

Computational study of Raney nickel type catalysts for the alkaline oxygen evolution reaction

CJ Thesner



orcid.org 0000-0001-9914-7392

Dissertation accepted in fulfilment of the requirements for the degree *Master of Science in Chemistry* at the North-West University

Supervisor: Prof CGCE van Sittert

Co-supervisor: Dr A Falch

Graduation October 2023

23515074

Declaration

I, Cherise Joanne Thesner, declare that the dissertation entitled: "Computational study of Raney nickel type catalysts for the alkaline oxygen evolution reaction", submitted in fulfilment of the requirements for the degree Master of Science in Chemistry, is my original and independent work under the supervision of Prof CGCE van Sittert and Dr A Falch, except where acknowledged in the text, and has not been submitted in whole or in part to any other tertiary institution.

Signed at North-West University (Potchefstroom Campus)

Acknowledgements

Anything is possible when you have the right people there to support you

~ Misty Copeland ~

- To my supervisors, Prof CGCE van Sittert and Dr A Falch, thank you for your continued guidance and support throughout my research and the accompanying growing pains. Without the guidance of good leaders such as yourselves, I would not have come this far. I could not have asked for better supervisors.
- To my immediate family, thank you for the coffee, the ear, the shoulder, and the support that you have given me through this time. You kept me motivated and pushing forward even when I felt that I wanted to give up. To the rest of my family, thank you for your support from afar and for checking in occasionally.
- To my friends, thank you for checking in on me and for your support, the little online chats and the resultant laughs helped me keep my head about me.
- To my fellow students, thank you for all the discussions and sharing of opinions which in many cases helped me realise and correct possible errors in my work.
- I would like to thank the North-West University (NWU) and Chemical Resource Beneficiation (CRB) for the opportunity granted to me to do this research and acknowledge the financial support of NWU Postgraduate bursary program, which has made it possible.
- I would like to thank the Centre for High Performance Computing (CHPC) for the use of their facility for the computing power to run my calculations and Dr Krishna Govender for his continued assistance.
- The financial assistance of the National Research Foundation (NRF), under grant UID 117978, towards this research is hereby acknowledged. Opinions expressed and conclusions arrived at are those of the author and are not necessarily attributable to the NRF. This work is based on the research supported in part by the National Research Foundation of South Africa.

Abstract

The growth of the global population, together with an increase in pollution caused by the use of fossil fuels for energy production, has led to an environmental and energy crisis. This crisis necessitates the search for alternative sustainable and environmentally accommodating energy sources. One such alternative form of energy is hydrogen gas. Although hydrogen gas is a highly energy-dense and clean energy carrier, it does not occur naturally and needs to be produced. One of the cleanest hydrogen production methods is water electrolysis. However, much research is being conducted on the electrocatalysts that drive the two water electrolysis half-reactions, i.e. the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). The OER is more energy-intensive and requires an effective electrocatalyst. The material of these catalysts are dictated by the pH environment of the electrolysis. In an acidic environment, costly rare noble metals such as Ir and Ru are used. However, in an alkaline environment, base metals such as Ni, Co and Fe can be used.

Literature is abundant with studies showing Ni and Ni-based oxides as effective catalytic materials for the OER in an alkaline environment. One Ni-based electrocatalyst of interest to this study is Raney nickel. Raney nickel, a porous nickel structure, is prepared from a bimetallic precursor, typically with Al as a secondary metal. This secondary metal is selectively leached out using an alkaline solution leaving a porous structure. However, the composition and morphology of the precursor can influence the final structure and composition of Raney nickel. Previous studies (experimental and computational) of Raney nickel focused mainly on three compositions (phases), namely Ni_2Al_3 , NiAl and NiAl_3 . To gain a better understanding of the influence of the composition and the morphology of the precursor on the final structure of Raney nickel and, therefore, the catalytic activity of Raney nickel, there is a need to investigate a wider range of phases. That is what this study attempted to do by studying several $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase surface structures.

Before the $\text{Ni}_{1-x}\text{Al}_x$ bimetallic surfaces could be constructed and investigated, an inclusive computational model needed to be developed. A Density Functional Theory (DFT) based model was developed using pure Ni and Al bulk structures and (111) surfaces. The model made use of the CAMbridge Serial Total Energy Package (CASTEP) included in the BIOVIA Software, Materials Studio 2020 (MS2020). The bulk model was developed using $2 \times 2 \times 2$ supercells and validated by comparing the structural and electronic properties of these bulk structures with literature values. Surface slabs in the (111)-Miller plane were created for Ni and Al. Although most of the setting in the bulk model was used when surface slabs were optimised, the k-points were changed for the surface slab model. The surface slabs were validated by comparing the structural and electronic properties of the Ni (111)- and Al (111)-surface slabs with literature values.

Next, the $\text{Ni}_{1-x}\text{Al}_x$ bimetallic precursors were constructed using the Site Occupancy Disorder (SOD) program, which built all possible configurations with the given ratio of Ni and Al atoms (phases) and identified the unique configurations. The unique configurations were optimised using the General Utility Lattice Program (GULP). Further, SOD also allowed for the calculation of thermodynamic properties, such as probability distribution, configurational entropy, and the enthalpy of mixing. These properties were used to identify the most stable $\text{Ni}_{1-x}\text{Al}_x$ bimetallic ratio and atomic configurations for further study.

The bulk structures of the most thermodynamically stable unique configurations were optimised using the abovementioned DFT model. Surface slabs were generated by cleaving the optimised bulk structures along the (111)-Miller. These (111)-surface slabs were optimised and used to identify configurations for manually simulated leaching. The surface slabs for the manual leaching of Al were selected using calculated properties such as the work function, the surface energy, and the Ni and Al content. The manual leaching was done by removing a set of four Al atoms. The initial Al atom was selected by considering the nearest neighbour (NN) atoms on the surface and in the sub-surface layers. The subsequent Al atoms were chosen by considering NN atoms in the layers surrounding the cavity created by the previous removal. The leached surface slabs were optimised after each removal. The final leached surface slabs were those with the smallest average removal energy.

Lastly, the simulated adsorption of the OH^- species was studied on the pure Ni (111)-surface slab and the final leached bimetallic (111)-surface slabs. The adsorption data for the Ni (111)-surface slab showed that Ni exhibited optimal adsorption energies for an OER catalyst. Comparatively, the adsorption data of five manually selected adsorption positions showed that the bimetallic (111)-surface slabs of Ni_8Al_8 , Ni_9Al_7 , and $\text{Ni}_{11}\text{Al}_5$ could be active catalysts for the OER. Of these $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases, Ni_8Al_8 (NiAl) has been studied previously. However, Ni_9Al_7 and $\text{Ni}_{11}\text{Al}_5$ are newly identified phases that could be used for future studies of precursor composition and morphology influences on Raney nickel.

Keywords: Oxygen Evolution Reaction, Raney nickel precursor, aluminium leaching, hydroxide adsorption, Site Occupation Disorder

Opsomming

Die groei van die wêreldbevolking tesame met 'n toename in besoedeling wat veroorsaak word deur die gebruik van fossielbrandstowwe vir energieproduksie, dra by tot die huidige globale omgewings- en energiekrisis. Hierdie krisis noodsaak die soeke na alternatiewe volhoubare en omgewingsvriendelike energiebronne. Een só 'n alternatiewe energiebron is waterstofgas. Alhoewel waterstofgas 'n hoogsenergie-digte en skoon energiedraer is, kom dit nie natuurlik voor nie en moet dit vervaardig word. 'n Skoon waterstofvervaardigingsmetode is watersplyting. Daar word egter baie navorsing met betrekking tot die elektrokatalisatore, wat die twee watersplytingshalfreaksies, naamlik die waterstofvrystellingsreaksie (HVR) en suurstofvrystellingsreaksie (SVR) aandryf, gedoen. Die SVR is meer energie-intensief en benodig 'n effektiewe elektrokatalisator. Die keuse van elektrokatalisatormateriale word egter bepaal deur die pH van die watersplytings omgewing. In 'n suur omgewing word duur en skaars edelmetale soos Ir en Ru gebruik. In 'n alkaliese omgewing kan basismetale soos Ni, Co en Fe egter gebruik word.

Literatuur is volop met studies wat Ni- en Ni-gebaseerde oksiede as effektiewe katalitiese materiale vir die SVR in 'n alkaliese omgewing aantoon. Een Ni-gebaseerde elektrokatalisator wat vir hierdie studie van belang is, is Raney-nikkel. Raney-nikkel is 'n poreuse Ni-struktuur wat vanaf 'n bimetaalvoorloper voorberei word, tipies met Al as sekondêre metaal. Hierdie sekondêre metaal word selektief uitgeloog met behulp van 'n alkaliese oplossing wat 'n poreuse struktuur laat. Die samestelling en morfologie van die voorloper kan egter die finale struktuur van die Raney-nikkel beïnvloed. Vorige studies (eksperimenteel en rekenaarmatig) van Raney-nikkel het hoofsaaklik op drie samestellings (fases), naamlik Ni_2Al_3 , NiAl en NiAl_3 gefokus. Om 'n beter begrip van die invloed van die samestelling en die morfologie van die voorloper op die finale struktuur van Raney-nikkel en dus die katalitiese aktiwiteit van Raney-nikkel te kry, is daar 'n behoefte om 'n groter verskeidenheid fases te ondersoek. Dit is wat hierdie studie gepoog het om te doen deur verskeie $\text{Ni}_{1-x}\text{Al}_x$ bimetaalfase oppervlakstrukture te bestudeer.

Voordat die $\text{Ni}_{1-x}\text{Al}_x$ bimetaaloppervlaktes gebou en ondersoek kon word, moes 'n omvattende berekeningsmodel ontwikkel word. 'n Digtheidfunksionaalteorie-model (DFT-model) is met behulp van suiwer Ni- en Al-strukture ontwikkel. Die DFT-model het van die "Cambridge Serial Total Energy Package" (CASTEP), wat in die BIOVIA-sagteware, "Materials Studio 2020" (MS2020) ingesluit is, gebruik gemaak. Die uitgebreide-struktuur model, wat ontwikkel is met behulp van $2 \times 2 \times 2$ superselle, is gevalideer deur die strukturele en elektroniese eienskappe van die uitgebreide-strukture met literatuurwaardes te vergelyk. Oppervlakstrukture in die (111)-Millervlak is geskep vir Ni en Al. Die uitgebreide-struktuur model is aangepas en gevalideer vir oppervlakstrukture deur die strukturele en elektroniese eienskappe van die Ni (111)- en Al (111)-oppervlakstrukture met literatuurwaardes te vergelyk.

Vervolgens is die $\text{Ni}_{1-x}\text{Al}_x$ -bimetaalvoorlopers met behulp van die “Site Occupancy Disorder”-program (SOD), wat verskeie samestellings met die gegewe verhouding van Ni- en Al-atome (fases) gee, gebou en die unieke samestellings is geïdentifiseer. Die unieke samestellings is met behulp van die “General Utility Lattice Program” (GULP) geoptimeer. Verder het die SOD-program ook vir die berekening van termodinamiese eienskappe, soos waarskynlikheidsverspreidings, samestellings-entropie en die entalpie van vermenging voorsiening gemaak. Hierdie eienskappe is gebruik om die mees termodinamies stabiele $\text{Ni}_{1-x}\text{Al}_x$ -bimetaalverhoudings en atoomsamestellings te identifiseer vir verdere evaluering.

Die uitgebreide strukture van die mees termodinamies stabiele samestellings is met die bogenoemde DFT-model geoptimeer. Hierdie geoptimeerde uitgebreide strukture is in die (111)-Millerlak gesny en geoptimeer. Hierdie geoptimeerde (111)-oppervlakstrukture is gebruik om samestellings vir handmatig gesimuleerde logging te identifiseer. Die oppervlakstrukture vir die handmatige logging van Al is met behulp van berekende eienskappe soos die werkfunksie, die oppervlakenergie en die Ni- en Al-inhoud gekies. Die handmatige logging is gedoen deur 'n stel van vier Al-atome te verwyder en die geloogde oppervlakstruktuur na elke verwydering te optimeer. Die finale geloogde oppervlakstrukture was dié met die kleinste gemiddelde verwyderingsenergie.

Laastens, is gesimuleerde adsorpsie van die OH^- spesie op die suiwer Ni (111)-oppervlakstruktuur en die finale geloogde bimetaal-(111)-oppervlakstrukture toegepas. Die adsorpsiedata vir die Ni (111)-opperstruktuur het aangetoon dat Ni optimale adsorpsie-energieë vir 'n SVR-katalisator toon. Soortgelyk het die adsorpsie-data van vyf handmatig gekiesde adsorpsie-posisies aangetoon dat die bimetaal-(111)-oppervlakstrukture van Ni_8Al_8 , Ni_9Al_7 en $\text{Ni}_{11}\text{Al}_5$ aktiewe katalisatore vir die SVR kan wees. Van hierdie $\text{Ni}_{1-x}\text{Al}_x$ bimetaalfases is Ni_8Al_8 (NiAl) voorheen bestudeer. Ni_9Al_7 en $\text{Ni}_{11}\text{Al}_5$ is egter nuut geïdentifiseerde fases wat gebruik kan word vir toekomstige studies van voorlopersamestellings- en morfologie-invloede op Raney-nikkel.

Sleutelwoorde: Suurstofvrystellingreaksie, Raney-nikkelvoorloper, aluminiumlogging, hidroksied-adsorpsie, “site occupation disorder”

Table of contents

Declaration	i
Acknowledgements	iii
Abstract	v
Opsomming	vii
List of Tables	xiii
List of Figures	xix
List of Abbreviations	xxv
List of symbols	xxvii
Preface	xxix
Outline of the dissertation	xxix
Contribution to article(s)/manuscript(s)	xxx
Formatting and status of article(s)/manuscript(s)	xxx
Consent by co-authors	xxxi
List of conference oral presentations	xxxi
List of conference poster presentations	xxxi
References	xxxi
CHAPTER 1 Introduction	1
1.1 Background and rationale	2
1.2 Problem statement	3
1.3 Aim of the study	4
1.4 Objectives of the study	4
1.5 Methodology of the study	5
References	6
CHAPTER 2 Literature review	9
2.1 Energy and environmental crisis	10
2.2 Water electrolysis	10
2.2.1 Acidic OER	11
2.2.2 Alkaline OER	12
2.3 Raney nickel	13
2.3.1 Precursor effect on the morphology of Raney nickel	13
2.3.2 Preparation of Raney nickel	14
2.3.3 Summary of previous findings	17
2.4 Computational background	17
2.4.1 The density functional theory (DFT)	17
2.4.2 Site occupation disorder program (SOD)	21
2.4.3 The general utility lattice program (GULP)	22
References	22

CHAPTER 3 DFT model development using pure metals	29
3.1 Introduction.....	30
3.2 Computational Method	31
3.2.1 Model development for bulk structures	31
3.2.2 Sampling and optimisation of (111) surfaces	32
3.2.3 Surface and electronic properties of Ni (111) and Al (111) surfaces	33
3.3 Results and discussion	33
3.3.1 Model development for bulk structures	33
3.3.2 Sampling and optimisation of (111) surfaces	36
3.3.3 Surface and electronic properties of Ni (111) and Al (111) surfaces	38
3.4 Conclusion	40
References	40
CHAPTER 4 Using Site Occupation Disorder to build bulk structures of $Ni_{1-x}Al_x^*$	43
4.1 Introduction.....	44
4.2 Computational method	45
4.2.1 Configurations built with SOD	45
4.2.2 Boltzmann probability distributions.....	45
4.2.3 Stability of configurations.....	46
4.3 Results and Discussion.....	46
4.3.1 Configurations built with SOD	46
4.3.2 Boltzmann probability distributions.....	47
4.3.3 Stability of configurations.....	49
4.4 Conclusion	51
4.5 Supplementary Information.....	52
4.6 Acknowledgements	52
References	52
CHAPTER 5 A DFT study of the $Ni_{1-x}Al_x$ bimetallic phase structures.....	55
5.1 Introduction.....	56
5.2 Computational method	58
5.2.1 Bulk and (111)-surface slab optimisation	59
5.2.2 Leaching behaviour and simulation	59
5.2.3 Simulated adsorption.....	60
5.3 Results and discussions	61
5.3.1 Bulk and (111)-surface slab optimisation	61
5.3.2 Leaching behaviour and simulation	67
5.3.3 Simulated adsorption.....	83
5.4 Conclusion	87
References	88
CHAPTER 6 Conclusions and Future work	93
6.1 Reiteration of the problem statement, aim and objectives	94
6.2 Achievement of study objectives	95
6.3 Recommendations for future work.....	99
References	99

Appendix A Additional dissertation data.....	A-1
A.1 Chapter 4 supplementary information	A-1
A.2 Chapter 5 supplementary information	A-2
Appendix B Published article(s)/manuscript(s).....	B-1
B.1 Published manuscript from Chapter 4.....	B-1
Appendix C Consent by the journal(s).....	C-1
C.1 Permission for the use of Published manuscript (Chapter 4).....	C-1
C.2 Permission for the use of phase diagram (Figure 5-1)	C-2
Appendix D Additional work.....	D-1
D.1 SOD and GULP Guide	D-1
Appendix E Final fractional coordinates for pure Ni and Al structures.....	E-1
E.1 Fractional coordinates for pure Ni and Al bulk structures	E-1
E.2 Fractional coordinates for pure Ni (111) and Al (111) surface slab structures	E-3
Appendix F Final fractional coordinates for $Ni_{1-x}Al_x$ bimetallic phase structures	F-1
F.1 Fractional coordinates for Ni_3Al_{13} bulk and (111) surface slab structures	F-1
F.2 Fractional coordinates for Ni_4Al_{12} bulk and (111) surface slab structures	F-3
F.3 Fractional coordinates for Ni_5Al_{11} bulk and (111) surface slab structures	F-5
F.4 Fractional coordinates for Ni_7Al_9 bulk and (111) surface slab structures for configurations 65 and 61.....	F-8
F.5 Fractional coordinates for Ni_8Al_8 bulk and (111) surface slab structures.....	F-12
F.6 Fractional coordinates for Ni_9Al_7 bulk and (111) surface slab structures.....	F-14
F.7 Fractional coordinates for $Ni_{11}Al_5$ bulk and (111) surface slab structures	F-16
F.8 Fractional coordinates for $Ni_{12}Al_4$ bulk and (111) surface slab structures	F-19
F.9 Fractional coordinates for $Ni_{13}Al_3$ bulk and (111) surface slab structures	F-21
Appendix G Final fractional coordinates for $Ni_{1-x}Al_x$ bimetallic phase structures after each manual leaching step	G-1
G.1 Fractional coordinates for Ni_7Al_9 (111) surface slab structures after Al atom removal	G-1
G.2 Fractional coordinates for Ni_8Al_8 (111) surface slab structures after Al atom removal	G-6
G.3 Fractional coordinates for Ni_9Al_7 (111) surface slab structures after Al atom removal	G-12
G.4 Fractional coordinates for $Ni_{11}Al_5$ (111) surface slab structures after Al atom removal	G-18
Appendix H Final fractional coordinates for leached $Ni_{1-x}Al_x$ bimetallic phase structures after the adsorption of OH^-	H-1
H.1 Fractional coordinates for the leached Ni_7Al_9 (111) surface slab structures after the adsorption of OH^-	H-1

H.2 Fractional coordinates for the leached Ni_8Al_8 (111) surface slab structures after the adsorption of OH^-	H-8
H.3 Fractional coordinates for the leached Ni_9Al_7 (111) surface slab structures after the adsorption of OH^-	H-15
H.4 Fractional coordinates for the leached $\text{Ni}_{11}\text{Al}_5$ (111) surface slab structures after the adsorption of OH^-	H-22
<i>Appendix I Final fractional coordinates for leaching behaviour using Ni_8Al_8 (111) and pure Ni (111) adsorption, using OH^-</i>	<i>I-1</i>
I.1 Fractional coordinates for the leaching behaviour using the Ni_8Al_8 (111) surface slab.....	I-1
I.2 Fractional coordinates for adsorption of OH^- onto the Ni (111) surface slab.....	I-4

List of Tables

Table 3-1	k-point data for Ni and Al, including the k-point grid and the corresponding k-points, the relative free energy for each k-point grid and the difference between the relative energies between different k-point grids.	34
Table 3-2	OTFG Ultrasoft and Ultrasoft pseudopotential results for Al and Ni compared to computational literature values.....	36
Table 3-3	k-point data for Ni (111) and Al (111), including the k-point grid and the corresponding k-points, the relative free energy for each k-point grid and the difference between the relative energies between different k-point grids.....	38
Table 3-4	Surface and electronic properties for Ni (111).....	39
Table 3-5	Surface and electronic properties for Al (111)	39
Table 4-1	The configurations for various $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases	47
Table 5-1	The calculated spin moment (m_s) and some measured interatomic distances (d_x - d_x) for (111)-surface slabs are shown.	61
Table 5-2	Bond length of $\text{OH}^\cdot$ and interatomic distances and bond lengths of the atoms surrounding the initial top position of the $\text{OH}^\cdot$ species, before and after optimisation.....	68
Table 5-3	Bond lengths of $\text{OH}^\cdot$ and interatomic distances and bond lengths of the atoms surrounding the initial fcc position of the $\text{OH}^\cdot$ species, before and after optimisation.....	70
Table 5-4	The calculated Al removal energy (eV) for the Ni_7Al_9 bimetallic phase.	72
Table 5-5	The calculated Al removal energy (eV) for the Ni_8Al_8 bimetallic phase.	75
Table 5-6	The calculated Al removal energy (eV) for the Ni_9Al_7 bimetallic phase	78
Table 5-7	The calculated Al removal energy (eV) for the $\text{Ni}_{11}\text{Al}_5$ bimetallic phase	81
Table 5-8	Adsorption position depths from Figure 5-23.....	84
Table 5-9	Calculated d-band centres for each $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase and pure Ni (111)-surface slab before and after adsorption at the different positions.....	85

Table 5-10	Calculated adsorption energies in eV for each $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase and pure Ni (111)-surface slab at the different positions.	86
Table 5-11	Calculated average adsorption energies in eV per layer for each $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase and pure Ni (111)-surface slab.	86
Table 6-1	DFT settings used during computational model development	96
Table 6-2	The surface areas of the cleaved $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase (111)-surface slabs	97
Table E-1	Final fractional coordinates for the optimised pure Ni bulk structure.....	E-1
Table E-2	Final fractional coordinates for the optimised pure Al bulk structure.....	E-2
Table E-3	Final fractional coordinates for the optimised pure Ni (111) surface slab structure.....	E-3
Table E-4	Final fractional coordinates for the optimised pure Al (111) surface slab structure.....	E-4
Table F-1	Final fractional coordinates for the optimised $\text{Ni}_3\text{Al}_{13}$ bulk structure.....	F-1
Table F-2	Final fractional coordinates for the optimised $\text{Ni}_3\text{Al}_{13}$ (111) surface slab structure.....	F-2
Table F-3	Final fractional coordinates for the optimised $\text{Ni}_4\text{Al}_{12}$ bulk structure.....	F-3
Table F-4	Final fractional coordinates for the optimised $\text{Ni}_4\text{Al}_{12}$ (111) surface slab structure.....	F-4
Table F-5	Final fractional coordinates for the optimised $\text{Ni}_5\text{Al}_{11}$ bulk structure.....	F-5
Table F-6	Final fractional coordinates for the optimised $\text{Ni}_5\text{Al}_{11}$ (111) surface slab structure.....	F-6
Table F-7	Final fractional coordinates for the optimised Ni_7Al_9 , configuration 65, bulk structure.....	F-8
Table F-8	Final fractional coordinates for the optimised Ni_7Al_9 , configuration 65, (111) surface slab structure.....	F-8
Table F-9	Final fractional coordinates for the optimised Ni_7Al_9 , configuration 61, bulk structure.....	F-10

Table F-10	Final fractional coordinates for the optimised Ni_7Al_9 , configuration 61, (111) surface slab structure.....	F-11
Table F-11	Final fractional coordinates for the optimised Ni_8Al_8 bulk structure	F-12
Table F-12	Final fractional coordinates for the optimised Ni_8Al_8 (111) surface slab structure.....	F-13
Table F-13	Final fractional coordinates for the optimised Ni_9Al_7 bulk structure	F-14
Table F-14	Final fractional coordinates for the optimised Ni_9Al_7 (111) surface slab structure.....	F-15
Table F-15	Final fractional coordinates for the optimised $\text{Ni}_{11}\text{Al}_5$ bulk structure.....	F-16
Table F-16	Final fractional coordinates for the optimised $\text{Ni}_{11}\text{Al}_5$ (111) surface slab structure.....	F-17
Table F-17	Final fractional coordinates for the optimised $\text{Ni}_{12}\text{Al}_4$ bulk structure.....	F-19
Table F-18	Final fractional coordinates for the optimised $\text{Ni}_{12}\text{Al}_4$ (111) surface slab structure.....	F-19
Table F-19	Final fractional coordinates for the optimised $\text{Ni}_{13}\text{Al}_3$ bulk structure.....	F-21
Table F-20	Final fractional coordinates for the optimised $\text{Ni}_{13}\text{Al}_3$ (111) surface slab structure.....	F-22
Table G-1	Final fractional coordinates for the optimised Ni_7Al_9 (111) surface slab structure after the first Al atom removal.....	G-1
Table G-2	Final fractional coordinates for the optimised Ni_7Al_9 (111) surface slab structure after the second Al atom removal.....	G-2
Table G-3	Final fractional coordinates for the optimised Ni_7Al_9 (111) surface slab structure after the third Al atom removal	G-4
Table G-4	Final fractional coordinates for the optimised Ni_7Al_9 (111) surface slab structure after the fourth Al atom removal	G-5
Table G-5	Final fractional coordinates for the optimised Ni_8Al_8 (111) surface slab structure after the first Al atom removal.....	G-6

Table G-6	Final fractional coordinates for the optimised Ni_8Al_8 (111) surface slab structure after the second Al atom removal.....	G-8
Table G-7	Final fractional coordinates for the optimised Ni_8Al_8 (111) surface slab structure after the third Al atom removal	G-9
Table G-8	Final fractional coordinates for the optimised Ni_8Al_8 (111) surface slab structure after the fourth Al atom removal	G-11
Table G-9	Final fractional coordinates for the optimised Ni_9Al_7 (111) surface slab structure after the first Al atom removal.....	G-12
Table G-10	Final fractional coordinates for the optimised Ni_9Al_7 (111) surface slab structure after the second Al atom removal.....	G-13
Table G-11	Final fractional coordinates for the optimised Ni_9Al_7 (111) surface slab structure after the third Al atom removal	G-15
Table G-12	Final fractional coordinates for the optimised Ni_9Al_7 (111) surface slab structure after the fourth Al atom removal	G-16
Table G-13	Final fractional coordinates for the optimised $\text{Ni}_{11}\text{Al}_5$ (111) surface slab structure after the first Al atom removal.....	G-18
Table G-14	Final fractional coordinates for the optimised $\text{Ni}_{11}\text{Al}_5$ (111) surface slab structure after the second Al atom removal.....	G-19
Table G-15	Final fractional coordinates for the optimised $\text{Ni}_{11}\text{Al}_5$ (111) surface slab structure after the third Al atom removal	G-20
Table G-16	Final fractional coordinates for the optimised $\text{Ni}_{11}\text{Al}_5$ (111) surface slab structure after the fourth Al atom removal	G-22
Table H-1	Final fractional coordinates for the optimised leached Ni_7Al_9 (111) surface slab structure after the first adsorption position	H-1
Table H-2	Final fractional coordinates for the optimised leached Ni_7Al_9 (111) surface slab structure after the second adsorption position.....	H-2
Table H-3	Final fractional coordinates for the optimised leached Ni_7Al_9 (111) surface slab structure after the third adsorption position	H-4

Table H-4	Final fractional coordinates for the optimised leached Ni_7Al_9 (111) surface slab structure after the fourth adsorption position	H-5
Table H-5	Final fractional coordinates for the optimised leached Ni_7Al_9 (111) surface slab structure after the fifth adsorption position	H-6
Table H-6	Final fractional coordinates for the optimised leached Ni_8Al_8 (111) surface slab structure after the first adsorption position	H-8
Table H-7	Final fractional coordinates for the optimised leached Ni_8Al_8 (111) surface slab structure after the second adsorption position.....	H-9
Table H-8	Final fractional coordinates for the optimised leached Ni_8Al_8 (111) surface slab structure after the third adsorption position	H-11
Table H-9	Final fractional coordinates for the optimised leached Ni_8Al_8 (111) surface slab structure after the fourth adsorption position	H-12
Table H-10	Final fractional coordinates for the optimised leached Ni_8Al_8 (111) surface slab structure after the fifth adsorption position	H-13
Table H-11	Final fractional coordinates for the optimised leached Ni_9Al_7 (111) surface slab structure after the first adsorption position	H-15
Table H-12	Final fractional coordinates for the optimised leached Ni_9Al_7 (111) surface slab structure after the second adsorption position.....	H-16
Table H-13	Final fractional coordinates for the optimised leached Ni_9Al_7 (111) surface slab structure after the third adsorption position	H-18
Table H-14	Final fractional coordinates for the optimised leached Ni_9Al_7 (111) surface slab structure after the fourth adsorption position	H-19
Table H-15	Final fractional coordinates for the optimised leached Ni_9Al_7 (111) surface slab structure after the fifth adsorption position	H-20
Table H-16	Final fractional coordinates for the optimised leached $\text{Ni}_{11}\text{Al}_5$ (111) surface slab structure after the first adsorption position	H-22
Table H-17	Final fractional coordinates for the optimised leached $\text{Ni}_{11}\text{Al}_5$ (111) surface slab structure after the second adsorption position	H-23

Table H-18	Final fractional coordinates for the optimised leached $\text{Ni}_{11}\text{Al}_5$ (111) surface slab structure after the third adsorption position.....	H-25
Table H-19	Final fractional coordinates for the optimised leached $\text{Ni}_{11}\text{Al}_5$ (111) surface slab structure after the fourth adsorption position.....	H-26
Table H-20	Final fractional coordinates for the optimised leached $\text{Ni}_{11}\text{Al}_5$ (111) surface slab structure after the fifth adsorption position	H-27
Table I-1	Final fractional coordinates for the optimised leaching behaviour using the Ni_8Al_8 (111) surface slab structure for the top site	I-1
Table I-2	Final fractional coordinates for the optimised leaching behaviour using the Ni_8Al_8 (111) surface slab structure for the fcc site.....	I-2
Table I-3	Final fractional coordinates for the optimised Ni (111) surface slab structure after the top adsorption site.....	I-4
Table I-4	Final fractional coordinates for the optimised Ni (111) surface slab structure after the bridge adsorption site.....	I-5
Table I-5	Final fractional coordinates for the optimised Ni (111) surface slab structure after the fcc adsorption site	I-7

List of Figures

Figure 2-1	Representation of a positive (downward) d-band shift.....	19
Figure 2-2	The d-band centre (ϵ_d) can be determined using integration and a simple representation of the d-bandwidth.....	20
Figure 3-1	The free energy (relative to 1×1×1 energy), shown in eV for Ni (blue) and Al (magenta) as a function of the number of k-points in the chosen grid.	34
Figure 3-2	Bulk energy results from the dispersion scheme identification with Al (magenta) on the left-hand y-axis and Ni (blue) on the right-hand y-axis.....	35
Figure 3-3	Fractional thickness and fractional top settings of 2.0 for (a) the Ni surface slab top and side view, (b) the Al surface slab top and side view.....	37
Figure 3-4	(111)-surface k-point sampling results with the relative free energy in eV shown for Ni (blue) and Al (magenta) as a function of the number of k-points in the chosen grid.....	37
Figure 4-1	The number of configurations for the $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases over a temperature range of 0.1K – 1200K for (a) existence probabilities > 0% and (b) existence probabilities $\geq 1\%$. (Circle markers represent ratios where the Ni content is the highest, and triangle markers represent ratios where Al content is the highest.).....	48
Figure 4-2	The entropy of the different configurations (with the identifying number shown above the bar), with probabilities $\geq 10\%$ relative to Ni content at 700K.	50
Figure 4-3	(a) - (h) The atomic structures of the most stable unique configurations identified from the entropy. (Al = magenta atoms and Ni = blue atoms.)	50
Figure 4-4	The enthalpy of mixing for $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases. The most stable configuration images of $\text{Ni}_5\text{Al}_{11}$, Ni_8Al_8 , and $\text{Ni}_{11}\text{Al}_5$ are included.....	51
Figure 5-1	Thermodynamic binary phase diagram of a Ni-Al system. The yellow areas show the stable phases and the dashed red lines represent the Ni_xAl_y bimetallic phases used in the study by Luong <i>et al.</i> ² Reused with permission (Appendix C).	56
Figure 5-2	(a) - (h) The atomic structure of the eight most stable unique $\text{Ni}_{1-x}\text{Al}_x$ bimetallic configurations identified from entropy in Chapter 4. (Al = magenta atoms and	

Ni = blue atoms.) ⁷ Additional to the Chapter 4 results, the Ni at% is shown for each $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase.	57
Figure 5-3 Statistical entropy data from SOD calculations in Chapter 4, over a temperature range of 0.1K to 1200K, for the $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases.	58
Figure 5-4 (a) – (b) The atomic structure for the most stable unique $\text{Ni}_{1-x}\text{Al}_x$ bimetallic configurations, namely (a) 65 and (b) 61, of Ni_7Al_9 . (Al = magenta atoms and Ni = blue atoms.).....	58
Figure 5-5 Partial density of states for pure Al, $\text{Ni}_5\text{Al}_{11}$, $\text{Ni}_{11}\text{Al}_5$ and pure Ni. The positive y-axis represents the d-band DOS, while the negative y-axis represents the p-band DOS.....	62
Figure 5-6 (a) The top view of the Ni_8Al_8 (111)-surface slab structure. (b) An isosurface slice of the electron density distribution of the top layer of the Ni_8Al_8 (111)-surface slab structure. The isosurface scale indicates that blue shows low electron density, while red shows high electron density. (c) An isosurface slice of the atomic electron density difference distribution of the top layer of the Ni_8Al_8 (111)-surface slab structure. The isosurface scale indicates that blue shows electron depletion, while red shows electron accumulation. (Al = magenta atoms, and Ni = blue atoms.)	64
Figure 5-7 Work function (green) and surface energy (blue) for the $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase (111)-surface slabs in order of ascending Ni content from the left.	65
Figure 5-8 (a) – (d) Surface structures of configurations identified using DFT calculated properties for the subsequent leaching of Al. The work functions (Φ) and surface energies (γ) are also given.	67
Figure 5-9 The leaching behaviour of an $\text{OH}^\cdot$ species, before and after optimisation, where $\text{OH}^\cdot$ was placed directly over an Al atom (top site). (a) Side view before optimisation, (b) top view before optimisation, (c) side view after optimisation and (d) top view after optimisation.	68
Figure 5-10 The leaching behaviour of an $\text{OH}^\cdot$ species, before and after optimisation, where $\text{OH}^\cdot$ was placed in a position between two Al atoms and a Ni atom (fcc site). (a) Side view before optimisation, (b) top view before optimisation, (c) side view after optimisation and (d) top view after optimisation.	69

- Figure 5-11 (a) - (e) Al atoms identified to be removed from the Ni_7Al_9 surface. (a) The first and second atoms to be removed. (b) and (c) The third atoms to be removed. (d) The fourth atoms to be removed. (The smaller spheres represent the top layer atoms, while the crosshairs represent the second layer atoms. Al = magenta atoms and Ni = blue atoms.) 71
- Figure 5-12 Atomic electron density difference slices for the manual leaching of Ni_7Al_9 . (a) Top layer before Al atoms were leached. (b) Top layer after one atom has been removed. (c) Top layer after two atoms have been removed. (d) The second layer before Al atoms were leached. (e) The second layer after Al atoms were leached. (f) The third layer before Al atoms were leached. (g) The third layer after Al atoms were leached. (Al = magenta atoms and Ni = blue atoms.) 73
- Figure 5-13 (a) – (e) The structure changes of the surface slab for Ni_7Al_9 during leaching. (a) The surface slab structure before leaching. (b) - (e) The results of each sequential leaching step, from one to four Al atoms being removed. (Al = magenta atoms and Ni = blue atoms.) 74
- Figure 5-14 (a) – (d) Al atoms identified to be removed from the Ni_8Al_8 surface slab. (a) The first and second atoms to be removed. (b) The third atoms to be removed. (c) The fourth atoms to be removed (top layer). (d) The fourth atoms to be removed (second layer). The smaller spheres represent the top layer atoms. (Al = magenta atoms and Ni = blue atoms.) 74
- Figure 5-15 (a) - (f) Atomic electron density difference slices for the manual leaching of Ni_8Al_8 . (a) Top layer before Al atoms were leached. (b) Top layer after one atom has been removed. (c) Top layer after two atoms have been removed. (d) Top layer after three atoms have been removed. (e) The second layer before Al atoms were leached. (f) The second layer after one atom has been removed. (Al = magenta atoms and Ni = blue atoms.) 76
- Figure 5-16 (a) – (e) The structure changes of the surface slab for Ni_8Al_8 during leaching. (a) The surface slab structure before leaching. (b) - (e) The results of each sequential leaching step, from one to four Al atoms removed. (Al = magenta atoms and Ni = blue atoms.) 77
- Figure 5-17 (a) - (e) Al atoms identified to be removed from the Ni_9Al_7 surface. The first and second atoms to be removed are shown in (a), while (b) and (c) show the third atoms to be removed. (d) and (e) The fourth atoms to be removed. The

	smaller spheres represent the top layer atoms. (Al = magenta atoms and Ni = blue atoms.).....	77
Figure 5-18	(a) - (f) Atomic electron density difference slices for the manual leaching of Ni_9Al_7 . (a) Top layer before Al atoms were leached. (b) Top layer after one atom has been removed. (c) Top layer after two atoms have been removed. (d) Top layer after three atoms have been removed. (e) The second layer before Al atoms were leached. (f) The second layer after one atom has been removed. (Al = magenta atoms and Ni = blue atoms.)	79
Figure 5-19	(a) – (e) The structure changes of the surface slab for Ni_9Al_7 during leaching. (a) The unleached surface slab structure. (b) - (e) The results of each sequential leaching step, from one to four Al atoms removed. (Al = magenta atoms and Ni = blue atoms.)	80
Figure 5-20	(a) - (c) Al atoms identified to be removed from the $\text{Ni}_{11}\text{Al}_5$ surface. (a) The first and second atoms to be removed, while (b) shows the third atoms to be removed. The smaller spheres represent the top layer atoms. (Al = magenta atoms and Ni = blue atoms.)	80
Figure 5-21	(a) - (f) Atomic electron density difference slices for the manual leaching of $\text{Ni}_{11}\text{Al}_5$. (a) Top layer before Al atoms were leached. (b) Top layer after one atom has been removed. (c) Top layer after two atoms have been removed. (d) Top layer after three atoms have been removed. (e) The second layer before Al atoms were leached. (f) The second layer after one atom has been removed. (Al = magenta atoms and Ni = blue atoms.)	82
Figure 5-22	The structure changes of the surface slab for $\text{Ni}_{11}\text{Al}_5$, during leaching. (a) The surface slab structure before leaching. (b) - (e) The results of each sequential leaching step, from one to four Al atoms removed. (Al = magenta atoms and Ni = blue atoms.).....	83
Figure 5-23	Adsorption positions of $\text{OH}^\cdot$ onto final leached $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase (111)-surface slab structures, as well as the pure Ni (111)-surface slab. (Al = magenta atoms and Ni = blue atoms.)	84
Figure 5-24	Representation of a positive (downward) d-band shift by using Ni_7Al_9 data.	86
Figure A-1	(a) –(l)The entropy of the different configurations (the identifying number shown above the bar), with probabilities $\geq 10\%$ relative to Ni content at all temperatures 0.1K -1200K.....	A-2

Figure A-2	(a) - (d) Different configurations under the same $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase showing a configurational difference of only one or two atoms. (a) - (b) Configurations 88 and 89 under Ni_9Al_7 . (c) - (d) Configurations 25 and 26 under $\text{Ni}_{11}\text{Al}_5$	A-2
Figure A-3	Alpha and beta DOS for the pure Ni d-band, $\text{Ni}_{11}\text{Al}_5$ and $\text{Ni}_5\text{Al}_{11}$ d- and p-bands and the pure Al p-band.	A-3
Figure C-1	Permission granted through personal correspondence to publish manuscript (Chapter 4) in dissertation.....	C-1
Figure C-2	Open Access permission for the use of phase diagram in Figure 5-1. For full description the following link may be visited: https://www.mdpi.com/about/openaccess	C-2

List of Abbreviations

CASTEP	CAMbridge Serial Total Energy Package	NN	Nearest neighbour
CHPC	Centre for High Performance Computing	NRF	National Research Foundation
CoSAAMI	Conference of the South African Advanced Materials Initiative	NWU	North-West University
CRB	Chemical Resource Beneficiation	OER	Oxygen Evolution Reaction
DFT	Density Functional Theory	OTFG	On-the-fly generated
DFT-D	Density Functional Theory with Dispersion correction	PBE	Perdew, Burke and Ernzerhof
DNP	double numerical plus polarisation	PGM	Platinum group metal
DOS	Density of states	SCF	self-consistent field
EAM	Embedded atom model	SHE	Standard hydrogen electrode
fcc	face-centred cubic	SOD	Site Occupancy Disorder
Fm-3m	space group number 225	TPSD	Two-Point Steepest Descent
GGA	Generalized-gradient approximation	TS	Tkatchenko-Scheffler
GULP	General Utility Lattice Program	VASP	Vienna Ab initio Simulation Package
HER	Hydrogen Evolution Reaction	vdW	van der Waals
LCTA	Low-temperature chemical alloying	XRD	X-ray powder diffraction
LDA	local density approximation		
MAPS	Materials And Processes Simulations		
MD	Molecular dynamics		
MS2020	Materials Studio 2020		

List of symbols

$E_{adsorbate}$	adsorbate energy	h	hour
E_{ads}	adsorption energy	d_x-d_x	interatomic spacing
$E_{(adsorbate/surface\ slab)}$	adsorbate/surface slab system energy	J	joule
$\text{\AA}$	angstrom	K	Kelvin
ΔE_a^*	atomisation energy	m	metre
Atm	atmosphere	μ	micro
at%	atomic percentage	mm	millimetre
$E_{X\ removal}$	atom X removal energy	D_{KL}	Molecule dissociation energy
E_X	atom X energy	nm	nanometre
μB	Bohr magneton	N	number of atoms
k_B	Boltzmann's constant	$N_{bulk\ structure}$	number of atoms in bulk structure
$E_{bulk\ structure}$	bulk structure energy	N_{slab}	number of atoms in surface slab
Ω_m	configuration degeneracy	Z	partition function
E_m	configuration energy	Pa	Pascal
$H_m[Ni_{1-x}Al_x]$	configuration enthalpy	Ry	Rydberg energy units
S_m	configuration entropy	γ	surface energy
P_m	configuration probability	$E_{surface\ slab(a)}$	surface energy before atom removal
ϵ_d	d-band centre	$E_{surface\ slab(b)}$	surface energy after atom removal
$\Delta G - dispersion\ corrected\ atom$	dispersion corrected free energy	T	temperature
e^-	electron	$E_{surface\ slab}$	total energy of the surface slab
eV	electron volt	V	volt
φ	electrostatic potential close to the surface in vacuum	wt%	weight percentage
ΔH_{mix}	enthalpy of mixing	Φ	work function
$H[Ni_{1-x}Al_x]$	enthalpy of Ni _{1-x} Al _x bimetal		
$H[Al]$	enthalpy of pure Al		
$H[Ni]$	enthalpy of pure Ni		
E_F	Fermi energy level		
GPa	gigapascal		

Preface

The research and results presented in this dissertation contribute to the larger fields of computational chemistry and theoretical electrocatalyst design. In this dissertation, Raney nickel as a potential electrocatalyst for the water splitting process was investigated computationally. This investigation included the development of a computational model, the construction of precursor bimetallic phases consisting of Ni and Al, the evaluation of the stability of these constructed precursors, the subsequent leaching of the Al to form Raney nickel, and an OH⁻ adsorption onto the leached surfaces.

This dissertation is submitted in article format as permitted by the North-West University (NWU), following the guidelines set out in the Faculty of Natural and Agricultural Sciences: Quality Manual¹ and the Manual for Higher Degrees Studies², and it is written in British English. Following these guidelines, the information presented in the conventional “Experimental/Method” and “Results and Discussions” sections are included in the article(s) or manuscript(s), with each article or manuscript representing a chapter. Chapter 4 has been published³ as part of the Conference of the South African Advanced Materials Initiative (CoSAAMI) 2021, where an oral presentation of this chapter was given. The work of Chapter 4 was also presented as a poster at the Chem4Energy conference in 2023. Additional requirements for this submission format are that an introductory chapter, a literature review, and a concluding chapter be included.

Overall, due to the format in which this dissertation is submitted, repetition and overlap of figures, tables, text, and references may occur, including the content of the article(s) or manuscript(s), which follow as output from this dissertation. The dissertation was also sent for language editing, which may lead to chapters that differ from the published work.

Outline of the dissertation

This dissertation will include the following as outlined in the University’s Manual for Higher Degree Studies:²

- Title page
- Declaration
- Acknowledgements
- Table of contents
- A Preface
- Abstract
- Opsomming
- Chapter 1 Introduction
- Chapter 2 Literature review

- Chapter 3 DFT model development using pure metals
- Chapter 4 Using Site Occupation Disorder to build bulk structures of $\text{Ni}_{1-x}\text{Al}_x$ (published as an article)
- Chapter 5 A DFT study of the $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase structures
- Chapter 6 Conclusion and future work
- Appendix A Additional dissertation data
- Appendix B Published article(s)/manuscript(s)
- Appendix C Consent by the journal(s)
- Appendix D Additional work
- Appendix E Final fractional coordinates for pure Ni and Al structures
- Appendix F Final fractional coordinates for $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase structures
- Appendix G Final fractional coordinates for $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase structures after each manual leaching step
- Appendix H Final fractional coordinates for leached $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase structures after the adsorption of OH^-
- Appendix I Final fractional coordinates for leaching behaviour using Ni_8Al_8 (111) and pure Ni (111) adsorption, using OH^-

Contribution to article(s)/manuscript(s)

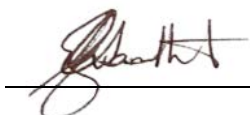
This work was conceptualised by Prof CGCE van Sittert (supervisor) and Dr A Falch (co-supervisor). I, Cherise J Thesner, did the research, calculation, conclusion, and compilation of the results within the dissertation and article(s) or manuscript(s) with the assistance and guidance of Prof CGCE van Sittert and Dr A Falch.

Formatting and status of article(s)/manuscript(s)

Although this dissertation is written in British English, the output article(s) or manuscript(s) are written in the journal's prescribed English. The published manuscript for Chapter 4 can be found in the Suid-Afrikaanse Tydskrif vir Natuurwetenskap en Tegnologie / South African Journal of Science and Technology (online ISSN 2222-4173),³ and the guidelines for the published manuscript can be found at <http://www.satnt.ac.za/index.php/satnt/about/submissions>. The manuscript is inserted into the dissertation in chapter format in Chapter 4, and the publication is in Appendix B in published format.

Consent by co-authors

The co-authors of the article(s) or manuscript(s) were informed that the MSc dissertation would be submitted in article format for examination, and they gave their consent.



I, Prof CGCE van Sittert, hereby give my permission that Cherise J Thesner may submit the article(s) or manuscript(s) for degree purposes.



I, Dr A Falch, hereby give my permission that Cherise J Thesner may submit the article(s) or manuscript(s) for degree purposes.

List of conference oral presentations

Using Site Occupation Disorder to build bulk structures of $Ni_{1-x}Al_x$, **Cherise J Thesner**, Anzel Falch and Cornelia GCE van Sittert, Conference of the South African Advanced Materials Initiative (CoSAAMI) 2021, Virtual, October 2021

List of conference poster presentations

Building $Ni_{1-x}Al_x$ bulk structures using the Site Occupation Disorder program, **Cherise J Thesner**, Anzel Falch and Cornelia GCE van Sittert, Chem4Energy Annual Conference – Sustainable Energy 2023, March 2023.

References

- (1) *Faculty of Natural and Agricultural Sciences: Quality Manual*; North-West University, 2020. <http://natural-sciences.nwu.ac.za/sites/natural-sciences.nwu.ac.za/files/files/FACULTY/fnas-quality-manual-2020.pdf> (accessed 2020-07-21).
- (2) *Manual for Higher Degrees Studies*; North-West University, 2020. http://studies.nwu.ac.za/sites/studies.nwu.ac.za/files/files/postgrad/Higher%20Degrees%20Manual_Senate_1Sept2020.pdf (accessed 2020-09-30).
- (3) Thesner, C.; Falch, A.; Van Sittert, C. G. C. E. Using Site Occupation Disorder to Build Bulk Structures of $Ni_{1-x}Al_x$. *Suid-Afrikaanse Tydskrif vir Natuurwetenskap en Tegnologie / South African Journal of Science and Technology* **2022**, 40 (1), 174–179. <https://doi.org/10.36303/SATNT.2021cosaami.33>.

CHAPTER 1 Introduction

The general theme of the dissertation is introduced in this chapter. This includes a background and rationale section explaining the significance of the OER and the necessity of researching potential catalyst improvements, particularly Raney nickel. Furthermore, a problem statement is also included that states the importance of investigating a novel range of precursor Ni-Al bimetallic phases. The aim and objectives of this study include a statement of the desired result and the approach used to achieve the outcome.

Please note that as this dissertation is in article format, there may be some overlap between the material cited in the following sections of Chapter 1 and the literature cited in the introductions to Chapters 2 to 6.

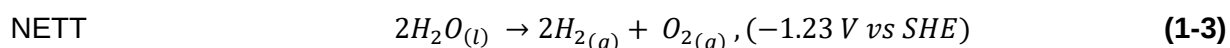
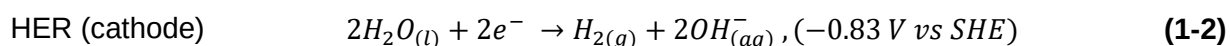
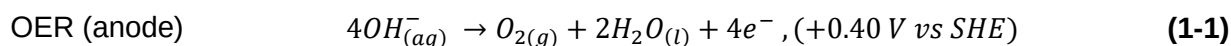
1.1 Background and rationale.....	2
1.2 Problem statement.....	3
1.3 Aim of the study.....	4
1.4 Objectives of the study.....	4
1.5 Methodology of the study	5
References	6

1.1 Background and rationale

The world's ever-increasing need for energy has led to the development of many alternative forms of energy production, with one such route being water electrolysis.^{1,2} During water electrolysis, water is split to produce molecular oxygen (O₂) and molecular hydrogen (H₂). The H₂, formed during water electrolysis, can be used as a high-energy fuel.³

Water electrolysis mainly occurs in an acidic or alkaline medium. Each of these media has certain advantages and disadvantages. The greatest advantage that alkaline electrolysis affords over acidic electrolysis is the possibility of using base metal catalysts, whereas rare noble metals are usually required for acidic electrolysis.⁴

In an alkaline medium, water electrolysis consists of the following two half-cell reactions, namely the oxygen evolution reaction (OER) (equation 1-1) and the hydrogen evolution reaction (HER) (equation 1-2).⁵



The energy barrier, i.e., overpotential required in addition to the minimum required energy (- 1.23 V (reaction 1-3)), limits the reaction rate, hence energy efficient water splitting.⁶ The HER and OER have certain limitations contributing to this net overpotential. The HER overpotential originates from the activation energy for water dissociation and hydrogen and hydroxyl binding energies.⁶ Comparing the simplest forms of reactions 1-1 and 1-2, it can be seen that the formation of one O₂ molecule (OER) involves twice the number of electrons as the formation of one H₂ molecule (HER). This four-electron transfer process required for O₂ evolution usually occurs as multi-step reactions, each requiring its own activation energy. Hence, the accumulation of the energy required for each step is known to result in sluggish kinetics (large overpotential) and requires an effective electrocatalyst to improve the reaction kinetics.^{7,8}

Ni and Ni-based oxides are effective materials as OER electrocatalysts.⁹ The effectiveness of Ni as an electrocatalyst for the OER can typically be increased by (i) adding additional materials (typically other transition metals) to alter the chemical composition or (ii) by inducing defects in the structure^{3,10} which can increase the surface area and hence the electrocatalytic efficacy.^{11,12} One material incorporating compositional variation and structural defects in Ni is Raney nickel, a porous, sponge-like form of Ni.⁷ The catalytic activity of the catalyst depends on the small amounts of Al/Zn content and the porosity of the Ni structure, which is influenced by the structure and composition of the precursor bimetal.¹²

Bimetal precursors used for Raney nickel production are usually Ni-M, where M represents Al or Zn. Al is commonly used since it shows better leaching results compared to Zn.^{3,13–18} The Ni-Al bimetal is most often studied in the ratios Ni₂Al₃, NiAl and NiAl₃, both experimentally and computationally, because these compositions are frequently observed experimentally.^{9,12,13,17,19–22} Al is selectively leached from the bulk structures of the bimetallic phases to produce the renowned porous structure of Raney nickel. The Al in different bimetal compositions will leach away at different rates, which leads to different surfaces because the leaching does not necessarily give exactly repeatable results.¹⁵ The amount of Al that is left unleached in the precursor can influence the catalytic activity of the Raney nickel, as well as its structural integrity. Bulk properties such as structural integrity can be considered for the overall longevity and stability of the Raney nickel catalyst. However, since the surface is the primary area of the catalyst involved in catalytic interactions the surface structure and composition are critical for the catalytic performance.

Studying the surface of a catalyst is of great importance since it can give an idea of important catalytic information, such as the activity, selectivity and stability.²³ Several catalytic properties can be influenced and optimised by manipulating the surface structure. These properties include adsorption energy, catalytic activity and stability. The catalytic activity is influenced by the electronic structure and charge of the surface, while the surface energy determines the stability.^{23,24}

For an electrocatalyst to be scalable for application purposes, it must be active, stable, selective, and reproducible. By applying computational modelling, insight can be gained into the mechanism or process of leaching and the most favourable Ni-Al ratio for water splitting (HER or OER or both).^{23,24} In this study, the focus will be placed on the (111)-surface, the most prominent surface before and after leaching of varying NiAl bimetal ratios.^{23,25–28} The crystal structures of both Ni and Al are face-centred cubic (fcc);^{29–31} therefore, the bimetal would also have this crystal structure. The smoothest, most uninterrupted surface to study at the atomic level is achieved by cleaving the Ni-Al bulk bimetal along the (111)-Miller plane.²⁴ By studying the surface the influence of the composition and structure on the activity, stability, and selectivity, especially with water adsorption can be elucidated. Finally, the activity of the leached bimetal surfaces, specifically towards the alkaline OER, will be tested.

1.2 Problem statement

For water electrolysis to be commercially viable, sustainable and affordable materials for electrocatalysts are needed. The materials available for use as electrocatalysts depend on the pH of the electrolyte.^{32,33} In an acidic medium, more inert materials like noble metals, such as Ir and Ru,³⁴ which are expensive and rare, are used, whereas in an alkaline medium, more sustainable and affordable materials can be used.^{32,33} One such material for the alkaline OER

reaction at 30°C is Raney nickel.³² Raney nickel is a porous Ni-Al bimetal formed from Ni-Al nanoparticles, where the Al has been leached from the Ni-Al bulk structure.^{12,17} However, the leaching of the Al from the Ni-Al bulk will not always be accurately reproducible¹⁵ as the degree of segregation of Al within the bulk and toward the surface of the Ni-Al bimetals varies.^{35–37} In addition, the amount of Al that remains after leaching could influence the performance and structural stability of the final Raney nickel catalyst.^{12,38} It is therefore beneficial to develop and evaluate a model for Raney nickel formation from precursor to final catalyst, to understand the leaching process and the influence of the surrounding factors on the final catalyst structure, composition, and activity towards the alkaline OER. Previous studies on Raney nickel, both computational and experimental, usually focused on the investigation of three bimetallic phases, namely Ni₂Al₃, NiAl, and NiAl₃.^{12,17,21} Thus, a more objective computational approach that includes a comprehensive spectrum of Ni-Al bimetallic phases (not just selecting the commonly used phases) will result in a more holistic and in-depth understanding of the characteristics of Raney nickel and its potential as an OER electrocatalyst.

1.3 Aim of the study

The study aims to develop and evaluate a model for the simulation of Raney nickel-type electrocatalysts and to investigate the activity towards the OER in alkaline media.

1.4 Objectives of the study

The following objectives will be addressed, to achieve the above-mentioned aim, namely:

- Scrutinise the available literature on hydrogen energy, water electrolysis as hydrogen production method, oxygen evolution reaction (OER) in alkaline media, and Raney nickel catalyst systems (experimental and computational) to assist with the model development.
- Develop a density functional theory (DFT) model by creating and optimising pure metal bulks for Ni and Al and their (111)-surfaces with the CAMbridge Serial Total Energy Package (CASTEP).³⁹ Validate the model by comparing the results to existing experimental and computational literature values.
- Construct several Ni_{1-x}Al_x bimetal bulk configurations with the Site-Occupancy Disorder (SOD)⁴ program. Optimise the constructed bimetal configurations using the General Utility Lattice Program (GULP)⁴⁰ and determine the most stable configurations with thermodynamic calculations.
- Optimise the most stable bimetallic bulk configurations with the CASTEP³⁹ model developed with pure metals. Using the most stable optimised bimetallic bulk configurations, create and optimise (111)-surfaces with CASTEP.³⁹ Investigate the electronic and magnetic properties of the most stable bimetal bulks and the (111)-surfaces. Identify the most suitable (111)-surface slabs using surface energy and surface properties. Leaching of Al was simulated by manually

removing Al from the (111)-surface slabs and the subsequent adsorption of the OER species ($\text{OH}\cdot$) onto the leached surfaces.

- Compare the findings of this study with available experimental and computational results found in the literature.

1.5 Methodology of the study

A comprehensive literature study will be conducted on the fundamental concepts of this work. Some topics that will be addressed are energy crises, water electrolysis (HER and OER), electrocatalysts for water electrolysis, Ni, Raney nickel, and solid-state catalysis studies using computational modelling. Additionally, the software and theoretical approaches used in this study, namely SOD⁴, GULP⁴⁰ and DFT, will be examined.

The pure metal bulks for Al and Ni will be constructed and optimised using CASTEP³⁹ to create a model for the bimetallic configurations. The (111)-surface slab for each metal will be created and optimised using CASTEP.³⁹ The electronic and magnetic properties as well as the surface energies will be calculated for these pure metals and their (111)-surface slabs.

The SOD⁴ program will be used to build $\text{Ni}_{1-x}\text{Al}_x$ bimetallic bulk configurations, which will be optimised using GULP.⁴⁰ These optimised structures will then be used to determine the most thermodynamically stable bimetallic configurations.

The CASTEP³⁹ model developed with the pure metals will then be used to optimise the most thermodynamically stable bimetallic bulk configurations. The (111)-surfaces of these optimised bulk configurations will be created and optimised using the previously mentioned CASTEP³⁹ model. Electronic and magnetic properties will be calculated, and the most suitable surface compositions will be determined by considering the surface energies, work functions, and the Ni and Al content. The leaching of Al from the most stable $\text{Ni}_{1-x}\text{Al}_x$ bimetallic surfaces will be simulated by manual removal of Al atoms, and the activity of the surface towards the first OER species ($\text{OH}\cdot$) will be evaluated via adsorption.

Lastly, the results of this study will be compared with literature findings where possible and be published in accredited journals fulfilling the requirements for completing a Master of Science degree.

The software used for the calculations is available on the Lengau cluster at the Centre for High Performance Computing (CHPC)⁴¹, where I am a registered user under the CHEM0778 program.

References

- (1) Doyle, R. L.; Lyons, M. E. G. The Oxygen Evolution Reaction: Mechanistic Concepts and Catalyst Design. In *Photoelectrochemical solar fuel production*; Springer, 2016; pp 41–104.
- (2) Dresselhaus, M. S.; Thomas, I. L. Alternative Energy Technologies. *Nature* **2001**, 414 (6861), 332–337. <https://doi.org/10.1038/35104599>.
- (3) Sapountzi, F. M.; Gracia, J. M.; Weststrate, C. J. (Kees-Jan).; Fredriksson, H. O. A.; Niemantsverdriet, J. W. (Hans). Electrocatalysts for the Generation of Hydrogen, Oxygen and Synthesis Gas. *Progress in Energy and Combustion Science*. Elsevier Ltd January 1, 2017, pp 1–35. <https://doi.org/10.1016/j.pecs.2016.09.001>.
- (4) Grau-Crespo, R.; Hamad, S.; Catlow, C. R. A.; De Leeuw, N. H. Symmetry-Adapted Configurational Modelling of Fractional Site Occupancy in Solids. *Journal of Physics: Condensed Matter* **2007**, 19 (25), 256201. <https://doi.org/10.1088/0953-8984/19/25/256201>.
- (5) Khan, M. A.; Zhao, H.; Zou, W.; Chen, Z.; Cao, W.; Fang, J.; Xu, J.; Zhang, L.; Zhang, J. Recent Progresses in Electrocatalysts for Water Electrolysis. *Electrochemical Energy Reviews* **2018**, 1 (4), 483–530.
- (6) Lao, M.; Li, P.; Jiang, Y.; Pan, H.; Dou, S. X.; Sun, W. From Fundamentals and Theories to Heterostructured Electrocatalyst Design: An in-Depth Understanding of Alkaline Hydrogen Evolution Reaction. *Nano Energy* **2022**, 98, 107231. <https://doi.org/10.1016/J.NANOEN.2022.107231>.
- (7) Lyu, F.; Wang, Q.; Choi, S. M.; Yin, Y. Noble-Metal-Free Electrocatalysts for Oxygen Evolution. *Small* **2019**, 15 (1), 1804201.
- (8) Shi, Q.; Zhu, C.; Du, D.; Lin, Y. Robust Noble Metal-Based Electrocatalysts for Oxygen Evolution Reaction. *Chem Soc Rev* **2019**, 48 (12), 3181–3192. <https://doi.org/10.1039/c8cs00671g>.
- (9) Smith, A. J.; Trimm, D. L. The Preparation of Skeletal Catalysts. *Annual Review of Materials Research*. 2005, pp 127–142. <https://doi.org/10.1146/annurev.matsci.35.102303.140758>.
- (10) Jamesh, M. I.; Sun, X. Recent Progress on Earth Abundant Electrocatalysts for Oxygen Evolution Reaction (OER) in Alkaline Medium to Achieve Efficient Water Splitting – A Review. *Journal of Power Sources*. Elsevier B.V. October 1, 2018, pp 31–68. <https://doi.org/10.1016/j.jpowsour.2018.07.125>.
- (11) Pierozynski, B.; Mikolajczyk, T.; Luba, M.; Zolfaghari, A. Kinetics of Oxygen Evolution Reaction on Nickel Foam and Platinum-Modified Nickel Foam Materials in Alkaline Solution. *Journal of Electroanalytical Chemistry* **2019**, 847, 113194. <https://doi.org/10.1016/j.jelechem.2019.113194>.
- (12) Schweizer, S.; Chaudret, R.; Low, J.; Subramanian, L. Molecular Modeling and Simulation of Raney Nickel: From Alloy Precursor to the Final Porous Catalyst. *Comput Mater Sci* **2015**, 99, 336–342.
- (13) Zeifert, B.; Blásquez, J. S.; Moreno, J. G. C.; Calderón, H. A. Raney-Nickel Catalysts Produced by Mechanical Alloying. *Reviews on Advanced Materials Science* **2008**, 18 (7), 633–639.
- (14) Gannon, W. J. F. F.; Dunnill, C. W. Raney Nickel 2.0: Development of a High-Performance Bifunctional Electrocatalyst. *Electrochim Acta* **2019**, 322, 134687. <https://doi.org/10.1016/j.electacta.2019.134687>.

- (15) Klein, J. C.; Hercules, D. M. Surface Analysis of Raney Nickel Alloys. *Anal Chem* **1981**, 53 (6), 754–758.
- (16) Fouilloux, P.; Martin, G. A.; Renouprez, A. J.; Moraweck, B.; Imelik, B.; Prettre, M. A Study of the Texture and Structure of Raney Nickel. *J Catal* **1972**, 25 (2), 212–222. [https://doi.org/10.1016/0021-9517\(72\)90220-5](https://doi.org/10.1016/0021-9517(72)90220-5).
- (17) Devred, F.; Gieske, A. H.; Adkins, N.; Dahlborg, U.; Bao, C. M.; Calvo-Dahlborg, M.; Bakker, J. W.; Nieuwenhuys, B. E. Influence of Phase Composition and Particle Size of Atomised Ni-Al Alloy Samples on the Catalytic Performance of Raney-Type Nickel Catalysts. *Appl Catal A Gen* **2009**, 356 (2), 154–161. <https://doi.org/10.1016/j.apcata.2008.12.039>.
- (18) Divisek, J.; Mergel, J.; Schmitz, H. Advanced Water Electrolysis and Catalyst Stability under Discontinuous Operation. *Int J Hydrogen Energy* **1990**, 15 (2), 105–114. [https://doi.org/10.1016/0360-3199\(90\)90032-T](https://doi.org/10.1016/0360-3199(90)90032-T).
- (19) Raney, M. Catalysts from Alloys: Nickel Catalysts. *Ind Eng Chem* **1940**, 32 (9), 1199–1203. <https://doi.org/10.1021/ie50369a030>.
- (20) Barnard, N. C.; Brown, S. G. R. Kinetic Monte Carlo Modelling the Leaching of Raney Ni-Al Alloys. In *WIT Transactions on Engineering Sciences*; 2007; Vol. 54, pp 53–62. <https://doi.org/10.2495/ECOR070061>.
- (21) Barnard, N. C.; Brown, S. G. R.; Devred, F.; Bakker, J. W.; Nieuwenhuys, B. E.; Adkins, N. J. A Quantitative Investigation of the Structure of Raney-Ni Catalyst Material Using Both Computer Simulation and Experimental Measurements. *J Catal* **2011**, 281 (2), 300–308. <https://doi.org/10.1016/j.jcat.2011.05.010>.
- (22) Lee, G. D.; Suh, C. S.; Park, J. H.; Park, S. S.; Hong, S. S. Raney Ni Catalysts Derived from Different Alloy Precursors (I) Morphology and Characterization. *Korean Journal of Chemical Engineering* **2005**, 22 (3), 375–381. <https://doi.org/10.1007/BF02719414>.
- (23) Yang, Y.; Luo, M.; Zhang, W.; Sun, Y.; Chen, X.; Guo, S. Metal Surface and Interface Energy Electrocatalysis: Fundamentals, Performance Engineering, and Opportunities. *Chem*. Elsevier Inc September 13, 2018, pp 2054–2083. <https://doi.org/10.1016/j.chempr.2018.05.019>.
- (24) Garlyyev, B.; Fichtner, J.; Piqué, O.; Schneider, O.; Bandarenka, A. S.; Calle-Vallejo, F. Revealing the Nature of Active Sites in Electrocatalysis. *Chemical Science*. Royal Society of Chemistry 2019, pp 8060–8075. <https://doi.org/10.1039/c9sc02654a>.
- (25) Oura, K.; Lifshits, V. G.; Saranin, A. A.; Zotov, A. v; Katayama, M. *Surface Science: An Introduction*; Springer Berlin Heidelberg, 2013.
- (26) Kim, J.-E.; Bae, K.-K.; Park, C.-S.; Jeong, S.-U.; Baik, K.-H.; Kim, J.-W.; Kang, K.-S.; Lee, K.-B.; Kim, Y.-H. Electrochemical Characterization of Raney Nickel Electrodes Prepared by Atmospheric Plasma Spraying for Alkaline Water Electrolysis. **2018**. <https://doi.org/10.1016/j.jiec.2018.10.010>.
- (27) Ge, X.; Pan, J.-B.; Qian, C.; Feng, L.; Chen, Y.-B.; Chen, X.-Z. Mechanism Study on Raney Nickel-Catalyzed Amination of Resorcinol. **2013**. <https://doi.org/10.1016/j.catcom.2013.12.021>.
- (28) Ma, X.; Liu, S.; Liu, Y.; Li, X.; Li, Q.; Gu, G.; Xia, C. Promoted Liquid-Phase Hydrodechlorination of Chlorophenol over Raney Ni via Controlling Base: Performance, Mechanism, and Application. **2019**. <https://doi.org/10.1016/j.chemosphere.2019.125202>.
- (29) nglos324 - aluminum. <https://www.princeton.edu/~maelabs/mae324/glos324/aluminum.htm> (accessed 2020-06-18).

- (30) nglos324 - nickel. <https://www.princeton.edu/~maelabs/mae324/glos324/nickel.htm> (accessed 2020-06-18).
- (31) Haynes, W. M. *CRC Handbook of Chemistry and Physics*, 97th ed.; CRC Press, 2016.
- (32) Colli, A. N.; Girault, H. H.; Battistel, A. Non-Precious Electrodes for Practical Alkaline Water Electrolysis. *Materials* **2019**, *12* (8), 1336. <https://doi.org/10.3390/ma12081336>.
- (33) Fabbri, E.; Haberer, A.; Waltar, K.; Kötzt, R.; Schmidt, T. J. Developments and Perspectives of Oxide-Based Catalysts for the Oxygen Evolution Reaction. *Catal Sci Technol* **2014**, *4* (11), 3800–3821. <https://doi.org/10.1039/c4cy00669k>.
- (34) Botha, L. M.; Santos-Carballal, D.; Terranova, U.; Quesne, M. G.; Ungerer, M. J.; Van Sittert, C. G. C. E.; De Leeuw, N. H. Mixing Thermodynamics and Electronic Structure of the Pt_{1-x}Ni_x (0 ≤ x ≤ 1) Bimetallic Alloy. *RSC Adv* **2019**, *9* (30), 16948–16954. <https://doi.org/10.1039/c9ra02320h>.
- (35) Manzoor, A.; Pandey, S.; Chakraborty, D.; Phillpot, S. R.; Aidhy, D. S. Entropy Contributions to Phase Stability in Binary Random Solid Solutions. *NPJ Comput Mater* **2018**, *4* (1). <https://doi.org/10.1038/s41524-018-0102-y>.
- (36) Fultz, B. Vibrational Thermodynamics of Materials. *Progress in Materials Science*. Pergamon May 1, 2010, pp 247–352. <https://doi.org/10.1016/j.pmatsci.2009.05.002>.
- (37) Ma, E. Alloys Created between Immiscible Elements. *Prog Mater Sci* **2005**, *50* (4). <https://doi.org/10.1016/j.pmatsci.2004.07.001>.
- (38) Schweizer, S.; Chaudret, R.; Spyriouni, T.; Low, J.; Subramanian, L. Influence of the Precursor Composition and Reaction Conditions on Raney-Nickel Catalytic System. In *Foundations of Molecular Modeling and Simulation: Select Papers from FOMMS 2015*; Snurr, R. Q., Adjiman, C. S., Kofke, D. A., Eds.; Springer Singapore: Singapore, 2016; pp 125–135. https://doi.org/10.1007/978-981-10-1128-3_8.
- (39) Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. I. J.; Refson, K.; Payne, M. C. First Principles Methods Using CASTEP. *Zeitschrift für Kristallographie-Crystalline Materials* **2005**, *220* (5/6), 567–570.
- (40) Gale, J. D.; Rohl, A. L. The General Utility Lattice Program (GULP). *Mol Simul* **2003**, *29* (5), 291–341. <https://doi.org/10.1080/0892702031000104887>.
- (41) Centre for high performance computing . <https://www.chpc.ac.za/index.php/resources/lengau-cluster>.

CHAPTER 2 Literature review

The world's energy and environmental crisis has led to the search for alternative energy sources. Hydrogen gas, being highly energy-dense, has been identified as a valuable alternative. There are several ways in which hydrogen gas can be produced. However, water electrolysis has the potential to be the cleanest method for hydrogen production, with oxygen as the only by-product. The oxygen evolution reaction (OER), a very important reaction occurring during water electrolysis, exhibits sluggish performance and requires an electrocatalyst to improve the overall efficiency of water electrolysis. Nickel and nickel-based oxides are good electrocatalysts, but they can be enhanced by adding defects within the structure of the catalyst. A nickel structure that incorporates such defects is porous Raney nickel. The porosity of the Raney nickel structure is influenced by the precursor materials used to synthesise the Raney nickel. Typical precursors for Raney nickel synthesis are NiAl, NiAl₃ and Ni₂Al₃.

2.1 Energy and environmental crisis.....	10
2.2 Water electrolysis	10
2.2.1 Acidic OER	11
2.2.2 Alkaline OER	12
2.3 Raney nickel.....	13
2.3.1 Precursor effect on the morphology of Raney nickel	13
2.3.2 Preparation of Raney nickel	14
2.3.2.1 Precursor alloy preparation	14
2.3.2.2 Leaching of the active metal.....	16
2.3.3 Summary of previous findings	17
2.4 Computational background.....	17
2.4.1 The density functional theory (DFT)	17
2.4.1.1 Electronic property calculation	18
2.4.1.2 Atomic removal energy.....	20
2.4.1.3 Adsorption energy	20
2.4.2 Site occupation disorder program (SOD)	21
2.4.3 The general utility lattice program (GULP)	22
References	22

2.1 Energy and environmental crisis

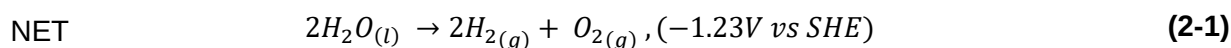
The world population is growing and so is the global demand for energy. This leads to an energy and environmental crisis, as most of the energy production relies on fossil fuels, which are used for up to 65% of global energy production. Fossil fuels are, however, not only slowly depleting, but also polluting the planet with greenhouse gas emissions.¹ Therefore, many studies have explored alternative forms of energy production that are clean and sustainable.

Some alternative energy sources that have been identified are solar, wind, hydro, and hydrogen. The first three sources have the disadvantage of being very variable in energy production.² This variation in production is due to the variability of nature; the sun does not shine always, and the wind does not always blow. Further, hydro energy is limited by location and can also be affected by wind. On the other hand, hydrogen energy is promising as an alternative energy source as it is not influenced by seasonal variability or location and has a very high energy density.² However, hydrogen is not readily available in nature in a useful form (namely H₂ gas) and it needs to be produced.

There are many methods of producing hydrogen, such as the reforming of natural gas and the gasification of coal and heavy oils.³ However, these methods still contribute to pollution, and a better method is needed. One such method is water electrolysis. Water electrolysis holds the promise to be a sustainable and clean method to produce hydrogen. The only by-product of water electrolysis is oxygen gas, which can later react with hydrogen to produce water and energy in a fuel cell.^{2,4-6} Water electrolysis is even more appealing since it can be powered by renewable energy sources like solar, wind and hydro energy.^{2,3,7}

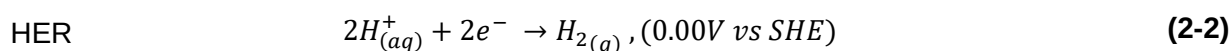
2.2 Water electrolysis

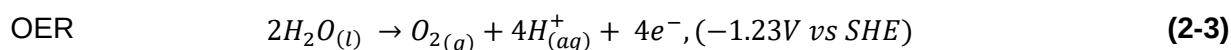
Water electrolysis is the splitting of water into molecular hydrogen (H₂) and oxygen (O₂).^{5,6,8} This water splitting occurs via the hydrogen evolution reaction (HER) at the cathode and the oxygen evolution reaction (OER) at the anode in an electrolyser.⁴⁻⁶ The reaction equation 2-1 shows the net reaction during water electrolysis.³ For this reaction to occur, a minimum potential of -1.23V is theoretically required.



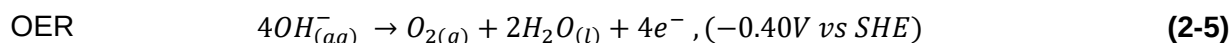
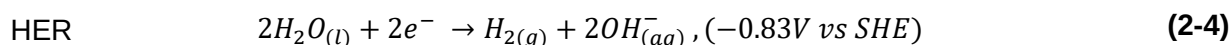
Water electrolysis can occur in an acidic or alkaline environment at 273 K and 1 atm, with each environment having distinct half-reactions.^{9,10}

In an acidic environment, the HER and OER have reactions and standard potentials, as shown in equations 2-2 and 2-3.^{11,12}





In an alkaline environment, the HER and OER have reactions and standard potentials, as shown in equations 2-4 and 2-5.^{6,11,12}



The theoretical potential for water electrolysis is -1.23 V. However, additional potential (overpotential) is required to overcome the kinetic limitations of both the HER and OER.^{8,13} The kinetic limitations refer to the intermediate species involved in each electron-transfer step, as well as the hydrogen binding energy, hydroxyl binding energy and the activation energy for the dissociation of water.¹⁴ The environment's pH influences the mechanistic steps of the adsorption of reaction intermediates.^{15,16} For the HER, the intermediate adsorbate is $^*H$, in both acidic and alkaline environments.^{17,18} For the OER, three intermediate adsorbates, namely $^*O$, $^*OH$, and $^*OOH$, accompany this four-electron transfer process in acidic and alkaline environments.^{1,15,19,20} The four-electron transfer reaction for the OER results in sluggish kinetics.⁷

In both environments, the formation of one mol of O_2 gas involves double the number of electrons needed during the formation of one mol of H_2 gas. In reaction equations 2-6 - 2-13 the extended forms of the OER reactions for acidic and alkaline environments are shown. The importance of the extended form of the reactions, as given in reaction equations 2-10 - 2-13, is to show that the four-electron transfer process consists of four separate reactions, each with its own electron transfer.⁵

2.2.1 Acidic OER

In an acidic environment, the water molecules (H_2O) are oxidised to produce $\text{O}_{2(g)}$, $\text{H}_{(aq)}^+$ and e^- (see the net reaction in equation 2-3).¹⁵ The mechanism involved in the acidic OER is shown in equations 2-6 - 2-9. The H_2O is dissociated on the surface of the metal and oxidises the surface by binding to it. This dissociation and binding lead to the adsorbed hydroxyl group ($^*OH$), which further oxidises to form adsorbed oxygen ($^*O$). The adsorbed oxygen reacts with H_2O to form $^*OOH$ species on the surface. This $^*OOH$ species is transformed into molecular oxygen.



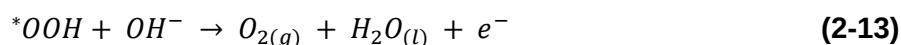
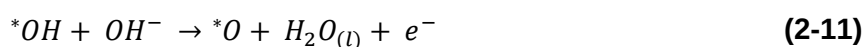
An advantage afforded by the acidic environment is the faster reaction kinetics.²¹

The main disadvantage of the acidic environment is the use of platinum group metals (PGMs), such as Pt, Ru, Pd and Ir, in electrocatalyst production,^{7,21,22} because base metals tend to

dissolve (corrode) under acidic OER conditions. This corrosion leads to catalyst instability.²³ The disadvantage comes from the high cost and increased rarity of these materials.²¹

2.2.2 Alkaline OER

In an alkaline environment, hydroxyl groups (OH^-) are converted into $\text{H}_2\text{O}_{(l)}$ and $\text{O}_{2(g)}$ (see the net reaction in 2-5).¹⁵ The mechanism involved in the alkaline OER is shown in equations 2-10 - 2-13. An OH^- is adsorbed onto the metal surface to form $^*\text{OH}$, which then reacts with a second OH^- to form adsorbed oxygen ($^*\text{O}$) and H_2O , by transfer of an electron and a proton. Finally, a third OH^- reacts with the adsorbed oxygen to form the adsorbed peroxide ($^*\text{OOH}$), which reacts with a fourth OH^- to form molecular oxygen (O_2) and H_2O . The O_2 desorbs from the metal surface.



The oxygen that adsorbs to the electrocatalytic surface changes the oxidation state of the catalyst, making any detailed computational study of the energy states difficult.¹⁹

The greatest advantage of alkaline electrolysis over acidic electrolysis is that the catalysts can be developed from less expensive materials, such as transition metals and their oxides.^{7,9,10} Transition metals studied as materials for OER electrocatalysts include Fe, Co, Mn and Ni.¹ Of these, Ni is considered the state-of-the-art material for OER catalyst design due to having more d-electrons available than the other transition metals.^{2,5,24} The effectiveness of Ni as an electrocatalyst for the OER can be increased by adding secondary materials (typically other transition metals) or adding defects in the structure.^{2,25} These defects can increase the surface area, increasing the electrocatalytic efficacy.^{26,27} Raney nickel, which is a porous Ni structure, is a material that incorporates these defects.¹

However, the most important consideration between the acidic and alkaline environments is the pH influence on the material used in the electrocatalyst design.¹⁵ A more alkaline pH has been found to be more favourable in terms of efficiency than an acidic or neutral pH.^{28,29}

Sustainable and affordable electrocatalysts need to be developed to lower the overpotential and improve the reaction kinetics of the OER. A suitable electrocatalyst for the OER should have an ideal adsorption energy of -3.2eV. This value was determined based on the scaling relation of the free energy of $^*\text{OH}$ to $^*\text{OOH}$.³⁰

2.3 Raney nickel

Raney nickel is a porous or "spongy" Ni structure, first introduced by Murray Raney in 1925.^{31,32} It is a popular catalyst for industrial processes such as the hydrogenation of various compounds, dehalogenation reactions and reduction reactions. This catalyst has also been employed to catalyse hydrogen production in water electrolysis and the decomposition of ammonia.^{27,33–36} Raney nickel is usually prepared from a Ni-M alloy precursor, where M is selectively leached out.³⁷ The metals (M) that have been used to produce the Ni-M alloy precursors are Zn and Al, with Al showing better leaching results than Zn.^{2,36,38–42}

Raney nickel is mainly prepared from a 50:50 weight percentage (wt%) Ni:Al alloy precursor, corresponding to 31.5:68.5 atomic percentage (at%) Ni:Al alloy.^{27,32,41,43} Within this alloy precursor ratio, the following alloy phases are observed, NiAl₃, Ni₂Al₃, NiAl and Ni₃Al. It has been seen that those phases within the ~30 wt% and ~60 wt% Ni content range are ideal for Raney nickel production.^{27,33,37} Devred *et al.*⁴¹ did a study with 40:60 at% Ni:Al, 31.5:68.5 at% Ni:Al and 25:75 at% Ni:Al. This study found that the first ratio only showed the pure Ni₂Al₃ alloy phase, while the other two ratios both showed NiAl, Ni₂Al₃ and Al alloy phases. According to Lee *et al.*³³, non-homogeneity is an ideal quality of Raney nickel precursors.

Studying the surface of Raney nickel is crucial for catalysis because it is where catalytic interactions occur. Experimental XRD data showed that the (111)-surface is the most dominant surface before and after Al leaching from the precursor.^{44,45} A Monte Carlo study of Raney nickel also showed that the (111)-surface and possibly the (100)-surface, are the most prevalent after leaching.⁴⁶ In this study the precursor materials will be referred to as bimetals, while the literature structures will be referred to as alloys where appropriate, because the properties related to alloy formation were not investigated.

2.3.1 Precursor effect on the morphology of Raney nickel

The alloy precursor composition is of critical importance since different phases show different leaching behaviours.⁴⁷ The temperature at which the alloy precursor is prepared influences the alloy phases that are present, determining the precursor's leachability.^{41,48} The precursor alloy composition determines how easily the Al is leached out and determines the final structure's structural integrity and catalytic activity.³⁴ Precursors with higher concentrations of Al could potentially be too friable for practical use due to the small amount of Ni to uphold the structure.⁴⁹ The alloy precursor shown to offer the highest activity is the NiAl₃ phase since Al leaches readily from this phase at lower temperatures (274 – 323 K).⁴⁹ However, other studies have shown that NiAl₃ is not a good precursor material since it does not have any structural integrity once the Al is leached out.^{37,49} The alloy phase Ni₂Al₃ is unreactive in the temperature range in which NiAl₃ leaches readily. Ni₂Al₃ leaches in the temperature range of 343 – 380 K.⁴⁹ Kim *et al.*⁴⁸ found that heat treatment on a Ni-Al alloy precursor containing, NiAl₃, Ni₂Al₃ and NiAl causes the NiAl phase

to dissociate, leaving only NiAl_3 and Ni_2Al_3 . This dissociation leads to faster and more complete leaching of the precursor since it was found that Al leaches faster from the alloy phases, NiAl_3 and Ni_2Al_3 .^{48,50} This faster and more complete leaching of Al leads to larger surface areas.

2.3.2 Preparation of Raney nickel

For the preparation of the Ni-Al alloy precursors, there are four main experimental methods, namely cast-and-crush^{41,51}, gas atomisation⁴¹, mechanical alloying with ball-milling^{36,52} and low-temperature chemical alloying.^{34,53–55} The first two methods involve high energies because they require melting the elemental materials. These alloy precursors are exposed to an alkaline solution to leach out the Al. The specific alloy phase, the temperature at which leaching takes place, the leaching time, and the leaching liquid concentration all affect the morphology of the final Raney nickel structure.^{2,37,47} The alloy phase dependency comes from the different leaching tendencies of different phases.^{41,47}

Additionally, a computational study of chemical systems, such as the influence of the alloy phase on the final Raney nickel structure, could be beneficial for a better understanding of the atomic level behaviour. This study could suggest ways to improve catalytic surfaces experimentally.

2.3.2.1 Precursor alloy preparation

Experimental

The experimental preparation methods can be divided into two types, namely mechanical types (cast-and-crush, gas atomisation, and mechanical alloying with ball-milling) and chemical types (low-temperature chemical alloying (LTCA)). The mechanical methods are very energy-intensive methods. However, the mechanical alloying with ball-milling and the chemical method probably are the least energy-intensive methods for Ni-Al precursor production.

Cast-and-crush⁵¹ is a method where a mixture of molten metals is cast into ingots and annealed at a specific temperature in a hydrogen gas-containing environment to prevent the oxidation of the metals.⁵⁴ The annealed ingots are crushed and ground into powder. The powder is sifted for desired particle sizes, depending on the application.^{37,41,55} Since this method employs the molten form of each of the metals, it is essential to consider the melting temperatures of each. In the case of Ni and Al, the values are 1728.15 K (1455 °C)^{56,57} and 933.47 K (660.32 °C)^{53,58}, respectively. These high temperatures make this method an expensive process.⁵⁵ This method also produces coarse microstructures that are irreproducible with a poor leachability.⁵¹ Bakker et al.⁴⁹ re-melted single-phase alloy precursors, namely NiAl_3 and Ni_2Al_3 , and annealed the re-cast ingots under flowing hydrogen for 24 hours at temperatures of 1103 K and 1363 K, respectively. These annealing temperatures were chosen to be slightly below the peritectic decomposition points for each phase.

Gas atomisation⁴¹ is a method where a stream of molten metal is injected into an atomisation chamber. Mullis *et al.*⁵⁹ used a 2 mm diameter nozzle to inject the molten metal into the chamber and applied a pressure of 40 kPa to ensure a smooth flow. The introduced molten metal stream is disrupted by an inert gas (atomisation gas) to produce liquid droplets. Argon gas can be used as the atomisation gas to prevent oxidation of the molten metal.⁵⁹ The produced droplets are then propelled away from the region in which atomisation takes place. This causes the droplets to rapidly solidify to give a very fine powder with a wide range of particles from 1 – 250 μm .^{41,59,60} This rapid solidification produces useful metastable phases. Gas atomisation produces almost perfectly spherical particle grains.⁶¹

The methods mentioned above require very high energies to melt the alloying elements or alloyed powders due to Ni having a high melting temperature of 1728.15 K (1455 °C).^{56,57} However, the gas atomisation method produces a finer powder than the cast-and-crush method.

Mechanical alloying with ball-milling^{36,52} is a method that employs elemental powders (in the desired wt% ratios) or master alloy powders and mills them using high-energy ball-milling equipment. The employment of master alloys reduces the oxidations of reactive alloy species such as Al. The milling occurs under continuous argon or hydrogen gas flow to create a protective atmosphere that averts contamination. The milling is done with steel balls, with a carefully selected ball-to-powder weight ratio. Due to the continuous collisions of the steel ball with the powders, the powders are alloyed. The finished product must be carefully removed from the ball mill to prevent combustion. The most significant advantage of mechanical alloying is that it produces smaller particles leading to larger surface areas.³⁶ In the case of the Ni-Al system, the steel balls have a diameter of 3.2 mm, and a ball-to-powder weight ratio of 30:1 is used.³⁶ This method can be energy-intensive, although the milling is done at room temperature.

Low-temperature chemical alloying (LTCA)^{34,53–55} is a method specifically designed to reduce the cost of Ni-Al alloy preparation by reducing the temperature at which these alloys are prepared.^{34,55} This method uses AlCl_3 as an activator to lower the reaction temperature to below the melting temperature of Al (933.47 K = 660.32 °C).^{53,58} Lee *et al.*⁵⁵ applied this synthesis method to $\text{Ni}_{1-x}\text{Al}_x$ ($x = 5, 15, 30$ and 50 wt%). The authors mixed the $\text{Ni}_{1-x}\text{Al}_x$ powder with AlCl_3 and placed it into a sealed quartz reactor under a vacuum of 10 Pa pressure. The reactor was then heated to 773 K (500 °C) and maintained for 20h before cooling it to room temperature.

Computational

Some computational studies have investigated the effect of the precursor structure on the Ni-Al alloy synthesis. Schweizer *et al.*⁴⁷ used the MAPS software platform to generate Ni-Al precursors with different Ni content. The authors started with a $2 \times 2 \times 2$ supercell of a NiAl_3 and randomly replaced Ni and Al atoms to obtain compositions with wt%'s of Ni of 40%, 50%, 60% and 70 %. These structures were then quenched to 300K from an unspecified annealing temperature and

subjected to molecular dynamics before further calculations. Another paper used kinetic Monte Carlo and Metropolis Monte Carlo algorithms to study the structure of Raney nickel catalyst materials based on the NiAl_3 alloy phase. This Ni-Al alloy phase was constructed by assuming a 1:3 atomic ratio of Ni:Al and modelled using an AuCu_3 structure as an approximation.⁴⁶

2.3.2.2 Leaching of the active metal

Experimental

The Al is leached out of the Ni-Al precursor using alkaline solutions such as NaOH and KOH.^{32,34,41,51,55} Parameters such as leaching time, temperature, and concentration affect how Al is leached and determines the properties of the final Raney nickel structure.^{33,34,62,63} During the leaching process, hydrogen gas is produced.⁶² Al is also known to undergo pitting corrosion.⁶⁴

The leaching process commonly involves adding the Ni-Al alloy precursor to the leaching solution (20 wt% NaOH, 40 wt% NaOH, 30 wt% KOH, all aqueous solutions).^{32,34,63,65} The reaction is maintained at a constant temperature and allowed to run to completion (when no more hydrogen gas is released). This process takes approximately three hours with a leaching solution of 20 wt% NaOH.⁴¹ In other cases, the leaching is only done for a certain amount of time and removed to avoid over-leaching.³⁴ Over-leaching occurs when all or too much of the Al is removed, leading to structural weakness. The final product is washed with distilled or deionised water to remove the alkaline leaching solution and then dried.^{32,41,55}

The parameters mentioned earlier have a variety of effects. Higher wt% concentrations of NaOH are typically used to prevent the formation of $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, which blocks the pores formed during Al leaching.⁴¹ The leaching time determines the amount of Al leached.⁶² It has been found that leaving a small percentage of Al in the final Raney nickel structure ensures structural integrity.²⁷ The amount of Al left after leaching also strongly influences the catalytic activity. In the case of the hydrogen evolution reaction studied by Divisek *et al.*⁶⁶, the overvoltage increased significantly with a residual Al content below 0.5 at%. The leaching temperatures influence the pore sizes and structures, influencing the final properties.^{24,63} Leaching at higher temperatures leads to lower surface areas (smaller pore size), and lower leaching temperatures lead to higher surface areas (larger pore size) in the final Raney nickel catalyst.^{24,63,67} The lower surface areas at higher temperature leaching are due to structural rearrangements. However, compromise is usually made on the surface area since Al leaches slowly at a lower temperature.²⁴

Computational

Schweizer *et al.*⁴⁷ leached Al from the prepared Ni-Al alloy phases and considered three cases: 100% Al leached, 95% Al leached, and 90% Al leached. However, the authors did not specify the method of Al removal. Barnard *et al.*⁴⁶ used kinetic Monte Carlo and Metropolis Monte Carlo algorithms to simulate the leaching of the Al from the bulk alloy structures. The authors did not

provide a clear mechanism for this process. It was assumed that mechanisms involved the dissolution of Al and the simultaneous diffusion of the atoms Ni or Al atoms.

2.3.3 Summary of previous findings

Raney nickel-type catalysts, introduced by Murray Raney in 1925,^{31,32} have been widely used for many reactions, such as hydrogenation reactions of organic compounds, the decomposition of ammonia, and fuel cell reactions.^{33,67} Several experimental and computational studies have been done on the influence of the precursor on the morphology of the final Raney nickel product.⁴⁷ It has been found (computationally and experimentally) that the difference in leachability of different phases within the Ni-Al system can lead to different pore sizes.⁴⁷ The leaching temperature can also influence the morphology of the final Raney nickel catalyst. Higher temperatures give lower surface areas, whereas low temperatures give higher surface areas.^{24,63,67} A larger surface area benefits the adsorption of active species in electrocatalysts. Raney nickel has been applied to alkaline water electrolysis⁶⁸ and shown to be a good catalyst and a cathode for the HER.^{2,69} Raney nickel and porous nickel structures have also received increasing attention as possible anode catalysts for the OER.^{2,26,38,70} However, most studies have focused on NiAl₃, Ni₂Al₃, NiAl and Ni₃Al precursors, leaving other potential ideal phases unstudied.

2.4 Computational background

This study utilises the density functional theory (DFT)⁷¹, site occupation disorder (SOD)⁷², and general utility lattice program (GULP)⁷³ to construct and study the bimetallic precursors and Raney nickel structure.

2.4.1 The density functional theory (DFT)

Density Functional Theory (DFT)⁶⁸ is a simplified quantum-mechanical approach that uses electron density instead of a many-electron wave function.⁷¹ The total energy of a system is expressed as a unique functional of the electron density. The generalised-gradient approximation (GGA), an extension of the local density approximation (LDA), is used since it offers improvements to the atomisation energies, cohesive energies, total energies and energy barriers of solids and molecules.^{71,74} The PBE (Perdew, Burke and Ernzerhof) functional^{75,76} within the GGA, where all the parameters are fundamental constants, is widely used and validated for various systems.^{22,77–79} However, the GGA tends to underestimate very weak, long-range forces related to van der Waals (vdW) interactions and the bandgap.^{71,74} Considering noncovalent forces, such as the vdW interactions and, in some cases, hydrogen bonds, is essential for evaluating the formation and stability of molecules and solids and understanding their function.^{80,81} These shortcomings of the GGA can be corrected by taking dispersion into account, using methods such as the Tkatchenko-Scheffler (TS)⁸⁰ or Grimme⁸¹ correction scheme. Spin polarisation can also be considered in the model development.

The k-points of a system are points that are used in the calculations for sampling the Brillouin zone. The Brillouin zone of a given crystal is the unit cell constructed within the reciprocal crystal lattice that determines the symmetry of the system.⁸² In some cases, the Brillouin zone can be reduced to the irreducible Brillouin zone. This irreducible volume is the smallest possible cell constructed within the reciprocal space, representing the symmetry of the whole crystal structure. The k-points differ depending on whether a bulk or surface slab is considered. For a bulk, the k-points are typically given as a coordinate value of (x×y×z), while for a surface slab, the k-points are given as a coordinate value of (x×y×1). The higher the number of k-points, the more densely packed the points are, and the higher the accuracy is that is achieved for the overall cell symmetry.⁸³

A computational model needs to be comparable with the available literature to be valid. A comprehensive DFT based model for the study of pure Ni and Al metals (bulks and low-index surfaces) has been developed and subsequently applied to a Ni-Al system.

2.4.1.1 Electronic property calculation

Electronic properties of surfaces can be obtained through the measurement of the surface energies (γ), work function (Φ), and d-band centre (ϵ_d).

A system's surface energy (γ) is the energy required to cleave a new surface. This energy is calculated using equation 2-14⁸⁴, where γ is the surface energy of the unconstrained surface slab. $E_{surface\ slab}$ is the total energy of the surface slab, N is the ratio of the number of atoms in the surface slab to the number of atoms in the bulk structure ($N_{surface\ slab} : N_{bulk\ structure}$), $E_{bulk\ structure}$ is the energy of the bulk system, and A is the area of the surface slab.

$$\gamma = \frac{E_{surface\ slab} - NE_{bulk\ structure}}{2A} \quad (2-14)$$

Surfaces with lower surface energies are more stable, while surfaces with higher surface energies are less stable. It can be thought of as a measurement of the additional energy that surface atoms possess due to a variety of factors, such as broken bonds that result in lower coordination numbers.⁸⁵ Unstable surfaces have been shown to undergo surface reconstruction in order to gain stability.⁸⁶

The work function (Φ), which is related to the surface energy, is defined as the energy required to remove an electron from the bulk interior. Work functions have also been shown to give an indication of the ease of surface atomic species removal.⁸⁷ The work function is calculated using equation 2-15⁸⁴, where e is the electron charge, ϕ is the electrostatic potential close to the surface in a vacuum, and E_F is the Fermi energy level within the surface.

$$\Phi = -e\phi - E_F \quad (2-15)$$

When using the CAMbridge Serial Total Energy Package (CASTEP)⁸⁸, the work function is automatically calculated within the calculations of the potentials. These potentials are the averaged electrostatic potentials of the planes oriented perpendicular to the surface slabs normal.

The ability of a transition metal surface to form a bond with a species depends on the valence d-electrons of the metal on the slab's surface; the orbitals can be observed from the partial density of states (PDOS), specifically the d-states. The d-band centre has therefore been identified as a descriptor of the activity of catalyst surfaces.⁸⁹ By comparing the d-band centre of the metal surface before and after the adsorption of the species, the reactivity of a metal surface can be assessed.⁹⁰ An upward shift of the d-band centre towards the Fermi level corresponds to stronger surface-adsorbate binding, whereas a downward shift in the d-band centre (Figure 2-1) corresponds to a weaker surface-adsorbate binding.^{89,91} The d-band centre can be calculated from the d-bandwidth using the partial Density of States (PDOS) graph, as illustrated in Figure 2-2. This graph can be obtained by calculating the PDOS during geometric optimisations with DFT.

The calculation of the d-band centre is illustrated in Figure 2-2. The d-band centre is calculated from the d-bandwidth, and the area under the d-band curve is calculated by integrating over the xy-plane region bounded by this curve. The integral (I) value is then divided by 2 to find the mid-point of the d-band ($I/2$), which is the y-value, and the corresponding x-value is the d-band centre (ϵ_d).

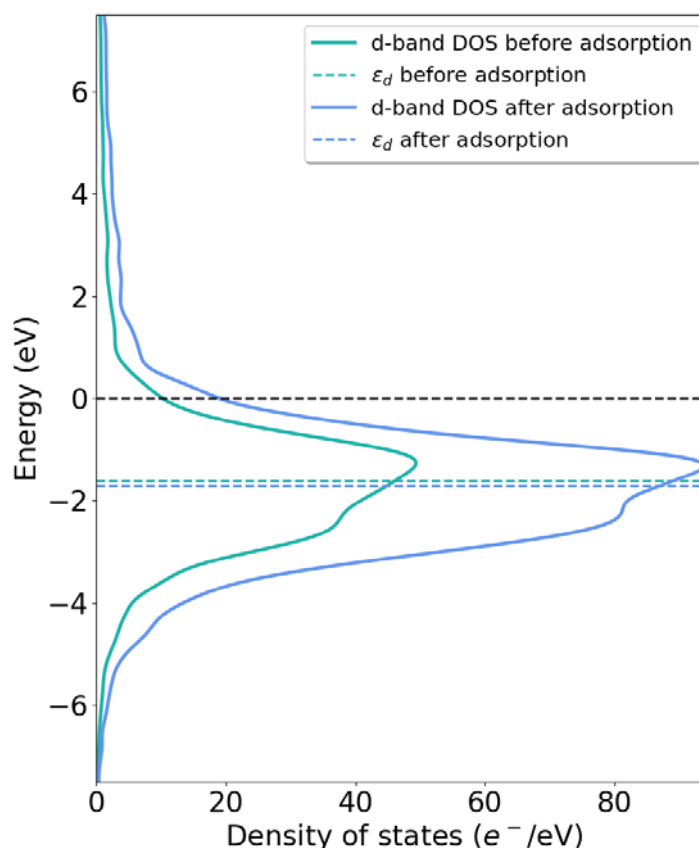


Figure 2-1 Representation of a positive (downward) d-band shift

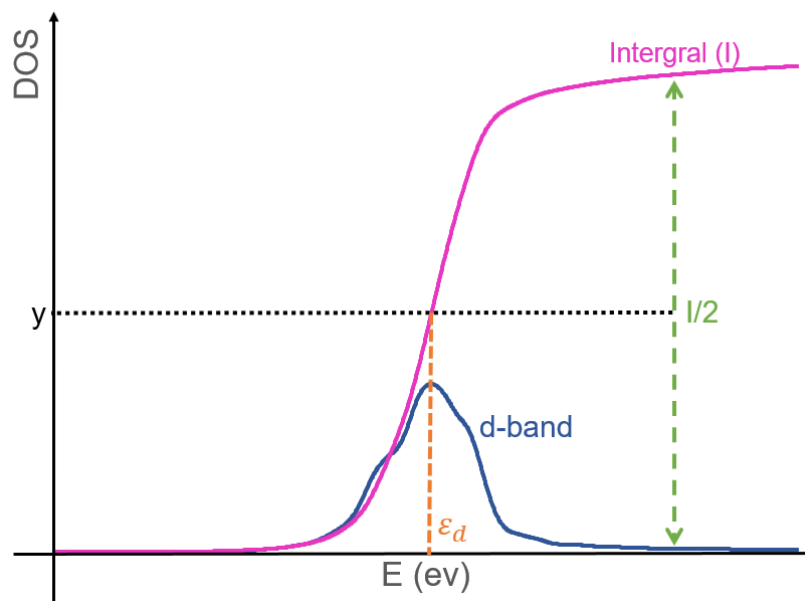


Figure 2-2 The d-band centre (ϵ_d) can be determined using integration and a simple representation of the d-band width.

2.4.1.2 Atomic removal energy

In this work, the manual leaching of atom X from the desired surface is done by selecting and deleting the chosen atoms. The energy required to remove atom X from the surface can be related to the bond dissociation energy (BDE).

For a molecule KL which dissociates to $K\cdot$ and $L\cdot$ the dissociation energy is given by equation 2-16:⁹²

$$D_{KL} = \Delta E_a^*(KL) - \Delta E_a^*(K\cdot) - \Delta E_a^*(L\cdot) \quad (2-16)$$

where D_{KL} is the dissociation energy of molecule KL , $\Delta E_a^*(KL)$ the atomisation energy of the ground-state molecule KL , $\Delta E_a^*(K\cdot)$ the atomisation energy of the ground-state free radical $K\cdot$, and $\Delta E_a^*(L\cdot)$ the atomisation energy of the ground-state free radical $L\cdot$.

Similarly, the energy required to remove atom X from a surface slab can then be calculated using the following general equation:

$$E_{X\text{ removal}} = E_{\text{surface slab}(b)} - E_{\text{surface slab}(a)} - E_X \quad (2-17)$$

where $E_{X\text{ removal}}$ is the energy required to remove atom X from the surface slab, $E_{\text{surface slab}(b)}$ is the energy of the optimised surface slab before the removal of atom X, $E_{\text{surface slab}(a)}$ is the energy of the optimised surface slab after the removal of atom X, and E_X is the energy of atom X.

2.4.1.3 Adsorption energy

The activity of the catalyst surface is determined with the d-band centre shift after the adsorption of a species (see section 2.4.1.1), along with the adsorption energy (E_{ads}) of a species onto the catalytic surface, calculated using the following equation:⁹³

$$E_{ads} = E_{(adsorbate/surface\ slab)} - E_{adsorbate} - E_{surface\ slab} \quad (2-18)$$

E_{ads} is the adsorption energy, $E_{(adsorbate/surface\ slab)}$ is the energy of the optimised adsorbate/surface slab system, $E_{adsorbate}$ is the energy of the optimised adsorbate species and $E_{surface\ slab}$ is the energy of the optimised surface slab before adsorption.

2.4.2 Site occupation disorder program (SOD)

The Site Occupation Disorder (SOD)⁷² program utilises the site occupancy disorder phenomenon in solid-state chemistry.⁷² This phenomenon is seen in the structures of solid mineral solutions, synthetic non-stoichiometric compounds, and metallic alloys. In the SOD program, a primary bulk structure is set up, and secondary elements are substituted into the available lattice positions to build new bulk structures. The size of the bulk structure determines the number of possible configurations.

First, a unit cell is set up using the primary element's lattice parameters (lattice length and angles) and the space-group data. The primary unit cell is then expanded to the desired supercell size. When expanding the cell, the computational cost must be considered since the larger the supercell, the higher the number of configurations built by SOD and the more costly the calculation. A set of geometric operators (translation, rotation, and reflection) are considered to reduce the number of configurations obtained. The space-group data helps to define the symmetry of the primary structure since it provides a reference point for these symmetry operators.⁹⁴ These operators work in conjunction with the symmetry of the crystal structure of the primary metal and allow for the identification of unique configurations. Symmetry-bound configurations tend to have similar atomic arrangements within the larger bulk structure; this leads to similar bulk energies. These similar energies are the reason that these configurations can be reduced to unique configurations, with a single configuration representing many. Each unique configuration is accompanied by a degeneracy value, Ω_m , which is the number of symmetry-bound configurations identified in the larger bulk structure.

The SOD program includes the calculations of thermodynamical properties for the configurations, such as the degeneracy entropy (S_m), the reduced energy ($\widetilde{E}_m$) (similar to Gibbs-free energy) and the probability of existence (P_m) via Boltzmann probability distributions by taking a temperature into account for the calculations.⁷² These properties can be calculated using the following equations:⁷²

$$S_m = k_B T \ln \Omega_m \quad (2-19)$$

$$\widetilde{E}_m = E_m - TS_m \quad (2-20)$$

$$P_m = \frac{1}{Z} \Omega_m e^{(-E_m/k_B T)} \quad (2-21)$$

where m is the specific configuration, k_B is Boltzmann's constant ($8.6173 \times 10^{-5} \text{ eV} \cdot \text{K}^{-1}$), T is the temperature, Ω_m the configuration degeneracy, $\widetilde{E}_m$ and E_m is the reduced and configuration energy, respectively. P_m is the Boltzmann probability distribution, and the partition function is given by Z in the following equation:

$$Z = \sum_{m=1}^N e^{(-E_m/k_B T)} \quad (2-22)$$

These thermodynamic considerations require an energy input, which can be calculated using a program such as the General Utility Lattice Program (GULP).

2.4.3 The general utility lattice program (GULP)

The General Utility Lattice Program (GULP)⁷³ is used to do approximated geometrical optimisations and provide the bulk energies of the optimised structures. GULP calculations use interatomic potentials (force fields) from the Sutton-Chen⁹⁵ library of potentials. These force-field methods for many-body systems lead to accurate descriptions of the metals and their bimetals.⁷³

References

- (1) Lyu, F.; Wang, Q.; Choi, S. M.; Yin, Y. Noble-Metal-Free Electrocatalysts for Oxygen Evolution. *Small* **2019**, *15* (1), 1804201.
- (2) Sapountzi, F. M.; Gracia, J. M.; Weststrate, C. J. (Kees-Jan).; Fredriksson, H. O. A.; Niemantsverdriet, J. W. (Hans). Electrocatalysts for the Generation of Hydrogen, Oxygen and Synthesis Gas. *Progress in Energy and Combustion Science*. Elsevier Ltd January 1, 2017, pp 1–35. <https://doi.org/10.1016/j.pecs.2016.09.001>.
- (3) Zeng, K.; Zhang, D. Recent Progress in Alkaline Water Electrolysis for Hydrogen Production and Applications. *Prog Energy Combust Sci* **2010**, *36* (3), 307–326. <https://doi.org/10.1016/j.pecs.2009.11.002>.
- (4) Mallouk, T. E. Water Electrolysis: Divide and Conquer. *Nat Chem* **2013**, *5* (5), 362–363.
- (5) Doyle, R. L.; Lyons, M. E. G. The Oxygen Evolution Reaction: Mechanistic Concepts and Catalyst Design. In *Photoelectrochemical solar fuel production*; Springer, 2016; pp 41–104.
- (6) Khan, M. A.; Zhao, H.; Zou, W.; Chen, Z.; Cao, W.; Fang, J.; Xu, J.; Zhang, L.; Zhang, J. Recent Progresses in Electrocatalysts for Water Electrolysis. *Electrochemical Energy Reviews* **2018**, *1* (4), 483–530.
- (7) Salonen, L. M.; Petrovykh, D. Y.; Kolen'ko, Y. V. Sustainable Catalysts for Water Electrolysis: Selected Strategies for Reduction and Replacement of Platinum-Group Metals. *Materials Today Sustainability* **2021**, 100060. <https://doi.org/10.1016/j.mtsust.2021.100060>.
- (8) Brauns, J.; Turek, T. Alkaline Water Electrolysis Powered by Renewable Energy: A Review. *Processes*. MDPI AG February 1, 2020. <https://doi.org/10.3390/pr8020248>.
- (9) Colli, A. N.; Girault, H. H.; Battistel, A. Non-Precious Electrodes for Practical Alkaline Water Electrolysis. *Materials* **2019**, *12* (8), 1336. <https://doi.org/10.3390/ma12081336>.

- (10) Fabbri, E.; Haberer, A.; Waltar, K.; Kötze, R.; Schmidt, T. J. Developments and Perspectives of Oxide-Based Catalysts for the Oxygen Evolution Reaction. *Catal Sci Technol* **2014**, 4 (11), 3800–3821. <https://doi.org/10.1039/c4cy00669k>.
- (11) Santos, D. M. F.; Sequeira, C. A. C.; Figueiredo, J. L. Hydrogen Production by Alkaline Water Electrolysis. *Quim Nova* **2013**, 36 (8), 1176–1193.
- (12) Atkins, P. W. (Peter W.; de Paula, Julio. *Atkins' Physical Chemistry*, 9th ed.; Oxford University Press, 2010.
- (13) Yang, J.; Jang, M. J.; Zeng, X.; Park, Y. S.; Lee, J.; Choi, S. M.; Yin, Y. Non-Precious Electrocatalysts for Oxygen Evolution Reaction in Anion Exchange Membrane Water Electrolysis: A Mini Review. *Electrochem commun* **2021**, 131, 107118. <https://doi.org/10.1016/J.ELECOM.2021.107118>.
- (14) Lao, M.; Li, P.; Jiang, Y.; Pan, H.; Dou, S. X.; Sun, W. From Fundamentals and Theories to Heterostructured Electrocatalyst Design: An in-Depth Understanding of Alkaline Hydrogen Evolution Reaction. *Nano Energy* **2022**, 98, 107231. <https://doi.org/10.1016/J.NANOEN.2022.107231>.
- (15) Liang, Q.; Brocks, G.; Bieberle-Hütter, A. Oxygen Evolution Reaction (OER) Mechanism under Alkaline and Acidic Conditions. *J Phys Energy* **2021**, 3 (2), 26001. <https://doi.org/10.1088/2515-7655/abdc85>.
- (16) Strmcnik, D.; Lopes, P. P.; Genorio, B.; Stamenkovic, V. R.; Markovic, N. M. Design Principles for Hydrogen Evolution Reaction Catalyst Materials. *Nano Energy* **2016**, 29, 29–36. <https://doi.org/10.1016/J.NANOEN.2016.04.017>.
- (17) Oyinbo, S. T.; Jen, T. C. Hydrogen Evolution Reaction in an Alkaline Environment through Nanoscale Ni, Pt, NiO, Fe/Ni and Pt/Ni Surfaces: Reactive Molecular Dynamics Simulation. *Mater Chem Phys* **2021**, 271, 124886. <https://doi.org/10.1016/J.MATCHEMPHYS.2021.124886>.
- (18) Lasia, A. Hydrogen Evolution Reaction. In *Handbook of Fuel Cells*; John Wiley & Sons, Ltd, 2010. <https://doi.org/10.1002/9780470974001.f204033>.
- (19) Schalenbach, M.; Zeradjian, A. R.; Kasian, O.; Cherevko, S.; Mayrhofer, K. J. J. A Perspective on Low-Temperature Water Electrolysis - Challenges in Alkaline and Acidic Technology. *Int J Electrochem Sci* **2018**, 13 (2), 1173–1226. <https://doi.org/10.20964/2018.02.26>.
- (20) Zhao, X.; Liu, X.; Huang, B.; Wang, P.; Pei, Y. Hydroxyl Group Modification Improves the Electrocatalytic ORR and OER Activity of Graphene Supported Single and Bi-Metal Atomic Catalysts (Ni, Co, and Fe). *J Mater Chem A Mater* **2019**, 7 (42), 24583–24593. <https://doi.org/10.1039/c9ta08661g>.
- (21) Lei, Z.; Wang, T.; Zhao, B.; Cai, W.; Liu, Y.; Jiao, S.; Li, Q.; Cao, R.; Liu, M. Recent Progress in Electrocatalysts for Acidic Water Oxidation. *Advanced Energy Materials*. Wiley-VCH Verlag June 1, 2020, p 2000478. <https://doi.org/10.1002/aenm.202000478>.
- (22) Botha, L. M.; Santos-Carballal, D.; Terranova, U.; Quesne, M. G.; Ungerer, M. J.; Van Sittert, C. G. C. E.; De Leeuw, N. H. Mixing Thermodynamics and Electronic Structure of the Pt_{1-x}Ni_x (0 ≤ x ≤ 1) Bimetallic Alloy. *RSC Adv* **2019**, 9 (30), 16948–16954. <https://doi.org/10.1039/c9ra02320h>.
- (23) Pan, S.; Li, H.; Liu, D.; Huang, R.; Pan, X.; Ren, D.; Li, J.; Shakouri, M.; Zhang, Q.; Wang, M.; Wei, C.; Mai, L.; Zhang, B.; Zhao, Y.; Wang, Z.; Graetzel, M.; Zhang, X. Efficient and

- Stable Noble-Metal-Free Catalyst for Acidic Water Oxidation. *Nat Commun* **2022**, 13 (1). <https://doi.org/10.1038/s41467-022-30064-6>.
- (24) Smith, A. J.; Wainwright, M. S. Skeletal Metal Catalysts. *Handbook of Heterogeneous Catalysis* **2008**, 92–100. <https://doi.org/10.1002/9783527610044.HETCAT0007>.
 - (25) Jamesh, M. I.; Sun, X. Recent Progress on Earth Abundant Electrocatalysts for Oxygen Evolution Reaction (OER) in Alkaline Medium to Achieve Efficient Water Splitting – A Review. *Journal of Power Sources*. Elsevier B.V. October 1, 2018, pp 31–68. <https://doi.org/10.1016/j.jpowsour.2018.07.125>.
 - (26) Pierozynski, B.; Mikolajczyk, T.; Luba, M.; Zolfaghari, A. Kinetics of Oxygen Evolution Reaction on Nickel Foam and Platinum-Modified Nickel Foam Materials in Alkaline Solution. *Journal of Electroanalytical Chemistry* **2019**, 847, 113194. <https://doi.org/10.1016/j.jelechem.2019.113194>.
 - (27) Schweizer, S.; Chaudret, R.; Low, J.; Subramanian, L. Molecular Modeling and Simulation of Raney Nickel: From Alloy Precursor to the Final Porous Catalyst. *Comput Mater Sci* **2015**, 99, 336–342.
 - (28) Vazhayil, A.; Vazhayal, L.; Thomas, J.; Ashok C, S.; Thomas, N. A Comprehensive Review on the Recent Developments in Transition Metal-Based Electrocatalysts for Oxygen Evolution Reaction. *Applied Surface Science Advances* **2021**, 6, 100184. <https://doi.org/10.1016/J.APSADV.2021.100184>.
 - (29) Schalenbach, M.; Tjarks, G.; Carmo, M.; Lueke, W.; Mueller, M.; Stolten, D. Acidic or Alkaline? Towards a New Perspective on the Efficiency of Water Electrolysis. *J Electrochem Soc* **2016**, 163 (11), F3197–F3208. <https://doi.org/10.1149/2.0271611jes>.
 - (30) Li, J. Oxygen Evolution Reaction in Energy Conversion and Storage: Design Strategies Under and Beyond the Energy Scaling Relationship. *Nano-Micro Letters*. Springer Science and Business Media B.V. December 1, 2022. <https://doi.org/10.1007/s40820-022-00857-x>.
 - (31) Raney, M. *Method of Producing Finely-Divided Nickel*; 1926.
 - (32) Raney, M. Catalysts from Alloys: Nickel Catalysts. *Ind Eng Chem* **1940**, 32 (9), 1199–1203. <https://doi.org/10.1021/ie50369a030>.
 - (33) Lee, G. D.; Suh, C. S.; Park, J. H.; Park, S. S.; Hong, S. S. Raney Ni Catalysts Derived from Different Alloy Precursors (I) Morphology and Characterization. *Korean Journal of Chemical Engineering* **2005**, 22 (3), 375–381. <https://doi.org/10.1007/BF02719414>.
 - (34) Lee, Y. J.; Lee, Y. S.; Cha, J. Y.; Jo, Y. S.; Jeong, H.; Sohn, H.; Yoon, C. W.; Kim, Y.; Kim, K. B.; Nam, S. W. Development of Porous Nickel Catalysts by Low-Temperature Ni–Al Chemical Alloying and Post Selective Al Leaching, and Their Application for Ammonia Decomposition. *Int J Hydrogen Energy* **2020**, 45 (38), 19181–19191. <https://doi.org/10.1016/j.ijhydene.2020.05.025>.
 - (35) Chiba, T.; Okimoto, M.; Nagai, H.; Takata, Y. Electrocatalytic Reduction Using Raney Nickel. *Bull Chem Soc Jpn* **1983**, 56 (3), 719–723. <https://doi.org/10.1246/bcsj.56.719>.
 - (36) Zeifert, B.; Blásquez, J. S.; Moreno, J. G. C.; Calderón, H. A. Raney-Nickel Catalysts Produced by Mechanical Alloying. *Reviews on Advanced Materials Science* **2008**, 18 (7), 633–639.
 - (37) Smith, A. J.; Trimm, D. L. The Preparation of Skeletal Catalysts. *Annual Review of Materials Research*. 2005, pp 127–142. <https://doi.org/10.1146/annurev.matsci.35.102303.140758>.

- (38) Gannon, W. J. F. F.; Dunnill, C. W. Raney Nickel 2.0: Development of a High-Performance Bifunctional Electrocatalyst. *Electrochim Acta* **2019**, 322, 134687. <https://doi.org/10.1016/j.electacta.2019.134687>.
- (39) Klein, J. C.; Hercules, D. M. Surface Analysis of Raney Nickel Alloys. *Anal Chem* **1981**, 53 (6), 754–758.
- (40) Fouilloux, P.; Martin, G. A.; Renouprez, A. J.; Moraweck, B.; Imelik, B.; Prettre, M. A Study of the Texture and Structure of Raney Nickel. *J Catal* **1972**, 25 (2), 212–222. [https://doi.org/10.1016/0021-9517\(72\)90220-5](https://doi.org/10.1016/0021-9517(72)90220-5).
- (41) Devred, F.; Gieske, A. H.; Adkins, N.; Dahlborg, U.; Bao, C. M.; Calvo-Dahlborg, M.; Bakker, J. W.; Nieuwenhuys, B. E. Influence of Phase Composition and Particle Size of Atomised Ni-Al Alloy Samples on the Catalytic Performance of Raney-Type Nickel Catalysts. *Appl Catal A Gen* **2009**, 356 (2), 154–161. <https://doi.org/10.1016/j.apcata.2008.12.039>.
- (42) Divisek, J.; Mergel, J.; Schmitz, H. Advanced Water Electrolysis and Catalyst Stability under Discontinuous Operation. *Int J Hydrogen Energy* **1990**, 15 (2), 105–114. [https://doi.org/10.1016/0360-3199\(90\)90032-T](https://doi.org/10.1016/0360-3199(90)90032-T).
- (43) Tanaka, S.; Hirose, N.; Tanaki, T.; Ogata, Y. H. Effect of Ni-Al Precursor Alloy on the Catalytic Activity for a Raney-Ni Cathode. *J Electrochem Soc* **2000**, 147 (6), 2242. <https://doi.org/10.1149/1.1393514>.
- (44) Yang, Y.; Luo, M.; Zhang, W.; Sun, Y.; Chen, X.; Guo, S. Metal Surface and Interface Energy Electrocatalysis: Fundamentals, Performance Engineering, and Opportunities. *Chem* **2018**, 4 (9), 2054–2083. <https://doi.org/10.1016/J.CHEMPR.2018.05.019>.
- (45) Oura, K.; Lifshits, V. G.; Saranin, A. A.; Zotov, A. v; Katayama, M. *Surface Science: An Introduction*; Springer Berlin Heidelberg, 2013.
- (46) Barnard, N. C.; Brown, S. G. R.; Devred, F.; Bakker, J. W.; Nieuwenhuys, B. E.; Adkins, N. J. A Quantitative Investigation of the Structure of Raney-Ni Catalyst Material Using Both Computer Simulation and Experimental Measurements. *J Catal* **2011**, 281 (2), 300–308. <https://doi.org/10.1016/j.jcat.2011.05.010>.
- (47) Schweizer, S.; Chaudret, R.; Spyriouni, T.; Low, J.; Subramanian, L. Influence of the Precursor Composition and Reaction Conditions on Raney-Nickel Catalytic System. In *Foundations of Molecular Modeling and Simulation: Select Papers from FOMMS 2015*; Snurr, R. Q., Adjiman, C. S., Kofke, D. A., Eds.; Springer Singapore: Singapore, 2016; pp 125–135. https://doi.org/10.1007/978-981-10-1128-3_8.
- (48) Kim, J.-E.; Bae, K.-K.; Park, C.-S.; Jeong, S.-U.; Baik, K.-H.; Kim, J.-W.; Kang, K.-S.; Lee, K.-B.; Kim, Y.-H. Electrochemical Characterization of Raney Nickel Electrodes Prepared by Atmospheric Plasma Spraying for Alkaline Water Electrolysis. **2018**. <https://doi.org/10.1016/j.jiec.2018.10.010>.
- (49) Bakker, M. L.; Young, D. J.; Wainwright, M. S. Selective Leaching of NiAl₃ and Ni₂Al₃ Intermetallics to Form Raney Nickels. *J Mater Sci* **1988**, 23 (11), 3921–3926. <https://doi.org/10.1007/BF01106814>.
- (50) Huang, W.; Chang, Y. A. A Thermodynamic Analysis of the Ni-Al System. *Intermetallics (Barking)* **1998**, 6 (6), 487–498. [https://doi.org/10.1016/S0966-9795\(97\)00099-X](https://doi.org/10.1016/S0966-9795(97)00099-X).
- (51) Jarvis, D. J.; Voss, D. IMPRESS Integrated Project—An Overview Paper. *Materials Science and Engineering: A* **2005**, 413–414. <https://doi.org/10.1016/j.msea.2005.09.066>.
- (52) Jones, A. R. Mechanical Alloying. In *Encyclopedia of Materials: Science and Technology*; Elsevier, 2001. <https://doi.org/10.1016/B0-08-043152-6/00912-8>.

- (53) Ham, H. C.; Maganyuk, A. P.; Han, J.; Yoon, S. P.; Nam, S. W.; Lim, T. H.; Hong, S. A. Preparation of Ni-Al Alloys at Reduced Temperature for Fuel Cell Applications. *J Alloys Compd* **2007**, *446–447*, 733–737. <https://doi.org/10.1016/j.jallcom.2007.02.096>.
- (54) Jang, S. C.; Lee, B. Y.; Nam, S. W.; Ham, H. C.; Han, J.; Yoon, S. P.; Oh, S. G. New Method for Low Temperature Fabrication of Ni–Al Alloy Powder for Molten Carbonate Fuel Cell Applications. *Int J Hydrogen Energy* **2014**, *39* (23), 12259–12265. <https://doi.org/10.1016/J.IJHYDENE.2014.01.097>.
- (55) Lee, Y. J.; Lee, B. Y.; Yoon, C. W.; Lee, Y. S.; Jeong, H.; Choi, S. H.; Kim, D. H.; Kim, Y.; Kim, K. B.; Nam, S. W. Facile Synthesis of Micro-Sized Ni–Al Alloy Powders through Low-Temperature Chemical Alloying. *J Alloys Compd* **2020**, *815*, 152392. <https://doi.org/10.1016/j.jallcom.2019.152392>.
- (56) Technical Data for the Element Nickel in the Periodic Table. <https://periodictable.com/Elements/028/data.html>.
- (57) Habashi, F. Nickel, Physical and Chemical Properties. In *Encyclopedia of Metalloproteins*; Springer New York, 2013; pp 1520–1520. https://doi.org/10.1007/978-1-4614-1533-6_338.
- (58) *Technical data for the element Aluminum in the Periodic Table*. <https://periodictable.com/Elements/013/data.html> (accessed 2020-10-15).
- (59) Mullis, A. M.; Bigg, T. D.; Adkins, N. J. A Microstructural Investigation of Gas Atomized Raney Type Al-27.5 at.% Ni Catalyst Precursor Alloys. *J Alloys Compd* **2015**, *648*, 139–148. <https://doi.org/10.1016/J.JALLCOM.2015.05.142>.
- (60) Afonso, C. R. M.; Spinelli, J. E.; Bolfarini, C.; Botta, W. J.; Kiminami, C. S.; Garcia, A. Rapid Solidification of an Al-5Ni Alloy Processed by Spray Forming. *Materials Research* **2012**, *15* (5), 779–785. <https://doi.org/10.1590/S1516-14392012005000044>.
- (61) Bao, C. M.; Dahlborg, U.; Adkins, N.; Calvo-Dahlborg, M. Structural Characterisation of Al–Ni Powders Produced by Gas Atomisation. *J Alloys Compd* **2009**, *481* (1–2), 199–206. <https://doi.org/10.1016/J.JALLCOM.2009.03.059>.
- (62) Fernandez, A. M.; Cano, U. Alkaline Electrolysis with Skeletal Ni Catalysts. In *Electrolysis*; InTech, 2012. <https://doi.org/10.5772/50617>.
- (63) Devred, F.; Hoffer, B. W.; Sloof, W. G.; Kooyman, P. J.; van Langeveld, A. D.; Zandbergen, H. W. The Genesis of the Active Phase in Raney-Type Catalysts: The Role of Leaching Parameters. *Appl Catal A Gen* **2003**, *244* (2), 291–300. [https://doi.org/10.1016/S0926-860X\(02\)00601-4](https://doi.org/10.1016/S0926-860X(02)00601-4).
- (64) Akpanyung, K. v.; Loto, R. T. Pitting Corrosion Evaluation: A Review. In *Journal of Physics: Conference Series*; Institute of Physics Publishing, 2019; Vol. 1378. <https://doi.org/10.1088/1742-6596/1378/2/022088>.
- (65) Young, D. J.; Wainwright, M. S.; Anderson, R. B. Raney Nickel-Copper Catalysts. I. Structure and Leaching Properties. *J Catal* **1980**, *64* (1), 116–123. [https://doi.org/10.1016/0021-9517\(80\)90484-4](https://doi.org/10.1016/0021-9517(80)90484-4).
- (66) Divisek, J.; Schmitz, H.; Steffen, B. Electrocatalyst Materials for Hydrogen Evolution. *Electrochim Acta* **1994**, *39* (11–12), 1723–1731. [https://doi.org/10.1016/0013-4686\(94\)85157-3](https://doi.org/10.1016/0013-4686(94)85157-3).
- (67) Fouilloux, P. The Nature of Raney Nickel, Its Adsorbed Hydrogen and Its Catalytic Activity for Hydrogenation Reactions (Review). *Appl Catal* **1983**, *8* (1), 1–42. [https://doi.org/10.1016/0166-9834\(83\)80051-7](https://doi.org/10.1016/0166-9834(83)80051-7).

- (68) Kim, J. E.; Bae, K. K.; Park, C. S.; Jeong, S. U.; Baik, K. H.; Kim, J. W.; Kang, K. S.; Lee, K. B.; Kim, Y. H. Electrochemical Characterization of Raney Nickel Electrodes Prepared by Atmospheric Plasma Spraying for Alkaline Water Electrolysis. *Journal of Industrial and Engineering Chemistry* **2019**, *70*, 160–168. <https://doi.org/10.1016/j.jiec.2018.10.010>.
- (69) Zhuang, L. Defect Engineering of Nonprecious Metal Based Catalysts for Oxygen Evolution Reaction. **2019**.
- (70) Delgado, D.; Bizzotto, F.; Zana, A.; Arenz, M. Accelerated Durability Test for High-Surface-Area Oxyhydroxide Nickel Supported on Raney Nickel as Catalyst for the Alkaline Oxygen Evolution Reaction. *ChemPhysChem* **2019**, *20* (22), 3147–3153. <https://doi.org/10.1002/cphc.201900195>.
- (71) Hasnip, P. J.; Refson, K.; Probert, M. I. J.; Yates, J. R.; Clark, S. J.; Pickard, C. J. Density Functional Theory in the Solid State. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*. The Royal Society Publishing March 13, 2014. <https://doi.org/10.1098/rsta.2013.0270>.
- (72) Grau-Crespo, R.; Hamad, S.; Catlow, C. R. A.; De Leeuw, N. H. Symmetry-Adapted Configurational Modelling of Fractional Site Occupancy in Solids. *Journal of Physics: Condensed Matter* **2007**, *19* (25), 256201. <https://doi.org/10.1088/0953-8984/19/25/256201>.
- (73) Gale, J. D.; Rohl, A. L. The General Utility Lattice Program (GULP). *Mol Simul* **2003**, *29* (5), 291–341. <https://doi.org/10.1080/0892702031000104887>.
- (74) Sousa, S. F.; Fernandes, P. A.; Ramos, M. J. General Performance of Density Functionals. *Journal of Physical Chemistry A* **2007**, *111* (42), 10439–10452. <https://doi.org/10.1021/jp0734474>.
- (75) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys Rev Lett* **1996**, *77* (18), 3865–3868. <https://doi.org/10.1103/PhysRevLett.77.3865>.
- (76) Perdew, J. P.; Burke, K.; Ernzerhof, M. Erratum: Generalized Gradient Approximation Made Simple (Physical Review Letters (1996) 77 (3865)). *Physical Review Letters*. American Physical Society February 17, 1997, p 1396. <https://doi.org/10.1103/PhysRevLett.78.1396>.
- (77) Vázquez-Lizardi, G. A.; Ruiz-Casanova, L. A.; Cruz-Sánchez, R. M.; Santana, J. A. Simulation of Metal-Supported Metal-Nanoislands: A Comparison of DFT Methods. *Surf Sci* **2021**, *712*, 121889. <https://doi.org/10.1016/j.susc.2021.121889>.
- (78) Pratap Khare, K.; Kathal, R.; Shukla, N.; Srivastava, R.; Srivastava, A. Copolymerization of Aniline and 9 Vinyl Carbazole: A DFT Study. *Mater Today Proc* **2021**. <https://doi.org/10.1016/j.matpr.2021.05.546>.
- (79) Chen, H.; Cox, D. F. CO Adsorption on MnO(100): Experimental Benchmarks Compared to DFT. *Surf Sci* **2021**, *707*, 121808. <https://doi.org/10.1016/j.susc.2021.121808>.
- (80) Tkatchenko, A.; Scheffler, M. Accurate Molecular van Der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data. *Phys Rev Lett* **2009**, *102* (7), 073005. <https://doi.org/10.1103/PHYSREVLETT.102.073005/FIGURES/2/MEDIUM>.
- (81) Grimme, S. Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. *J Comput Chem* **2006**, *27* (15), 1787–1799. <https://doi.org/10.1002/JCC.20495>.
- (82) Nakamura, K. G. Coherent Control of Optical Phonons in Solids. In *Encyclopedia of Interfacial Chemistry: Surface Science and Electrochemistry*; Elsevier, 2018; pp 334–337. <https://doi.org/10.1016/B978-0-12-409547-2.13236-6>.

- (83) Choudhary, K.; Tavazza, F. Convergence and Machine Learning Predictions of Monkhorst-Pack k-Points and Plane-Wave Cut-off in High-Throughput DFT Calculations. *Comput Mater Sci* **2019**, *161*, 300–308. <https://doi.org/10.1016/j.commatsci.2019.02.006>.
- (84) Wang, J.; Wang, S. Q. Surface Energy and Work Function of Fcc and Bcc Crystals: Density Functional Study. *Surf Sci* **2014**, *630*, 216–224. <https://doi.org/10.1016/j.susc.2014.08.017>.
- (85) Tran, R.; Xu, Z.; Radhakrishnan, B.; Winston, D.; Sun, W.; Persson, K. A.; Ong, S. P. Data Descriptor: Surface Energies of Elemental Crystals. *Sci Data* **2016**, *3*. <https://doi.org/10.1038/sdata.2016.80>.
- (86) Ramezani-Dakhel, H.; Mirau, P. A.; Naik, R. R.; Knecht, M. R.; Heinz, H. Stability, Surface Features, and Atom Leaching of Palladium Nanoparticles: Toward Prediction of Catalytic Functionality. *Physical Chemistry Chemical Physics* **2013**, *15* (15), 5488–5492. <https://doi.org/10.1039/c3cp00135k>.
- (87) Nie, Y.; Yang, L.; Sun, W.; Gao, Z.; Wang, Q. Increase in Gold Dissolution in Copper Ammonia Thiosulfate Solution via Cobalt Surface Modification. *Hydrometallurgy* **2020**, *197*. <https://doi.org/10.1016/j.hydromet.2020.105473>.
- (88) Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. I. J.; Refson, K.; Payne, M. C. First Principles Methods Using CASTEP. *Zeitschrift für Kristallographie-Crystalline Materials* **2005**, *220* (5/6), 567–570.
- (89) Bhattacharjee, S.; Waghmare, U. V.; Lee, S. C. An Improved D-Band Model of the Catalytic Activity of Magnetic Transition Metal Surfaces. *Sci Rep* **2016**, *6*. <https://doi.org/10.1038/srep35916>.
- (90) Hammer, B.; Nørskov, J. K. Theoretical Surface Science and Catalysis—Calculations and Concepts; 2000; Vol. 45, pp 71–129. [https://doi.org/10.1016/S0360-0564\(02\)45013-4](https://doi.org/10.1016/S0360-0564(02)45013-4).
- (91) Peck, M. A.; Santos-Carballal, D.; de Leeuw, N. H.; Claeys, M. Density Functional Theory Study of the Adsorption of Oxygen and Hydrogen on 3d Transition Metal Surfaces with Varying Magnetic Ordering. *South African Journal of Chemistry* **2021**, *74*, 69–72. <https://doi.org/10.17159/0379-4350/2021/V74A11>.
- (92) Fliszár, S. Bond Dissociation Energies; 1994; pp 69–84. https://doi.org/10.1007/978-3-642-51492-0_4.
- (93) Mohsenzadeh, A.; Bolton, K.; Richards, T. DFT Study of the Adsorption and Dissociation of Water on Ni(111), Ni(110) and Ni(100) Surfaces. *Surf Sci* **2014**, *627*, 1–10. <https://doi.org/10.1016/j.susc.2014.04.006>.
- (94) Ladd, M.; Palmer, R. *Structure Determination by X-Ray Crystallography: Analysis by X-Rays and Neutrons*; Springer US, 2013. <https://doi.org/10.1007/978-1-4614-3954-7>.
- (95) Kimura, Y.; Qi, Y.; Cagin, T.; Goddard III, W. A. *The Quantum Sutton-Chen Many-Body Potential for Properties of Fcc Metals*; 1998.

CHAPTER 3 DFT model development using pure metals

In this chapter, pure nickel (Ni) and aluminium (Al) metals were used to develop a Density Functional Theory (DFT) model for bulk optimisation, surface cleaving and optimisation, and calculation of the surface electronic and magnetic properties. The DFT model developed in this chapter was used to optimise Ni-Al bulk bimetallic phases identified in Chapter 4, the (111)-surface slabs of these bimetallic phases, and the leached forms of these (111)-surface slabs in Chapter 5. The model used the CAMbridge Serial Total Energy Package (CASTEP) within the Materials Studio 2020 software developed by the BIOVIA software company. The model also employed the generalised gradient approximation (GGA) by Perdew, Burke, and Ernzerhof (PBE), the Koelling-Harmon relativistic treatment, and the Two-Point Steepest Descent (TPSD) algorithm for geometric optimisation. Varied pseudopotentials were used to describe the interaction between the core and valence electrons, with a cut-off energy of 570 eV. For the optimisation of bulk structures, the Monkhorst-Pack k-point grid was varied for both the bulks and surfaces. The dispersion correction for the atomic system was also considered and varied.

3.1 Introduction.....	30
3.2 Computational Method	31
3.2.1 Model development for bulk structures	31
3.2.1.1 k-point sampling	32
3.2.1.2 Dispersion correction scheme sampling.....	32
3.2.1.3 Pseudopotentials scheme sampling.....	32
3.2.2 Sampling and optimisation of (111) surfaces	32
3.2.3 Surface and electronic properties of Ni (111) and Al (111) surfaces	33
3.3 Results and discussion	33
3.3.1 Model development for bulk structures	33
3.3.1.1 k-point sampling	33
3.3.1.2 Dispersion correction scheme sampling.....	35
3.3.1.3 Pseudopotentials scheme sampling.....	35
3.3.2 Sampling and optimisation of (111) surfaces	36
3.3.3 Surface and electronic properties of Ni (111) and Al (111) surfaces	38
3.4 Conclusion	40
References	40

3.1 Introduction

This study aimed to develop a valid computational model for the study of Raney-Nickel that accurately calculates the electronic properties and obtains parameters comparable with experimental or previously calculated parameters. To achieve this, computational studies for nickel (Ni) and aluminium (Al) with similar computational parameters and calculated electronic properties were identified as a starting point for developing the computational model.

Four studies were identified that modelled the Al bulk metal and its low-index surfaces; namely, Liu *et al.*¹, Zhou *et al.*², Singh-Miller *et al.*³ and Wei *et al.*⁴. These studies used different software packages, such as the Cambridge Serial Total Energy Package (CASTEP)⁵, Quantum-espresso and MedeA-VASP 5.4 to perform DFT calculations.¹⁻⁴ Liu *et al.*¹, Singh-Miller *et al.*³ and Wei *et al.*⁴ applied GGA PBE functionals, while Zhou *et al.*² applied the GGA PW91 functional. Liu *et al.*¹ and Zhou *et al.*² selected ultrasoft pseudopotentials, Singh-Miller *et al.*³ used norm-conserving pseudopotentials, and Wei *et al.*⁴ did not specify which pseudopotential scheme was used. Liu *et al.*¹ and Zhou *et al.*² used a k-point grid of 11×11×11 with an energy cut-off of 350 eV, and a 5×5×2 k-point grid with 410 eV for modelling Al bulks, respectively. However, Singh-Miller *et al.*³ and Wei *et al.*⁴ did not specify which k-point grids were used for the bulk determinations but they utilised energy cut-offs of 32 Ry (~435 eV) and 520 eV, respectively. For surface slab calculations, Liu *et al.*¹ calculated the Al (100)-surface with a 5-layer atomic thickness, a vacuum gap of 12 Å, and surface slab k-point grids of 3×3×1 and 4×4×1 with (2×2) and (3×3) supercells. For further optimisation, Liu *et al.*¹ used a 400 eV energy cut-off and a self-consistent field tolerance (SCF) of 1.0×10^{-5} eV/atom. They selected thresholds for the total energy (1.0×10^{-5} eV/atom), the maximum force (0.3 eV/nm), the maximum stress (0.05 GPa) and the maximum displacement (1.0×10^{-4} nm). While Zhou *et al.*² used SCF tolerance of 2.0×10^{-6} eV/atom. Further, they considered thresholds for the total energy change (2.0×10^{-5} eV/atom), the maximum force (0.05 eV/nm), the maximum stress (0.1 GPa) and the maximum displacement (0.002 Å). Singh-Miller *et al.*³ calculated the (111)-, (100)- and (110)-surface(s) each with a vacuum gap of 16 Å. Lastly, Wei *et al.*⁴ calculated the 4×4×1 k-point grid of the Al (111)-surface with six atomic layers and a vacuum gap of 12 Å.

Three studies were identified for the Ni bulk and its surfaces; namely, the studies of Botha *et al.*,⁶ Watson *et al.*⁷, and Zhang *et al.*⁸. These studies used different software packages, such as CASTEP,⁵ the Vienna Ab initio Simulation Program (VASP) and DMol³ to perform DFT calculations.⁶⁻⁸ Botha *et al.*⁶ and Watson *et al.*⁷ applied ultrasoft pseudopotentials and GGA PBE functionals. Watson *et al.*⁷ used a cut-off energy of 300 eV. Zhang *et al.*⁸ used the GGA PBE functional with a double numerical plus polarisation (DNP) basis set. For surface slab calculation, all three authors considered the (111)-surface.⁶⁻⁸ Zhang *et al.*⁸ used a (2×2) unit cell with a 4×4×1 k-point grid. Botha *et al.*⁶ and Watson *et al.*⁷ chose a 5×5×1 k-point grid, while they calculated slabs of four atomic layers and five atomic layers, respectively. Additionally, Botha *et al.*⁶ utilised

a vacuum gap of 12 Å and Watson *et al.*⁷ utilised a vacuum gap equivalent to the thickness of 3 atomic layers.

In this study, DFT calculations were done using CASTEP⁵ with GGA PBE as functional. The pseudopotentials were varied to find the best fit for the selected metals, with a cut-off energy of 570 eV. The k-point grids for both the bulks and surfaces were sampled over a range that included the settings of previous studies. To investigate the systems where these two metals are combined later in this study, a universal model must be developed for the pure components and the mixed structures to ensure consistency and comparability of the results.

Surface properties are crucial for catalyst study and development, as these properties determine the catalytic interactions. The (111)-surface, the most prominent surface for Raney nickel, was chosen for this study.^{9,10}

3.2 Computational Method

The CASTEP⁵ module within the Materials Studio 2020 (MS2020)¹¹ software developed by the BIOVIA software company was used to perform Density Functional Theory calculations. The dispersion correction (DFT-D) was selected for optimising the bulk structures to enable follow up surface interaction calculations for identified low-energy structures.

The computational model was applied to pure metal bulks and (111) Ni and Al surface slabs. The Computational Method section is divided into three subsections dealing with bulks (3.2.1) and surface slabs (3.2.2 - 3.2.3).

3.2.1 Model development for bulk structures

Face-centred cubic (fcc) pure Ni and Al crystal structures within the Fm-3m space group were used for the model development. A unit cell imported from the MS2020¹¹ structures library was expanded into a 2×2×2 supercell through the build function within MS2020.¹¹ The geometric optimisation used the GGA PBE functional and the various dispersion correction schemes (section 3.2.1.2). Due to the magnetic nature of nickel, spin polarisation was selected and set to collinear, and the formal spin was used as the initial value. The cell optimisation was set to full, with a fixed basis quality for the basis set for variable cell and medium compressibility. The optimisation was done with the TPSD algorithm. For the electronic property settings, the basis cut-off energy was 570.0 eV with a standard density, and the finite basis correction was set to smart. The SCF tolerance was left at the default value of 2.0×10^{-6} eV/atom, the electronic minimiser was set to density mixing, and no dipole correction was applied. The k-points were varied (see section 3.2.1.1). The pseudopotentials scheme was varied between OTFG ultrasoft and ultrasoft with a reciprocal space representation and a Koelling-Harmon relativistic treatment. The property of population analysis was selected, which analyses the electron population of the structure being optimised to gain spin properties.

3.2.1.1 k-point sampling

To obtain more accurate geometric optimisation results for the bulk structures within the $2\times 2\times 2$ supercell, the optimisations were done at various k-point settings. The rest of the settings were left constant, as mentioned in section 3.2.1. The k-point grid ranged from $1\times 1\times 1$ to $11\times 11\times 11$. This range of k-point grids was chosen to ensure that a high enough density of symmetry points for accurate energy calculations.

3.2.1.2 Dispersion correction scheme sampling

The two most used schemes for metals, TS and Grimme, were evaluated to ensure that the best dispersion correction scheme for the study was used. The pure metal bulk of Ni and Al were optimised with the settings as in section 3.2.1, at the same k-point grid with the addition of the DFT-D setting set to either TS or Grimme. The lowest optimised electronic energy was used to identify the best correction scheme for the metals.

3.2.1.3 Pseudopotentials scheme sampling

The pseudopotential scheme was considered because it is how the plane waves are calculated; it is an approximation method for the core electrons of an atom.¹² The pseudopotential was varied between the OTFG Ultrasoft and the Ultrasoft pseudopotentials to determine the most suitable pseudopotential for this study by comparing the outcome to literature values.

3.2.2 Sampling and optimisation of (111) surfaces

The cleave surface tool within the MS2020¹¹ software was used to create the (111)-surface slabs from the $2\times 2\times 2$ supercell. Within the cleave surface dialogue box, the cleave plane was set to the (111)-Miller plane. Furthermore, the Top setting determines the depth at which the surface is cleaved, while the thickness setting determines the thickness of the slab, i.e., how many layers of atoms are present in the slab. In this study, a four-layer slab was selected. The cleave rule was set to atomic, and the 'cap bonds on' was set to neither since there were no bonds dangling after the surface have been cleaved. The surface mesh settings and options were left at the default values. Once the bulk was cleaved at the desired surface, a vacuum slab with a thickness of 15 Å was built on top of the surface slab along the c-axis direction. This thickness was chosen to ensure enough space to prevent interaction of individual surfaces and to run simulations on the surface.

All the layers of the surface slabs were allowed to relax during optimisation using the settings in section 3.2.1 with the cell optimisation set to none, the dispersion correction scheme from the results of section 3.2.1.2 and the identified pseudopotentials algorithm from section 3.2.1.3, respectively. The k-points for the slab were varied from $1\times 1\times 1$ to $9\times 9\times 1$ to identify the best k-point density for accurate geometric calculations.

3.2.3 Surface and electronic properties of Ni (111) and Al (111) surfaces

The surface and electronic properties of Ni (111) and Al (111), including the surface energies, work functions, and d-band centres, were calculated using the settings mentioned in section 3.2.1. The optimised energies and calculated surface areas of the metals were used to calculate the surface energies using equation 3-1 (equation 2-14):¹³

$$\gamma = \frac{E_{slab} - NE_{bulk\ structure}}{2A} \quad (3-1)$$

where γ is the surface energy of the unconstrained surface slab. E_{slab} is the total energy of the surface slab, N is the ratio of the number of atoms in the surface slab to the number of atoms in the bulk structure ($N_{slab} : N_{bulk\ structure}$), $E_{bulk\ structure}$ is the energy of the bulk system, and A is the area of the surface slab. The work function, the minimum energy needed to remove an electron from the surface of the metal³, was obtained from potential files, which CASTEP⁵ automatically calculates during the optimisation of the surfaces.

The valence electrons are responsible for the bonding ability of metals and the orbitals can be observed from the density of states (DOS) graph. For Ni, these are the d-orbitals, while for Al, these are the p-orbitals. The centre of the d-band can be calculated from the d-bandwidth using the partial DOS (PDOS) graph. This calculation is done by first integrating across the area in the xy-plane bounded by the graph after loading PDOS data into a numerical data plotting tool. The d-bandwidth is then calculated by dividing the resulting integral by two, giving a y-value. Finally, the centre of the d-band is calculated by finding the corresponding x-value to the previously calculated y-value. This calculation can be done in software freely available such as QtGrace.¹⁴

3.3 Results and discussion

3.3.1 Model development for bulk structures

3.3.1.1 k-point sampling

To identify the optimal k-point grid for the optimisations of the pure metals (Ni and Al), the k-point grid ranged from 1×1×1 to 11×11×11. Figure 3-1 shows how the relative free energy varies as a function of the number of k-points for Ni (blue) and Al (magenta).

The 1×1×1 k-point grid (1 k-point or Γ point) for both Ni and Al is not an optimal choice. The relative energies for both were significantly lower at all other considered k-point grids. In the case of the Al bulk, the 3×3×3 k-point grid (27 k-points) had the lowest energy, but it was not yet converged since the energies increased again after that point. While the opposite was true in the case of Ni, the energies still decreased after that point. The 5×5×5 k-point grid (125 k-points) was also not converged since the energies increased for Ni and decreased for Al. However, for the 7×7×7 k-point grid (343 k-points) and beyond, convergence was observed.

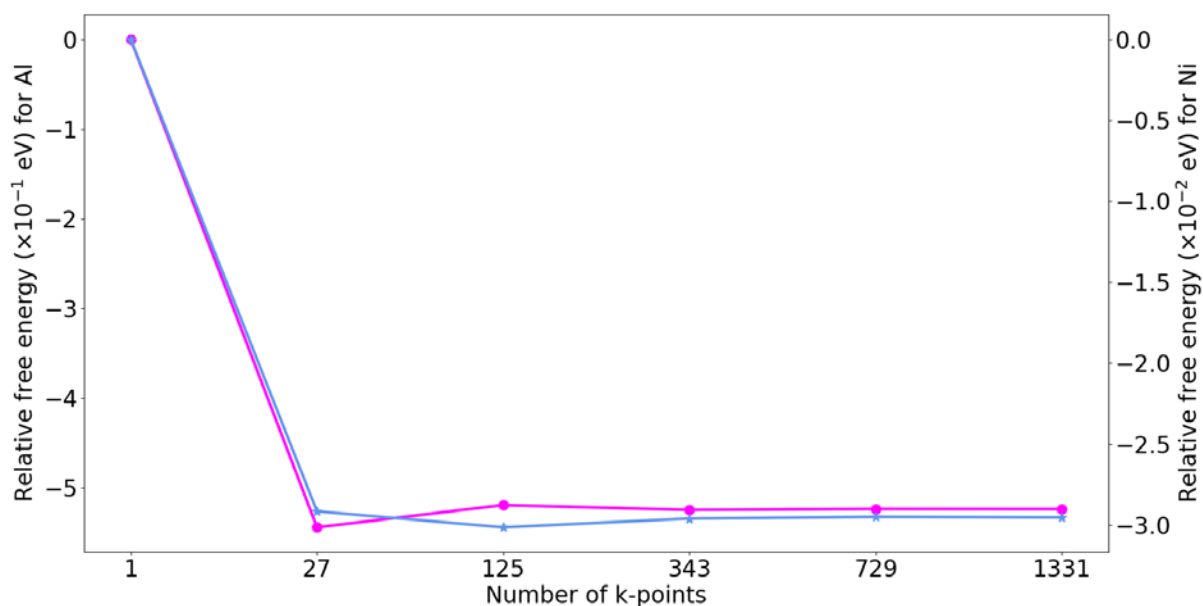


Figure 3-1 The free energy (relative to 1×1×1 energy), shown in eV for Ni (blue) and Al (magenta) as a function of the number of k-points in the chosen grid.

To determine the best k-point grid for further optimisations of the bulk structures, the difference between the relative energies was calculated between the 7×7×7 and 9×9×9 k-point grids (343 vs 729 k-points), and the 9×9×9 and 11×11×11 k-point grids (729 vs 1331 k-points) for Ni and Al individually. These values are listed in Table 3-1.

Table 3-1 k-point data for Ni and Al, including the k-point grid and the corresponding k-points, the relative free energy for each k-point grid and the difference between the relative energies between different k-point grids.

k-point grid (n×n×n)	Number of points (n ³)	Relative free energy (eV)	Difference in relative free energy (n – (n+2)) (eV)
k-point data for Ni			
1	1	0.00000	0.02916
3	27	-0.02916	0.00099
5	125	-0.03015	0.00054
7	343	-0.02960	0.00010
9	729	-0.02950	0.00003
11	1331	-0.02953	-
k-point data for Al			
1	1	0.00000	0.54430
3	27	-0.54430	0.02483
5	125	-0.51947	0.00544
7	343	-0.52491	0.00110
9	729	-0.52381	0.00015
11	1331	-0.52396	-

In the case of Ni, the relative free energy difference, between the 7×7×7 and 9×9×9 k-point grids, was an acceptable 0.0001 eV. Whereas, in the case of Al, the relative free energy difference was only 0.0011 eV between these k-points. However, the acceptable difference of 0.00015 eV was

observed between the 9×9×9 and 11×11×11 k-point grids. Since the model had to be applied to a mixture of Ni and Al later in this study, the 9×9×9 k-point grid was chosen for all further bulk calculations.

3.3.1.2 Dispersion correction scheme sampling

To identify the optimal dispersion correction scheme for the optimisations of Ni and Al, the scheme was varied between the Grimme and TS correction schemes. The corrected energies for Ni (blue) and Al (magenta) are shown in Figure 3-2. The uncorrected energy shows how the dispersion scheme inclusion changed the energies.

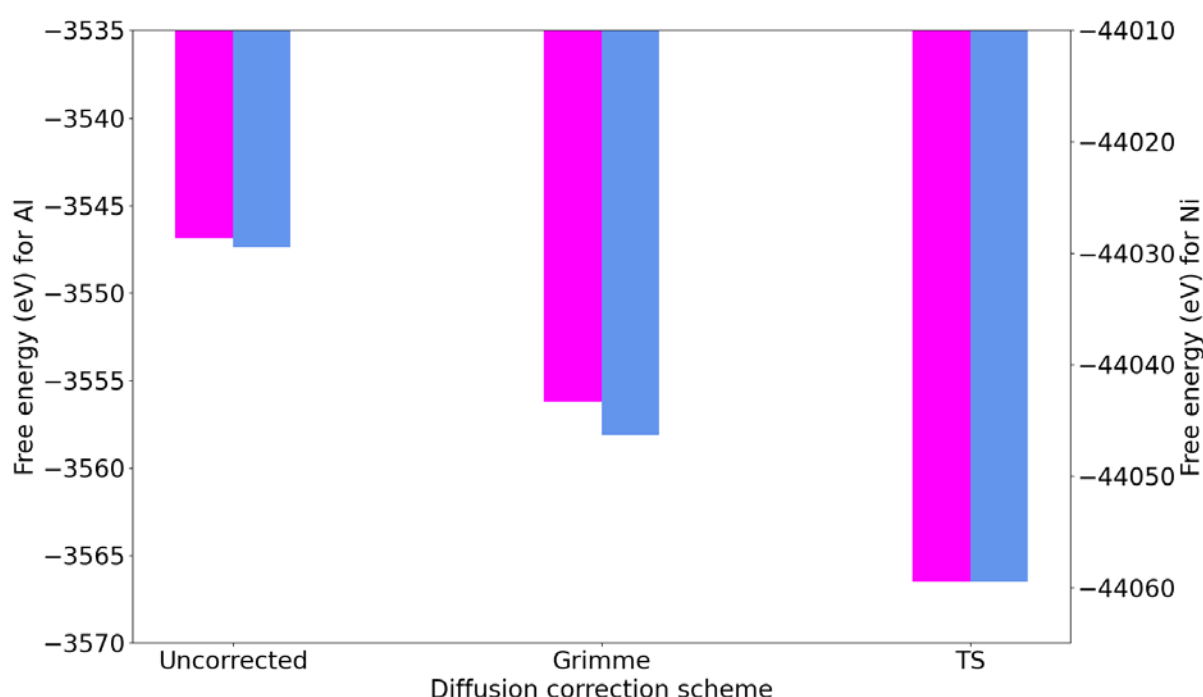


Figure 3-2 Bulk energy results from the dispersion scheme identification with Al (magenta) on the left-hand y-axis and Ni (blue) on the right-hand y-axis.

The Grimme correction scheme gave better results for the Ni than the Al. However, the TS correction scheme gave significantly lower optimised energy for Ni and Al. Since the model must be applied to a mixture of Ni and Al, the TS correction scheme was selected for all further optimisations.

3.3.1.3 Pseudopotentials scheme sampling

To identify the best pseudopotential for the optimisations of Ni and Al, the pseudopotential was varied between the OTFG Ultrasoft and Ultrasoft pseudopotentials. The calculated lattice parameters and bulk energies for Ni and Al, listed in Table 3-2, were compared to literature values.

The ultrasoft pseudopotential values for Ni and Al were the most accurate when compared to the literature values. In the case of the lattice parameter, the values obtained with the ultrasoft pseudopotential were closer to the literature values of $4.05 \text{ \AA}^{15}$ and $3.526 \text{ \AA}^{16,17}$ for Al and Ni,

respectively. While in the case of the bulk energies, the ultrasoft pseudopotential gave more stable energies than the OTFG ultrasoft pseudopotential. For Ni, the spin moment per atom compared well with the literature values of $0.62 \pm 0.01 \mu\text{B}$ (calculated with PBE).^{17,18} Therefore the ultrasoft pseudopotential was selected for all further optimisations.

Table 3-2 OTFG Ultrasoft and Ultrasoft pseudopotential results for Al and Ni compared to computational literature values.

Element	Al			Ni		
Pseudo potentials	OTFG Ultrasoft	Ultrasoft	Literature	OTFG Ultrasoft	Ultrasoft	Literature
a-lattice (Å)	3.920	3.927	4.05 ¹⁵	3.427	3.444	3.526 ^{16,17}
ΔG -dispersion corrected atom (eV/atom)	-111.454	-57.047	-	-1376.859	-1355.317	-1355.490 ¹⁹
Spin moment ($\mu\text{B}/\text{atom}$)	-	-	-	0.61	0.62	0.62 ± 0.01 ^{17,18}

For bulk structures, the closest values to the literature were produced using the $9 \times 9 \times 9$ k-point grid, the TS dispersion scheme and the ultrasoft pseudopotential. For the final bulk structure fractional coordinates, refer to Appendix E.

3.3.2 Sampling and optimisation of (111) surfaces

The optimised bulk structures of Ni and Al were cleaved at the (111)-Miller plane with a fractional thickness value of 2.0 (equivalent to 8.138 Å). This thickness value led to a four-atomic layer surface slab. A fractional top value of 2.0 (equivalent to 8.138 Å) was also chosen for the pure metal surface structures. Figure 3-3 (a) shows the top and side views of these surface slabs for the Ni, and Figure 3-3 (b) for the Al without the vacuum gap before optimisation. The cell length vectors for these surface slabs (including the vacuum layer) are a , $b = 9.740 \text{ Å}$ and $c = 20.965 \text{ Å}$ for the Ni surface slab and a , $b = 11.108 \text{ Å}$ and $c = 21.802 \text{ Å}$ for the Al surface slab.

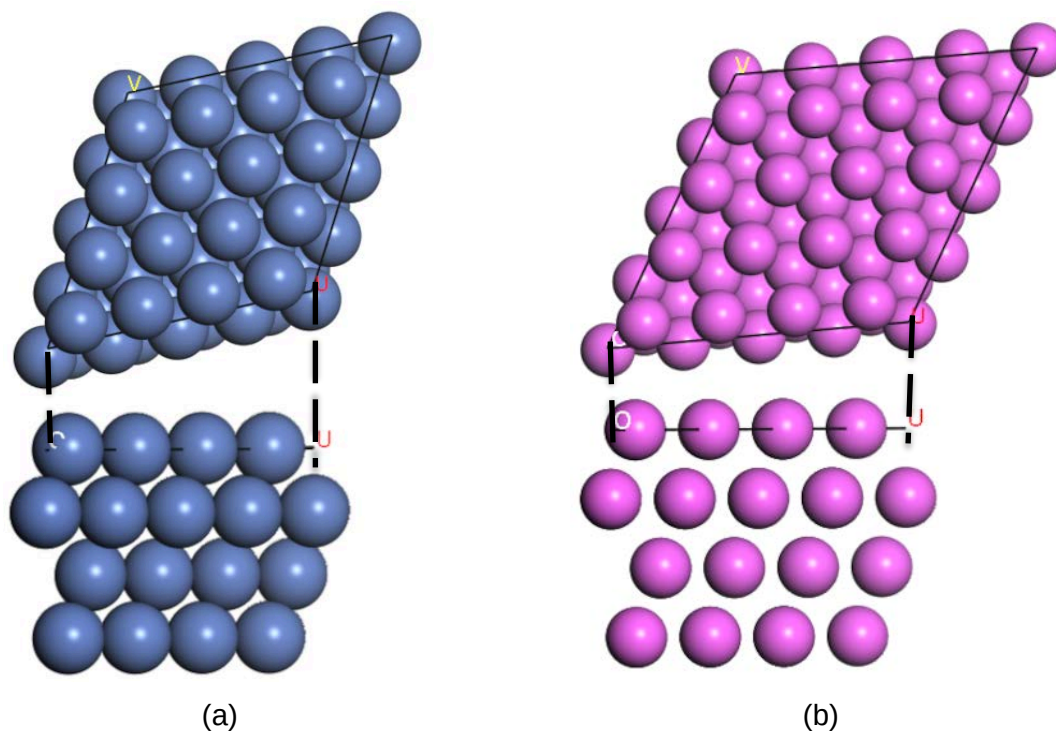


Figure 3-3 Fractional thickness and fractional top settings of 2.0 for (a) the Ni surface slab top and side view, (b) the Al surface slab top and side view.

For the identification of the optimal k-point grid for the optimisations of Ni and Al surface slabs, the k-point grid ranged from $1 \times 1 \times 1$ to $9 \times 9 \times 1$.

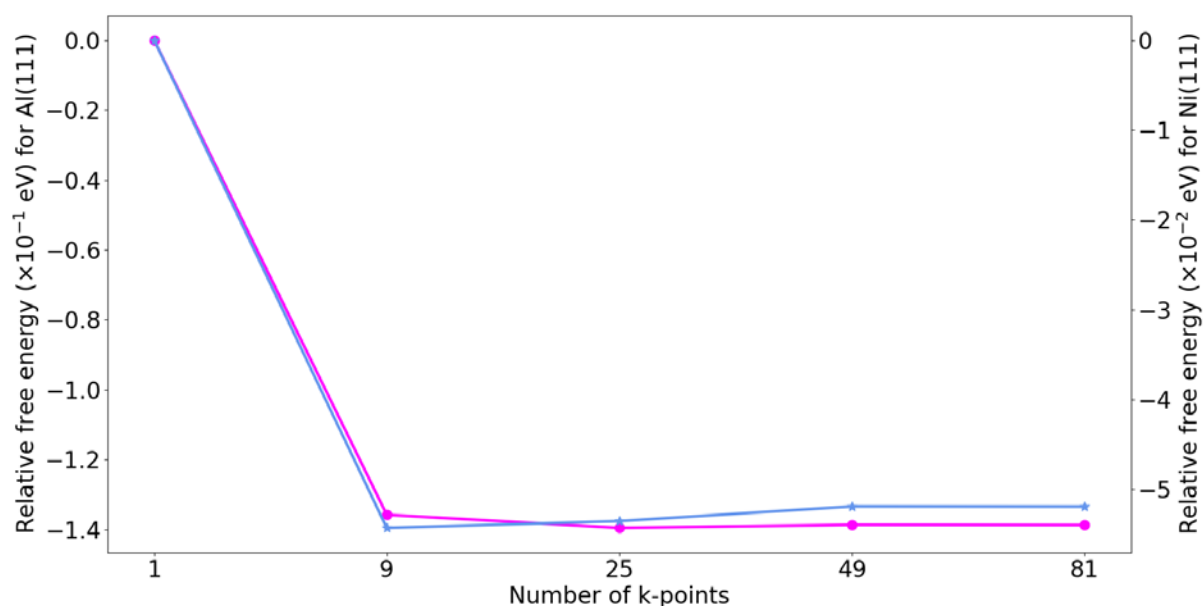


Figure 3-4 (111)-surface k-point sampling results with the relative free energy in eV shown for Ni (blue) and Al (magenta) as a function of the number of k-points in the chosen grid.

The $1 \times 1 \times 1$ k-point grid (1 k-point or Γ point) for both Ni (111) and Al (111) was not an optimal choice. The relative energies for Ni and Al were significantly lower at all other considered k-point grids. With the $3 \times 3 \times 1$ k-point grid (9 k-points) the energy was not yet converged for Al (111) since the energies decreased again after that point. While the opposite was true in the case of Ni (111); namely, the energies increased after that point. The $5 \times 5 \times 1$ k-point grid (25 k-points) did not yield

convergence since the energies slightly increased for Ni (111) and slightly decreased for Al (111). Considering the 7×7×1 k-point grid (49 k-points) and beyond, convergence was achieved for both Ni (111) and Al (111). To determine the best k-point grid for further optimisations of the surface slabs, the difference between the relative energies was calculated between the 5×5×1 and 7×7×1 k-point grids and 7×7×1 and 9×9×1 k-point grids. These values are listed in Table 3-3.

For both Ni (111) and Al (111), an acceptable difference of < 0.0001 eV was obtained between the relative free energies of the 5×5×1 and 7×7×1 k-point grids. While an even smaller difference in the relative free energy of the 7×7×1 and 9×9×1 k-point grids was obtained. Since the developed model had to be consistent, the 9×9×1 k-point grid was selected for all further calculations to keep the same calculation level as in the bulk structures.

Table 3-3 k-point data for Ni (111) and Al (111), including the k-point grid and the corresponding k-points, the relative free energy for each k-point grid and the difference between the relative energies between different k-point grids.

k-point grid (n×n×1)	Number of points (n ²)	Relative free energy (eV)	Difference in relative free energy (n – (n+2)) (eV)
k-point data for Ni (111)			
1	1	0.00000	0.06770
3	9	-0.06773	0.00150
5	25	-0.06623	0.00070
7	49	-0.06553	0.00004
9	81	-0.06549	-
k-point data for Al (111)			
1	1	0.00000	0.13660
3	9	-0.13664	0.00470
5	25	-0.14130	0.00010
7	49	-0.14125	0.00039
9	81	-0.14164	-

3.3.3 Surface and electronic properties of Ni (111) and Al (111) surfaces

The calculated surface and electronic properties of Ni (111) and Al (111), namely, surface energies (γ), work functions (Φ) and the d-band ($\mathcal{E}_d$) centres, are listed in Tables 3-4 and 3-5.

The work function of 5.144 eV calculated for the 9×9×1 k-point grid is comparable to the literature values for Ni (111), which were found to be 5.11 eV²⁰ and 5.35 eV.²¹ The measured interatomic spacing ($d_{Ni} - d_{Ni}$) value of 2.435 Å is comparable to literature values of 2.490 Å²² and 2.509 Å.⁶

Table 3-4 Surface and electronic properties for Ni (111)

k-point grid (n×n×1)	Number of points (n ²)	E (eV/atom)	ΔE (eV)	Φ (eV)	ε _d (eV)	m _s (μB/atom)
1	1	-1354.769	0.000	4.890	-1.631	0.705
3	9	-1354.714	-0.055	5.152	-1.599	0.655
5	25	-1354.715	-0.054	4.949	-1.617	0.650
7	49	-1354.717	-0.052	4.774	-1.598	0.660
9	81	-1354.717	-0.052	5.144	-1.597	0.655

The d-band centre values calculated within this study are comparable to the theoretical values of -1.477 eV⁶ and -1.56 eV²³, with the closest value reflected at the 9×9×1 k-point grid, for Ni (111). The spin moment, calculated using the Hirshfeld population analysis data, shows that the value of the 5×5×1 k-point grid (0.650 μB) was found to be the closest to that of Ni (111) (0.631 μB) (calculated using PBE, averaged).¹⁸ The 9×9×1 k-point grid value was acceptable, with a deviation of only 3.8%. Finally, according to the literature, the experimental surface energy for Ni (111) is between 2.370 J/m² and 2.450 J/m², and the theoretical values are between 1.633 J/m² and 2.600 J/m².^{6,24,25} Thus, the calculated value of 3.247 J/m² is 0.647 J/m² larger than the largest literature value²⁵ with a deviation of 24.88%. The surface energy was calculated for the 9×9×1 k-point grid to keep the calculation level consistent with the 9×9×9 k-point grid for bulks.

Table 3-5 Surface and electronic properties for Al (111)

k-point grid (n×n×1)	Number of points (n ²)	E (eV/atom)	ΔE (eV)	Φ (eV)	ε _p (eV)
1	1	-56.541	0.000	3.116	1.091
3	9	-56.677	-0.136	3.961	1.123
5	25	-56.681	-0.140	3.903	1.137
7	49	-56.680	-0.139	3.906	1.118
9	81	-56.680	-0.139	3.893	1.118

The calculated work function values of the surface slabs for Al (111) over the k-point grid range from 3×3×1 to 9×9×1 are comparable with literature values, 4.02 eV³, 4.12 eV⁴, and 4.24 eV²¹. In contrast, an interatomic spacing (d_{Al} – d_{Al}) of 2.777 Å was measured in this study, which is comparable to the literature, 2.864 Å.¹⁵ Since Al is a diamagnetic metal, it has an average spin moment of 0 μB. Lastly, an experimental value of 1.14 J/m² was obtained for the surface energy of Al, while other studies calculated the surface energy to be 1.02 J/m² and 0.67 J/m².^{3,4,24} The surface energy value of 1.524 J/m² calculated in this study is 0.384 J/m² larger than the largest literature value²⁴ with a deviation of 33.68%.

Thus, the most accurate surface slab structures were produced using the 9×9×1 k-point grid. Refer to Appendix E for the fractional coordinates of the final surface slab structure.

3.4 Conclusion

In this chapter, pure Ni and Al metals were optimised to develop a model for $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase precursors to Raney nickel, which will be identified in Chapter 4. To build the optimisation model for bulk structures, the k-point grid, dispersion scheme and pseudopotential were varied, and the results were validated against literature values. For the bulk optimisations, a $9 \times 9 \times 9$ k-point grid was found sufficient, as shown through comparison of free energy differences. The TS dispersion correction scheme gave more stable bulk energies compared to the Grimme dispersion scheme. Additionally, the Ultrasoft pseudopotential gave the most stable bulk energies which was validated using Ni and Al lattice parameters. For surface slabs, k-point grids greater than $7 \times 7 \times 1$ were found to be sufficient for surface optimisations but, electronic property calculation favoured the $9 \times 9 \times 1$ k-point grid the most. The work function calculated for the $9 \times 9 \times 1$ k-point grid of Ni is the most comparable with 5.15 eV^{21} , whereas the work function of Al that was calculated for most of the k-point grid range is comparable with 4.02 eV^3 . For surface slabs, a $9 \times 9 \times 1$ k-point grid was selected to keep the same computational level as for the bulks. In conclusion, the computational method developed in this chapter is suitable for optimising the Raney nickel precursor, $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase, bulks and surface slabs to be identified in Chapter 4.

References

- (1) Liu, J.; Zhang, X.; Chen, M.; Li, L.; Zhu, B.; Tang, J.; Liu, S. DFT Study on Surface Properties and Dissolution Trends of Al(1 0 0) Surfaces Doped with Zn, Ga, In, Sn and Pb. *Appl Surf Sci* **2011**, 257 (9), 4004–4009. <https://doi.org/10.1016/j.apsusc.2010.11.165>.
- (2) Zhou, X.; Zhao, C.; Wu, G.; Chen, J.; Li, Y. DFT Study on the Electronic Structure and Optical Properties of N, Al, and N-Al Doped Graphene. *Appl Surf Sci* **2018**, 459, 354–362. <https://doi.org/10.1016/j.apsusc.2018.08.015>.
- (3) Singh-Miller, N. E.; Marzari, N. Surface Energies, Work Functions, and Surface Relaxations of Low-Index Metallic Surfaces from First Principles. *Phys Rev B* **2009**, 80 (23), 235407. <https://doi.org/10.1103/PhysRevB.80.235407>.
- (4) Wei, X.; Dong, C.; Chen, Z.; Xiao, K.; Li, X. A DFT Study of the Adsorption of O₂ and H₂O on Al(111) Surfaces. *RSC Adv* **2016**, 6 (61), 56303–56312. <https://doi.org/10.1039/C6RA08958E>.
- (5) Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. I. J.; Refson, K.; Payne, M. C. First Principles Methods Using CASTEP. *Zeitschrift für Kristallographie-Crystalline Materials* **2005**, 220 (5/6), 567–570.
- (6) Botha, L. M.; Ungerer, M. J.; van Sittert, C. G. C. E. Catalytic Dissociation of a Water Molecule on the (1 1 1) Surfaces of Pt_{0.5}Ni_{0.5} Bimetal: Density Functional Theory (DFT) Study. *Appl Surf Sci* **2022**, 602, 154238. <https://doi.org/10.1016/j.apsusc.2022.154238>.
- (7) Watson, G. W.; Wells, R. P. K.; Willock, D. J.; Hutchings, G. J. A Comparison of the Adsorption and Diffusion of Hydrogen on the {111} Surfaces of Ni, Pd, and Pt from Density Functional Theory Calculations. *Journal of Physical Chemistry B* **2002**, 105 (21), 4889–4894. <https://doi.org/10.1021/JP002864C>.

- (8) Zhang, M.; Yang, K.; Zhang, X.; Yu, Y. Effect of Ni(111) Surface Alloying by Pt on Partial Oxidation of Methane to Syngas: A DFT Study. *Surf Sci* **2014**, *630*, 236–243. <https://doi.org/10.1016/j.susc.2014.08.023>.
- (9) Yang, Y.; Luo, M.; Zhang, W.; Sun, Y.; Chen, X.; Guo, S. Metal Surface and Interface Energy Electrocatalysis: Fundamentals, Performance Engineering, and Opportunities. *Chem* **2018**, *4* (9), 2054–2083. <https://doi.org/10.1016/J.CHEMPR.2018.05.019>.
- (10) Oura, K.; Lifshits, V. G.; Saranin, A. A.; Zotov, A. v; Katayama, M. *Surface Science: An Introduction*; Springer Berlin Heidelberg, 2013.
- (11) Dassault Systèmes BIOVIA, Materials Studio, 20.1.0.5, San Diego: Dassault Systèmes, 2020. Dassault Systèmes: San Diego 2020.
- (12) Kittel C. *Introduction to Solid State Physics, 8th Edition*; 2005.
- (13) Wang, J.; Wang, S. Q. Surface Energy and Work Function of Fcc and Bcc Crystals: Density Functional Study. *Surf Sci* **2014**, *630*, 216–224. <https://doi.org/10.1016/j.susc.2014.08.017>.
- (14) Grace Home. <https://plasma-gate.weizmann.ac.il/Grace/> (accessed 2022-09-04).
- (15) Zhukovskii, Y. F.; Mastrikov, Y.; Shunin, Y.; Jacobs, P. W. M.; Zhukovskii, Y. F.; Mastrikov, Y.; Shunin, Y. N. Bulk and Surface Properties of Metallic Aluminium: DFT Simulations. *Computer Modelling & New Technologies* **2002**, *6* (1), 7–28.
- (16) Watson, G. W.; Wells, R. P. K.; Willock, D. J.; Hutchings, G. J. A Comparison of the Adsorption and Diffusion of Hydrogen on the {111} Surfaces of Ni, Pd, and Pt from Density Functional Theory Calculations. *Journal of Physical Chemistry B* **2002**, *105* (21), 4889–4894. <https://doi.org/10.1021/jp002864c>.
- (17) Botha, L. M.; Santos-Carballal, D.; Terranova, U.; Quesne, M. G.; Ungerer, M. J.; van Sittert, C. G. C. E.; de Leeuw, N. H. Mixing Thermodynamics and Electronic Structure of the Pt_{1-x}Ni_x (0 ≤ x ≤ 1) Bimetallic Alloy. *RSC Adv* **2019**, *9* (30), 16948–16954. <https://doi.org/10.1039/c9ra02320h>.
- (18) Doll, K. Density Functional Study of Ni Bulk, Surfaces and the Adsorbate Systems Ni(1 1 1) ($\sqrt{3} \times \sqrt{3}$)R30°-Cl, and Ni(1 1 1)(2 × 2)-K. *Surf Sci* **2003**, *544* (1), 103–120. <https://doi.org/10.1016/j.susc.2003.07.008>.
- (19) Botha, L. Screening of Pt/Ni Bimetallic Electrocatalysts Using DFT Calculations. Doctoral, North-West University, 2020.
- (20) Mittendorfer, F.; Eichler, A.; Hafner, J. *Structural, Electronic and Magnetic Properties of Nickel Surfaces*; 1999; Vol. 423.
- (21) Michaelson, H. B. The Work Function of the Elements and Its Periodicity. *J Appl Phys* **1977**, *48* (11), 4729–4733. <https://doi.org/10.1063/1.323539>.
- (22) Kitchin, J. R.; Khan, N. A.; Barteau, M. A.; Chen, J. G.; Yakshinskiy, B.; Madey, T. E. Elucidation of the Active Surface and Origin of the Weak Metal-Hydrogen Bond on Ni/Pt(1 1 1) Bimetallic Surfaces: A Surface Science and Density Functional Theory Study. *Surf Sci* **2003**, *544* (2–3), 295–308. <https://doi.org/10.1016/j.susc.2003.09.007>.
- (23) Greeley, J.; Mavrikakis, M. Surface and Subsurface Hydrogen: Adsorption Properties on Transition Metals and near-Surface Alloys. *Journal of Physical Chemistry B* **2005**, *109* (8), 3460–3471. <https://doi.org/10.1021/jp046540q>.
- (24) Tyson, W. R.; Miller, W. A. Surface Free Energies of Solid Metals: Estimation from Liquid Surface Tension Measurements. *Surf Sci* **1977**, *62* (1), 267–276. [https://doi.org/10.1016/0039-6028\(77\)90442-3](https://doi.org/10.1016/0039-6028(77)90442-3).

- (25) Lee, J. Y.; Punkkinen, M. P. J.; Schönecker, S.; Nabi, Z.; Kádas, K.; Zólyomi, V.; Koo, Y. M.; Hu, Q. M.; Ahuja, R.; Johansson, B.; Kollár, J.; Vitos, L.; Kwon, S. K. The Surface Energy and Stress of Metals. *Surf Sci* **2018**, *674*, 51–68. <https://doi.org/10.1016/J.SUSC.2018.03.008>.

CHAPTER 4 Using Site Occupation Disorder to build bulk structures of $\text{Ni}_{1-x}\text{Al}_x$ *

* This chapter was adapted and published as a manuscript and an oral presentation at the CoSAAMI 2021

* Thesner, C.; Falch, A.; Van Sittert, C. G. C. E. Using Site Occupation Disorder to Build Bulk Structures of $\text{Ni}_{1-x}\text{Al}_x$. *Suid-Afrikaanse Tydskrif vir Natuurwetenskap en Tegnologie / South African Journal of Science and Technology* **2022**, 40 (1), 174–179. <https://doi.org/10.36303/SATNT.2021cosaami.33>.

Potential exists for Raney nickel as an oxygen evolution reaction (OER) electrocatalyst. Raney nickel's catalytic activity, however, varies depending on its characteristics. These properties are related to the composition of the initial bimetallic precursor used to synthesise Raney nickel. The bimetallic precursor consists of a combination of bimetallic phases. Various studies have been done on the well-known bimetallic phases, namely, Ni_2Al_3 , NiAl , and NiAl_3 . However, a larger spectrum of bimetallic phases needs to be evaluated to understand the influence of the bimetallic precursor on the properties of Raney nickel. The Site Occupation Disorder (SOD) program was used in this study to build solid-state structures (bimetallic phases) with various $\text{Ni}_{1-x}\text{Al}_x$ bimetallic ratios. These $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases were evaluated, and unique configurations for each $\text{Ni}_{1-x}\text{Al}_x$ bimetallic ratio were obtained. The unique configurations were geometrically optimised using the General Utility Lattice Program (GULP) at 0K. These optimised unique configurations were thermodynamically evaluated over a range of 0.1K – 1200K, and the most stable configurations, with a probability higher than 10%, were identified. This study found that the stable non-homogeneous configurations fall within 20% - 80% Ni content. A weight average combination of these configurations of the bimetallic phases will produce a non-homogeneous precursor with an average Ni content of 20% - 80%, which is in close agreement with experimental results. The approach in this study enables researchers to obtain a larger, computationally repeatable spectrum of bimetallic phases for the investigation of Raney nickel precursors.

4.1 Introduction.....	44
4.2 Computational method	45
4.2.1 Configurations built with SOD	45
4.2.2 Boltzmann probability distributions.....	45
4.2.3 Stability of configurations.....	46
4.3 Results and Discussion.....	46
4.3.1 Configurations built with SOD	46
4.3.2 Boltzmann probability distributions.....	47
4.3.3 Stability of configurations.....	49
4.4 Conclusion	51
4.5 Supplementary Information.....	52
4.6 Acknowledgements	52
References	52

4.1 Introduction

The world is facing an energy and environmental crisis, which has led to a need to develop various alternative forms of energy production.^{1–3} Hydrogen gas (H_2) has been identified as a clean, sustainable, and highly energy-dense energy source. However, H_2 is not found naturally.⁴ There are several methods to produce H_2 . The most prominent methods include reforming natural gas, coal gasification, and water electrolysis.^{5,6} Water electrolysis is a highly sustainable and clean way to produce H_2 of high purity with only oxygen gas (O_2) as a by-product.^{5–8}

Water electrolysis consists of two half-cell reactions: the OER and the hydrogen evolution reaction (HER)^{8,9}. The OER is the rate-determining reaction of these two reactions and therefore requires an efficient electrocatalyst⁷. Studies have shown that Raney nickel, a porous Ni structure, is a possible electrocatalyst for the OER in an alkaline environment.⁹

However, the activity and selectivity of Raney nickel towards OER vary with the morphological properties of the final synthesised Raney nickel. The morphological properties of Raney nickel depend on the synthesis method,^{10–13} which is influenced by the composition of the bimetallic precursor and the final porous structure.^{13–15} During the synthesis of Raney nickel, the primary metal (Ni) is combined with a secondary metal (usually zinc (Zn) or aluminium (Al)) to form a bimetallic precursor containing various bimetallic phases followed by a leaching step.^{16,17} The secondary metal in the bimetallic precursor is more active towards the leaching step than the Ni. Of the two secondary metals mentioned above, Al produced the best results for leachability without influencing Ni's integrity.^{17,18}

The most studied $Ni_{1-x}Al_x$ bimetallic phases which form during the synthesis of Raney nickel, both experimentally and computationally, are Ni_2Al_3 , $NiAl$, and $NiAl_3$. These studies usually started with a specific bimetallic phase within an alloy or a bimetallic precursor.^{11,14,17,19,20} However, to get a more comprehensive understanding of the influence of the bimetallic precursor on the morphological properties of Raney nickel, a larger spectrum of possible bimetallic phases needs to be evaluated. The bimetallic phases could be evaluated separately or combined in one bimetallic precursor structure.

The Site Occupation Disorder (SOD)²¹ program can be used for a more systematic approach to building and modelling a spectrum of $Ni_{1-x}Al_x$ bimetallic phases. This program utilises the site occupancy disorder phenomenon seen in solid-state chemistry.²¹ In the SOD²¹ program, the secondary metal (Al) atoms are systematically substituted into each of the available lattice spaces of the bulk structure of the pure primary metal (Ni), according to a pre-defined $Ni_{1-x}Al_x$ bimetallic ratio at 0K. This substitution leads to several configurations directly proportional to the size of the bulk structure. To reduce the number of configurations obtained, only the unique configurations are identified by applying a set of geometric operators (translation, rotation, and reflection) that work in conjunction with the symmetry of the crystal structure of the primary metal.

Each unique configuration is accompanied by a degeneracy value, Ω_m , which is the number of symmetry-bound configurations identified in the larger bulk structure. These symmetry-bound configurations have the same energy due to similar atomic arrangements within the larger bulk structure. Only one of these symmetry-bound configurations is listed as output for the SOD²¹ program, namely the unique configuration.

The unique configurations were geometrically optimised at 0 K, using the General Utility Lattice Program (GULP), to find the most stable geometric orientation for the configurations.^{22,23} These optimised structures were submitted to thermodynamic calculations with a statistical SOD.²¹ These calculations require an input file with the temperatures at which the data should be calculated. The thermodynamic calculations include the Boltzmann probability distributions, the configurational entropy, and the enthalpy of mixing.

In this study, a larger spectrum of potential $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases that may influence the morphology and, thus, the synthesis and activity properties of Raney nickel were investigated using the SOD²¹ program.

4.2 Computational method

4.2.1 Configurations built with SOD

The face-centred cubic (fcc) unit cell for Ni, within the space group Fm-3m, was constructed using the following lattice parameters: a, b, and c of 3.524 Å; and cell angles of 90.0°.²⁴ The unit cell was expanded into a 2×2×1 supercell. The 2×2×1 cell contains 16 atoms, where each atom represents 6.25% of the cell. Using the SOD²¹ program at 0K resulted in numerous symmetry-bound configurations for a specific $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase. Symmetry operations reduced these symmetry-bound configurations to unique configurations, geometrically optimised using GULP²³ with the interatomic many-body potentials from the Sutton-Chen library.²² The Boltzmann probability distributions, the configurational entropy, and enthalpy of mixing were calculated for a temperature range of 0.1 K – 1200 K, in steps of 100 K.

4.2.2 Boltzmann probability distributions

The Boltzmann probability distribution was calculated using the following equation:²¹

$$P_m = \frac{1}{Z} \Omega_m e^{(-E_m/k_B T)} \quad (4-1)$$

where m is the specific configuration, E_m is the configuration energy, Ω_m the configuration degeneracy showing the number of times the unique configuration is observed, k_B is Boltzmann's constant ($8.6173 \times 10^{-5} \text{ eV} \cdot \text{K}^{-1}$), and Z is the partition function in the following equation:

$$Z = \sum_{m=1}^N e^{(-E_m/k_B T)} . \quad (4-2)$$

4.2.3 Stability of configurations

The stability of the configurations was determined by studying the entropy, which is calculated using the following equation:²¹

$$S_m = k_B T \ln \Omega_m , \quad (4-3)$$

where T is temperature, and the rest of the terms are as defined earlier.

The morphology of the various bimetallic phases could be explained with reference to the enthalpy of mixing.²⁵

$$\Delta H_{mix} = E[Ni_{1-x}Al_x] - (1-x)E[Ni] - xE[Al] , \quad (4-4)$$

where $E[Ni_{1-x}Al_x]$ is the total energy of a specific $Ni_{1-x}Al_x$ bimetallic phase bulk, and $E[Ni]$ and $E[Al]$ are the energies of the pure metals. The $E[Ni_{1-x}Al_x]$ can be calculated as a weight average from the configuration energy:²¹

$$E[Ni_{1-x}Al_x] = \sum_{m=1}^N P_m E_m [Ni_{1-x}Al_x], \quad (4-5)$$

where $E_m[Ni_{1-x}Al_x]$ is the configuration energy, and the rest of the terms are as defined earlier.

4.3 Results and Discussion

4.3.1 Configurations built with SOD

The total number of symmetry-bound configurations and the unique configurations for various $Ni_{1-x}Al_x$ bimetallic phases are listed in Table 4-1. For example, in the case of the 1:1 atomic ratio (bimetallic phase Ni_8Al_8), the total number of symmetry-bound configurations was 12870, of which only 153 configurations were unique. The number of configurations for all the bimetallic phases investigated was distributed symmetrically around the Ni_8Al_8 bimetallic phase. This distribution was observed since there was little or no influence outside the bulk structure (periodic supercell).

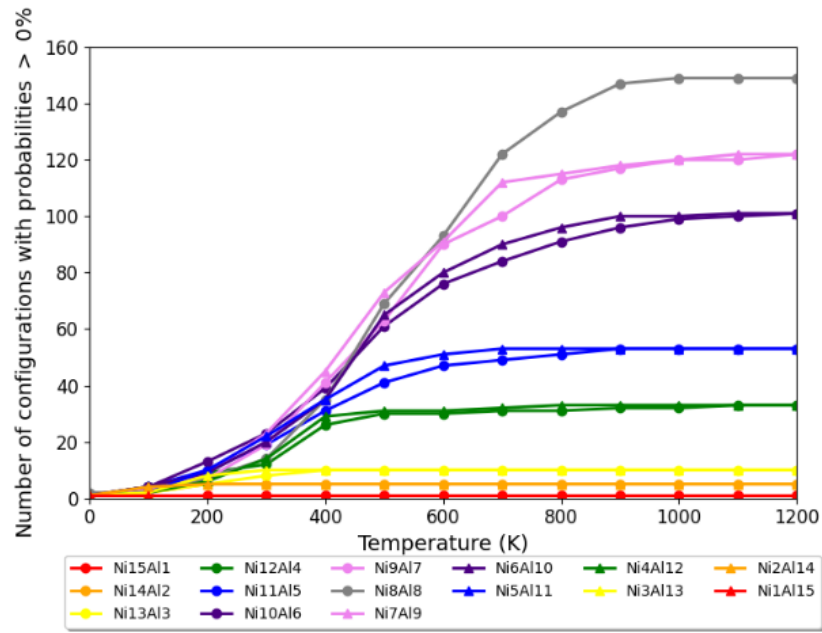
Initially, the various symmetry-bound configurations were built at 0 K. However, Raney nickel is prepared at higher temperatures. Therefore, the temperature influence on the probability distribution was considered, and it was observed that the number of unique configurations increased as the temperature increased.

Table 4-1 The configurations for various Ni_{1-x}Al_x bimetallic phases

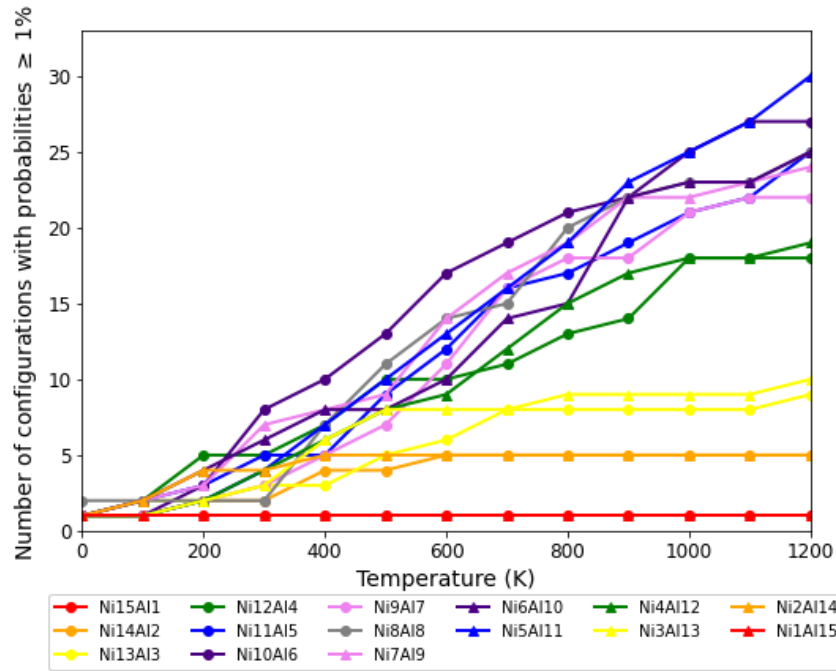
Bimetallic phase	Total number of symmetry-bound configurations	Unique configurations	Unique configurations probable at 0K
Ni ₁₅ Al ₁	16	1	1
Ni ₁₄ Al ₂	120	5	1
Ni ₁₃ Al ₃	560	10	1
Ni ₁₂ Al ₄	1820	33	1
Ni ₁₁ Al ₅	4368	53	1
Ni ₁₀ Al ₆	8008	101	1
Ni ₉ Al ₇	11440	122	1
Ni ₈ Al ₈	12870	153	2
Ni ₇ Al ₉	11440	122	1
Ni ₆ Al ₁₀	8008	101	1
Ni ₅ Al ₁₁	4368	53	1
Ni ₄ Al ₁₂	1820	33	1
Ni ₃ Al ₁₃	560	10	1
Ni ₂ Al ₁₄	120	5	1
Ni ₁ Al ₁₅	16	1	1

4.3.2 Boltzmann probability distributions

Figure 4-1 shows the number of unique configurations for the various Ni_{1-x}Al_x bimetallic phases over a temperature range of 0.1 K – 1200 K. Figure 4-1 (a) shows the number of unique configurations with a probability of existence higher than 0%. The number of unique configurations increased in a sigmoidal trend as the temperature increased and reached a plateau when the maximum number of unique configurations was above a 0% existence range. The first range is from 0K – 200K. In this temperature range, there was a gradual increase in the number of configurations for most Ni_{1-x}Al_x bimetallic phases. At 200 K, the bimetallic phases outside the Ni₁₂Al₄ to Ni₄Al₁₂ (with a Ni content of 81.25% to 18.75%) range reached their maximum number of unique configurations. The second temperature range is from 200 K – 900 K; there was a linear increase in the number of unique configurations in this temperature range. The final temperature range is from 900 K – 1200 K. In this temperature range, all the bimetallic phases in the Ni₁₂Al₄ to Ni₄Al₁₂ range reached a plateau for the unique configurations. The plateaus indicate that at 900 K, the maximum number of unique configurations was no longer influenced by temperature. It should also be noted that a high percentage of the unique configurations above 200 K had a probability of existence of less than 1%.



(a)



(b)

Figure 4-1 The number of configurations for the $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases over a temperature range of 0.1K – 1200K for (a) existence probabilities > 0% and (b) existence probabilities $\geq 1\%$. (Circle markers represent ratios where the Ni content is the highest, and triangle markers represent ratios where Al content is the highest.)

Figure 4-1(b) shows the number of unique configurations with probabilities of existence $\geq 1\%$ as the temperature increased. The bimetallic phases outside the $\text{Ni}_{12}\text{Al}_4$ to $\text{Ni}_4\text{Al}_{12}$ range reached their maximum number of unique configurations at much lower temperatures than the bimetallic phases in the $\text{Ni}_{12}\text{Al}_4$ to $\text{Ni}_4\text{Al}_{12}$ range, as seen in Figure 4-1(a). None of the bimetallic phases in the $\text{Ni}_{12}\text{Al}_4$ to $\text{Ni}_4\text{Al}_{12}$ range reached their maximum number of unique configurations in Figure 4-1(b). However, the bimetallic phases in the $\text{Ni}_{12}\text{Al}_4$ to $\text{Ni}_4\text{Al}_{12}$ range had more unique

configurations over the 600 K – 1200 K temperature range than the bimetallic phases outside of this range. Since there were fewer unique configurations for all the $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases, the influence of temperature on the number of unique configurations could be seen more clearly. Additionally, the influence of temperature on the existence probability of the two inverse-ratio $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases, namely, $\text{Ni}_2\text{Al}_{14}$ and $\text{Ni}_{14}\text{Al}_2$, or $\text{Ni}_3\text{Al}_{13}$ and $\text{Ni}_{13}\text{Al}_3$, is seen in Figure 4-1(b).

The number of unique configurations could be further reduced by increasing the probability of existence cut-off. Therefore, unique configurations with probabilities $\geq 10\%$ were considered in the rest of the chapter.

4.3.3 Stability of configurations

Studies on high entropy alloys show that the larger the entropy of the substance, the greater the stability thereof.²⁶ This observation follows from the fact that higher entropies lead to lower Gibbs-free energies. Figure 4-2 shows the entropy for the unique configurations with a probability of existence cut-off of $\geq 10\%$ relative to the Ni content at 700 K. The unique configuration data shows a parabolic trend across the Ni content range, centred around the 1:1 atomic ratio. The entropy for the unique configurations over this range of temperatures shows the same parabolic relationship with Ni content in the unique configurations as in Figure 4-2. The unique configurations with the highest entropy are in the 18.75% to 81.25% Ni content range for 700 K. The ten configurations showing the highest entropies at 700 K in Figure 4-2 are also seen at 800 K. Additionally, 80% of these highest entropy configurations at 700 K were also observed in the 600 K – 1100 K range. Entropy graphs for other temperatures over the entire 0.1 K – 1200 K range are available in Appendix A.

The unique configurations of the bimetallic phases observed at 700 K had an average Ni content of 20% - 80%. This range agreed with experimental studies showing the effective Raney nickel precursors to contain bimetallic phases in the 40% to 60% Ni range.^{16,27}

Although ten unique configurations with the highest entropy were identified in Figure 4-2, the atomic arrangement of only eight of these configurations are shown in Figure 4-3. Only eight are shown because the atomic arrangement in configurations 88 and 89 under Ni_9Al_7 , and in configurations 25 and 26 under $\text{Ni}_{11}\text{Al}_5$, are very similar for each respective $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase. It is observed in Figure 4-3 (a) – (h) that there was a tendency of like-atoms to form clusters, which indicate the preference of the pure metals to separate. This clustering tendency led to patterns of non-homogeneous mixtures within the unique configurations.

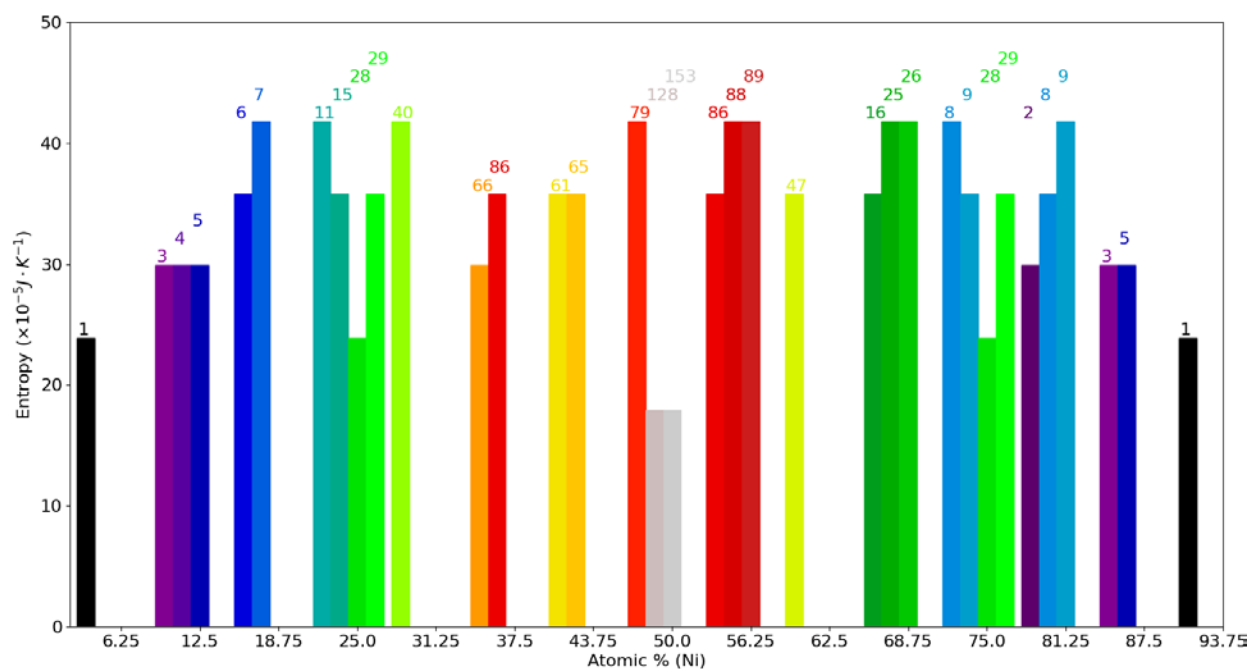


Figure 4-2 The entropy of the different configurations (with the identifying number shown above the bar), with probabilities $\geq 10\%$ relative to Ni content at 700K.

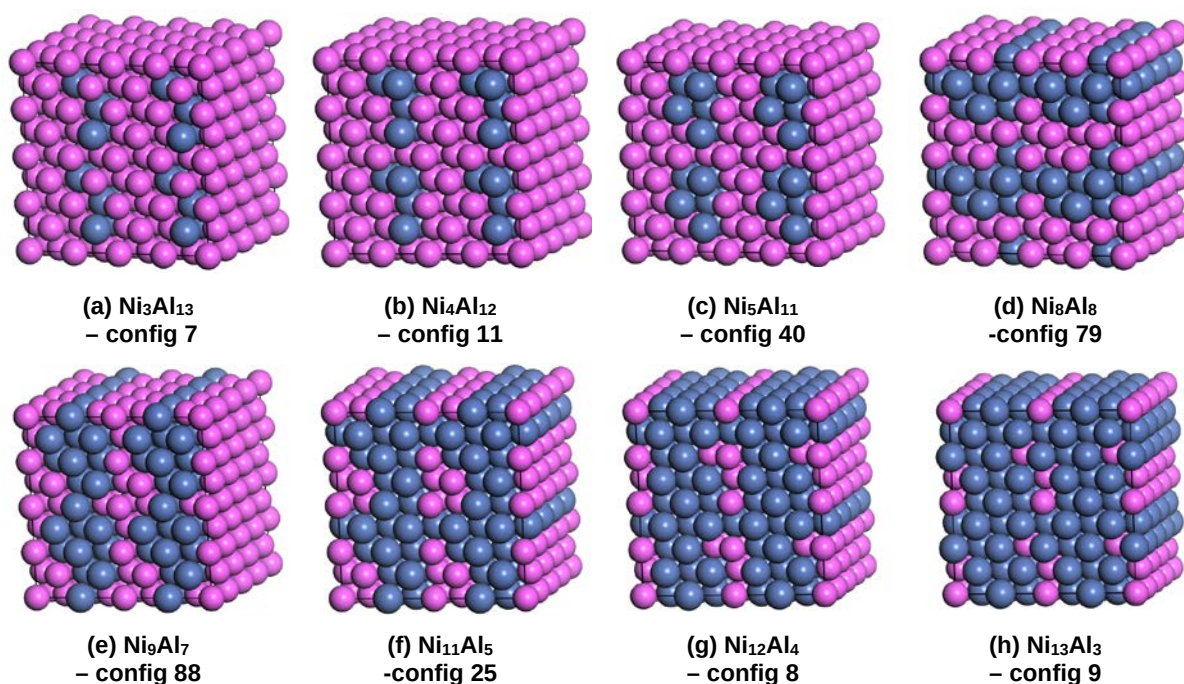


Figure 4-3 (a) - (h) The atomic structures of the most stable unique configurations identified from the entropy. (Al = magenta atoms and Ni = blue atoms.)

The expectation was that the combination of non-homogeneous bimetallic phases will form a non-homogeneous bimetallic precursor. This expectation was found to be true, which agreed with previous observations in literature.²⁸ The non-homogeneity of the bimetallic phases was further investigated by calculating the enthalpy of mixing of the bimetallic phases, as shown in equation 4-4. The enthalpy of mixing for the bimetallic phases was positive, as shown in Figure 4-4.

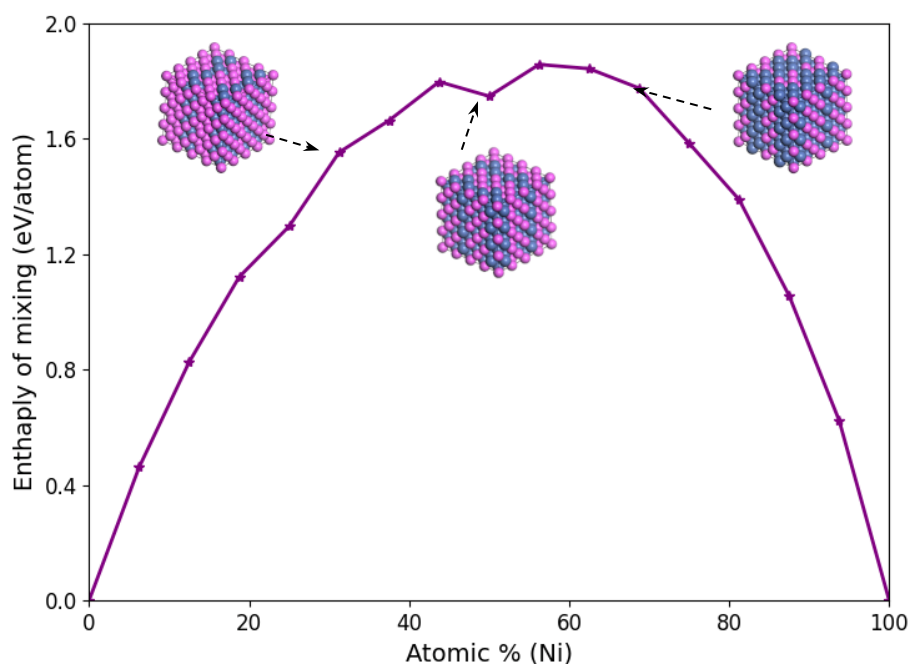


Figure 4-4 The enthalpy of mixing for $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases. The most stable configuration images of $\text{Ni}_5\text{Al}_{11}$, Ni_8Al_8 , and $\text{Ni}_{11}\text{Al}_5$ are included.

A positive enthalpy of mixing indicates that the bimetallic phases are chemically unmixed.^{27,29} Chemical unmixing refers to the segregation of Ni and Al. This segregation leads to the formation of short-to-medium range chemical and topological ordering or clustering.³⁰ This observation supports the clustering observed in Figure 4-3. However, in the case of the 1:1 atomic ratio (bimetallic phase Ni_8Al_8), a slight decrease in the enthalpy of mixing was observed. While all the configurations of the ratios surrounding the 1:1 atomic ratio showed non-homogeneity, the configuration corresponding to the 1:1 ratio showed a slightly more homogenous atomic arrangement (see inclusions in Figure 4-4), leading to a lower enthalpy of mixing.

4.4 Conclusion

In this chapter, a full spectrum of $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases was built using the SOD program. From the results, it can be concluded that using SOD to build the $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases led to the identification of configurations that included the Ni content (40% - 60%) and agreed with the non-homogeneity of Raney nickel precursors that have been used successfully in previous experimental and computational studies of OER.^{14,19,28,29} Therefore, the SOD program provided a reliable spectrum of configurations that can be used for a more in-depth study of the influence of the precursor (containing various $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases) on the properties of Raney nickel. The next step in the study of Raney nickel will be to investigate the leaching of Al from the separate $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases or from a bimetallic precursor structure constructed by combining these $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases. These $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases will be studied further in Chapter 5 using the DFT model developed in Chapter 3.

4.5 Supplementary Information

Supplementary Information to this chapter can be found in Appendix A.

4.6 Acknowledgements

The financial assistance of the North-West University (NWU) and the National Research Foundation (NRF), under grant UID 117978, towards this research is hereby acknowledged. The opinions expressed, and conclusions arrived at are those of the authors and are not necessarily to be attributed to the NRF. Additionally, the authors would like to thank Jabus van den Berg for technical support. This work was performed using the computational facilities of the Centre for High-Performance Computing (CHPC) of South Africa.

References

- (1) Coyle D., E.; Simmons A., R. *Understanding the Global Energy Crisis*; 2014. https://doi.org/10.26530/oopen_469619.
- (2) Demirbas, A. Global Renewable Energy Projections. *Energy Sources, Part B: Economics, Planning and Policy* **2009**, 4 (2), 212–224. <https://doi.org/10.1080/15567240701620499>.
- (3) Dresselhaus, M. S.; Thomas, I. L. Alternative Energy Technologies. *Nature* **2001**, 414 (6861), 332–337. <https://doi.org/10.1038/35104599>.
- (4) Cheng, Y.; Jiang, S. P. Advances in Electrocatalysts for Oxygen Evolution Reaction of Water Electrolysis-from Metal Oxides to Carbon Nanotubes. *Progress in Natural Science: Materials International* **2015**, 25 (6), 545–553. <https://doi.org/10.1016/j.pnsc.2015.11.008>.
- (5) Doyle, R. L.; Lyons, M. E. G. The Oxygen Evolution Reaction: Mechanistic Concepts and Catalyst Design. In *Photoelectrochemical solar fuel production*; Springer, 2016; pp 41–104.
- (6) Santos, D. M. F.; Sequeira, C. A. C.; Figueiredo, J. L. Hydrogen Production by Alkaline Water Electrolysis. *Química Nova* **2013**, 36 (8), 1176–1193.
- (7) Lyu, F.; Wang, Q.; Choi, S. M.; Yin, Y. Noble-Metal-Free Electrocatalysts for Oxygen Evolution. *Small* **2019**, 15 (1), 1804201.
- (8) Khan, M. A.; Zhao, H.; Zou, W.; Chen, Z.; Cao, W.; Fang, J.; Xu, J.; Zhang, L.; Zhang, J. Recent Progresses in Electrocatalysts for Water Electrolysis. *Electrochemical Energy Reviews* **2018**, 1 (4), 483–530.
- (9) Colli, A. N.; Girault, H. H.; Battistel, A. Non-Precious Electrodes for Practical Alkaline Water Electrolysis. *Materials* **2019**, 12 (8), 1336. <https://doi.org/10.3390/ma12081336>.

- (10) Klein, J. C.; Hercules, D. M. Surface Analysis of Raney Nickel Alloys. *Analytical Chemistry* **1981**, 53 (6), 754–758.
- (11) Zeifert, B.; Blásquez, J. S.; Moreno, J. G. C.; Calderón, H. A. Raney-Nickel Catalysts Produced by Mechanical Alloying. *Reviews on Advanced Materials Science* **2008**, 18 (7), 633–639.
- (12) Tanaka, S.; Hirose, N.; Tanaki, T. Evaluation of Raney-Nickel Cathodes Prepared with Aluminum Powder and Tin Powder. *International Journal of Hydrogen Energy* **2000**. [https://doi.org/10.1016/S0360-3199\(99\)00052-X](https://doi.org/10.1016/S0360-3199(99)00052-X).
- (13) Devred, F.; Gieske, A. H.; Adkins, N.; Dahlborg, U.; Bao, C. M.; Calvo-Dahlborg, M.; Bakker, J. W.; Nieuwenhuys, B. E. Influence of Phase Composition and Particle Size of Atomised Ni-Al Alloy Samples on the Catalytic Performance of Raney-Type Nickel Catalysts. *Applied Catalysis A: General* **2009**, 356 (2), 154–161. <https://doi.org/10.1016/j.apcata.2008.12.039>.
- (14) Schweizer, S.; Chaudret, R.; Low, J.; Subramanian, L. Molecular Modeling and Simulation of Raney Nickel: From Alloy Precursor to the Final Porous Catalyst. *Computational Materials Science* **2015**, 99, 336–342.
- (15) Schweizer, S.; Chaudret, R.; Spyriouni, T.; Low, J.; Subramanian, L. Influence of the Precursor Composition and Reaction Conditions on Raney-Nickel Catalytic System. In *Foundations of Molecular Modeling and Simulation: Select Papers from FOMMS 2015*; Snurr, R. Q., Adjiman, C. S., Kofke, D. A., Eds.; Springer Singapore: Singapore, 2016; pp 125–135. https://doi.org/10.1007/978-981-10-1128-3_8.
- (16) Divisek, J.; Mergel, J.; Schmitz, H. Advanced Water Electrolysis and Catalyst Stability under Discontinuous Operation. *International Journal of Hydrogen Energy* **1990**, 15 (2), 105–114. [https://doi.org/10.1016/0360-3199\(90\)90032-T](https://doi.org/10.1016/0360-3199(90)90032-T).
- (17) Raney, M. Catalysts from Alloys: Nickel Catalysts. *Industrial and Engineering Chemistry* **1940**, 32 (9), 1199–1203. <https://doi.org/10.1021/ie50369a030>.
- (18) Smith, A. J.; Trimm, D. L. The Preparation of Skeletal Catalysts. *Annual Review of Materials Research*. 2005, pp 127–142. <https://doi.org/10.1146/annurev.matsci.35.102303.140758>.
- (19) Barnard, N. C.; Brown, S. G. R. Kinetic Monte Carlo Modelling the Leaching of Raney Ni-Al Alloys. In *WIT Transactions on Engineering Sciences*; 2007; Vol. 54, pp 53–62. <https://doi.org/10.2495/ECOR070061>.
- (20) Barnard, N. C.; Brown, S. G. R.; Devred, F.; Bakker, J. W.; Nieuwenhuys, B. E.; Adkins, N. J. A Quantitative Investigation of the Structure of Raney-Ni Catalyst Material Using Both Computer Simulation and Experimental Measurements. *Journal of Catalysis* **2011**, 281 (2), 300–308. <https://doi.org/10.1016/j.jcat.2011.05.010>.

- (21) Grau-Crespo, R.; Hamad, S.; Catlow, C. R. A. R. A.; de Leeuw, N. H. Symmetry-Adapted Configurational Modelling of Fractional Site Occupancy in Solids. *Journal of Physics: Condensed Matter* **2007**, 19 (25), 256201. <https://doi.org/10.1088/0953-8984/19/25/256201>.
- (22) Kimura, Y.; Qi, Y.; Cagin, T.; Goddard III, W. A. *CALTECH ASCI TECHNICAL REPORT 003 The Quantum Sutton-Chen Many-Body Potential for Properties of Fcc Metals*; 1998.
- (23) Gale, J. D.; Rohl, A. L. The General Utility Lattice Program (GULP). *Molecular Simulation* **2003**, 29 (5), 291–341. <https://doi.org/10.1080/0892702031000104887>.
- (24) Technical Data for the Element Nickel in the Periodic Table. <https://periodictable.com/Elements/028/data.html>.
- (25) Wang, Q.; Grau-Crespo, R.; de Leeuw, N. H. Mixing Thermodynamics of the Calcite-Structured (Mn,Ca)CO₃ Solid Solution: A Computer Simulation Study. *Journal of Physical Chemistry B* **2011**, 115 (47), 13854–13861. <https://doi.org/10.1021/jp200378q>.
- (26) Zhang, Y. *High-Entropy Materials*; Springer Singapore: Singapore, 2019. <https://doi.org/10.1007/978-981-13-8526-1>.
- (27) Manzoor, A.; Pandey, S.; Chakraborty, D.; Phillpot, S. R.; Aidhy, D. S. Entropy Contributions to Phase Stability in Binary Random Solid Solutions. *npj Computational Materials* **2018**, 4 (1). <https://doi.org/10.1038/s41524-018-0102-y>.
- (28) Lee, G. D.; Suh, C. S.; Park, J. H.; Park, S. S.; Hong, S. S. Raney Ni Catalysts Derived from Different Alloy Precursors (I) Morphology and Characterization. *Korean Journal of Chemical Engineering* **2005**, 22 (3), 375–381. <https://doi.org/10.1007/BF02719414>.
- (29) Fultz, B. Vibrational Thermodynamics of Materials. *Progress in Materials Science*. Pergamon May 1, 2010, pp 247–352. <https://doi.org/10.1016/j.pmatsci.2009.05.002>.
- (30) MA, E. Alloys Created between Immiscible Elements. *Progress in Materials Science* **2005**, 50 (4). <https://doi.org/10.1016/j.pmatsci.2004.07.001>.

CHAPTER 5 A DFT study of the $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase structures

In this chapter, several configurations of $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase structures were geometrically optimised with the DFT model developed in Chapter 3. These bimetallic phase configurations include the eight configurations identified from configurational SOD data in Chapter 4, as well as two additional configurations identified from the statistical SOD data. These configurations' bulks and (111)-surface slabs were optimised. Various properties of the (111)-surface slabs were calculated using an energy calculation with the same settings as the optimisation. Adsorption of the $\text{OH}\cdot$ radical on a pure Ni (111)-surface slab was studied at three adsorption sites for comparison to literature and leached surfaces. Surfaces for leaching were identified using calculated properties, such as the work function, surface energy, and Ni and Al content. The leaching of Al from these surfaces was investigated using a manual approach. After the leaching, five adsorption positions on the newly leached surface slabs were selected. Adsorption at these positions was investigated using a manual approach. Finally, evaluating these results led to recommendations on whether the identified precursors were suitable for synthesising high-activity Raney nickel catalysts.

5.1 Introduction.....	56
5.2 Computational method	58
5.2.1 Bulk and (111)-surface slab optimisation	59
5.2.1.1 Bimetallic bulk structures.....	59
5.2.1.2 Bimetallic (111)-surface slab structures	59
5.2.2 Leaching behaviour and simulation	59
5.2.2.1 Leaching behaviour	59
5.2.2.2 Leaching simulation.....	60
5.2.3 Simulated adsorption.....	60
5.3 Results and discussions	61
5.3.1 Bulk and (111)-surface slab optimisation	61
5.3.2 Leaching behaviour and simulation	67
5.3.2.1 Leaching behaviour	67
5.3.2.2 Leaching simulation.....	70
5.3.2.2.1 (111)-surface slab of Ni_7Al_9	70
5.3.2.2.2 (111)-surface slab of Ni_8Al_8	74
5.3.2.2.3 (111)-surface slab of Ni_9Al_7	77
5.3.2.2.4 (111)-surface slab of $\text{Ni}_{11}\text{Al}_5$	80
5.3.3 Simulated adsorption.....	83
5.4 Conclusion	87
References	88

5.1 Introduction

The properties of Raney nickel depend on the leachability of the precursor bimetal used in its preparation.¹ Thermodynamic binary phase diagrams, such as Figure 5-1², show stable phases within a bimetallic system. This diagram shows the binary Ni-Al system for a temperature range of ~300°C to ~1700°C (~573.15K to ~1973.15K). It contains the two pure metals and several bimetallic phases, namely NiAl₃, Ni₂Al₃, Ni₂Al₄, NiAl, Ni₅Al₃ and Ni₃Al. Of these phases, Ni₂Al₃, NiAl, Ni₅Al₃ and Ni₃Al are the most stable bimetallic phases, indicated by larger areas on the phase diagram. However, depending on the preparation temperature, a wider range of bimetallic phases with different atomic % (at%) Ni than those shown in the phase diagram is possible.

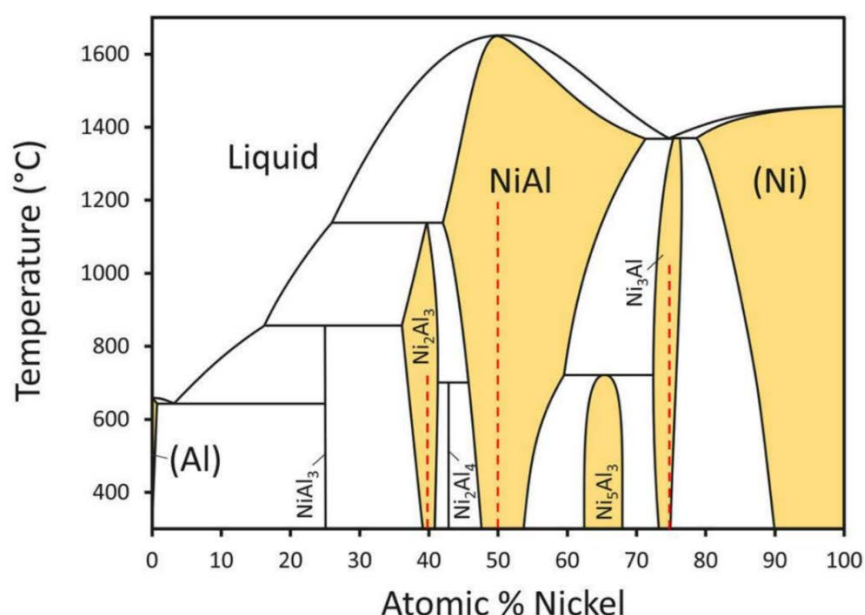


Figure 5-1 Thermodynamic binary phase diagram of a Ni-Al system. The yellow areas show the stable phases and the dashed red lines represent the Ni_xAl_y bimetallic phases used in the study by Luong *et al.*² Reused with permission (Appendix C).

Thus, a wider range of potential bimetallic phases needs to be evaluated to gain a more comprehensive understanding of the influence of the bimetallic precursor on the morphological properties of Raney nickel. As a result, in the previous chapter (Chapter 4), a full spectrum of Ni_{1-x}Al_x bimetallic phases were constructed using the Site Occupation Disorder (SOD) program.³ From the results in Chapter 4, the ten most stable unique Ni_{1-x}Al_x bimetallic configurations included in the bimetallic phases within the 40%–60% Ni content range were identified. These agreed with the non-homogeneity of Raney nickel precursors that have been used successfully in earlier experimental and computational studies of the Oxygen Evolution Reaction (OER).^{1,4–6} Two of the ten unique Ni_{1-x}Al_x bimetallic configurations could be eliminated based on the observation that these configurations have very similar atomic arrangements to two other configurations under the same Ni_{1-x}Al_x bimetallic phase, with the only difference being the position of one or two atoms (See Figure A-2 in Appendix A). The remaining eight unique Ni_{1-x}Al_x bimetallic configurations are reiterated in Figure 5-2.

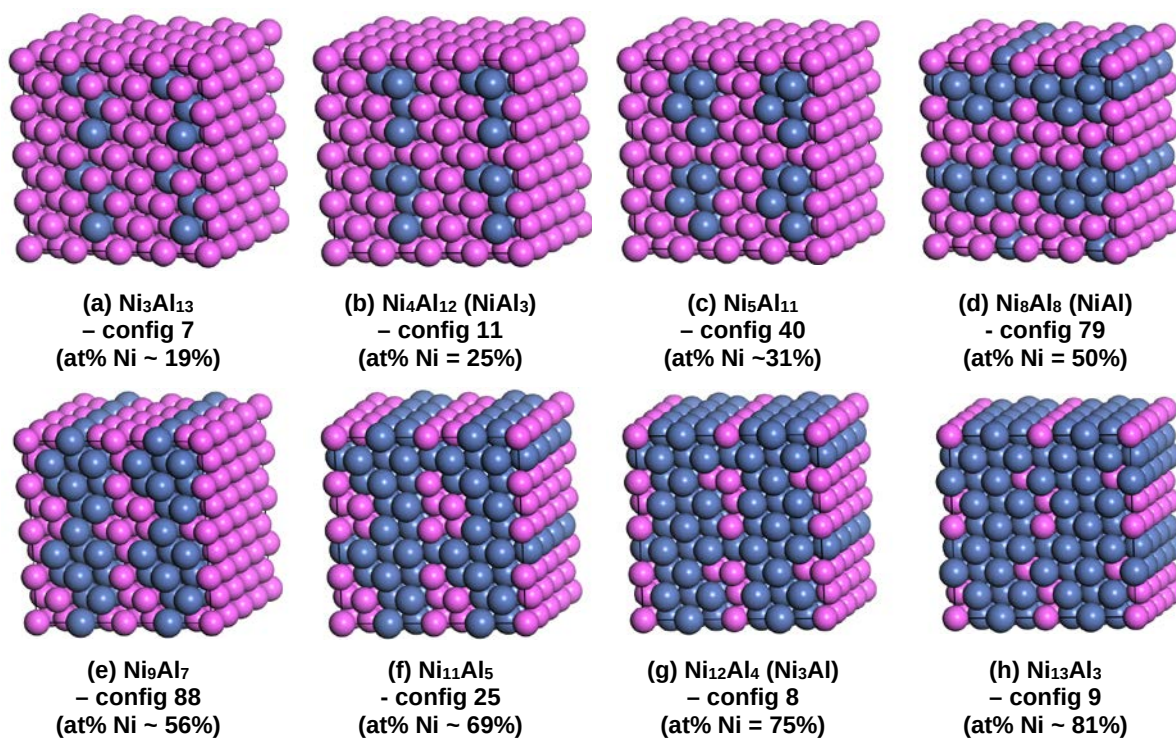


Figure 5-2 (a) - (h) The atomic structure of the eight most stable unique $\text{Ni}_{1-x}\text{Al}_x$ bimetallic configurations identified from entropy in Chapter 4. (Al = magenta atoms and Ni = blue atoms.)⁷ Additional to the Chapter 4 results, the Ni at% is shown for each $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase.

Additionally, from the statistical SOD data (Figure 5-3), Ni_7Al_9 (black dashed line) was identified as the bimetallic phase with the highest entropy across most temperature ranges. By comparing the entropy of all the unique configurations of Ni_7Al_9 , built with SOD, the two most stable unique $\text{Ni}_{1-x}\text{Al}_x$ bimetallic configurations were identified (Figure 5-4). These bimetallic configurations will be included in the rest of this study. Furthermore, the locations of the bimetallic phases (grey dashed lines), which are present in the phase diagram (Figure 5-1), and the bimetallic phases identified in Chapter 4 (sea green dashed lines), are indicated in Figure 5-3.

In this study, the bulk structures of the ten identified unique $\text{Ni}_{1-x}\text{Al}_x$ bimetallic configurations were geometrically optimised and cleaved at the (111)-surface. These surface slabs were geometrically optimised, and the properties of the surface slabs were calculated. By comparative use of the calculated properties, bimetallic phase surface slab structures were identified, from which the leaching of Al was simulated. Subsequently, the $\text{OH}^\cdot$ species, the most widely accepted first adsorbate for alkaline OER,^{8,9} was adsorbed onto the leached surface slab. The electrocatalytic activity toward the $\text{OH}^\cdot$ species was evaluated for each identified surface slab. For this evaluation, the d-band centres of the leached surface slabs were compared before and after $\text{OH}^\cdot$ adsorption. For comparison, the $\text{OH}^\cdot$ adsorption and evaluation was also done on the pure Ni (111)-surface slab.

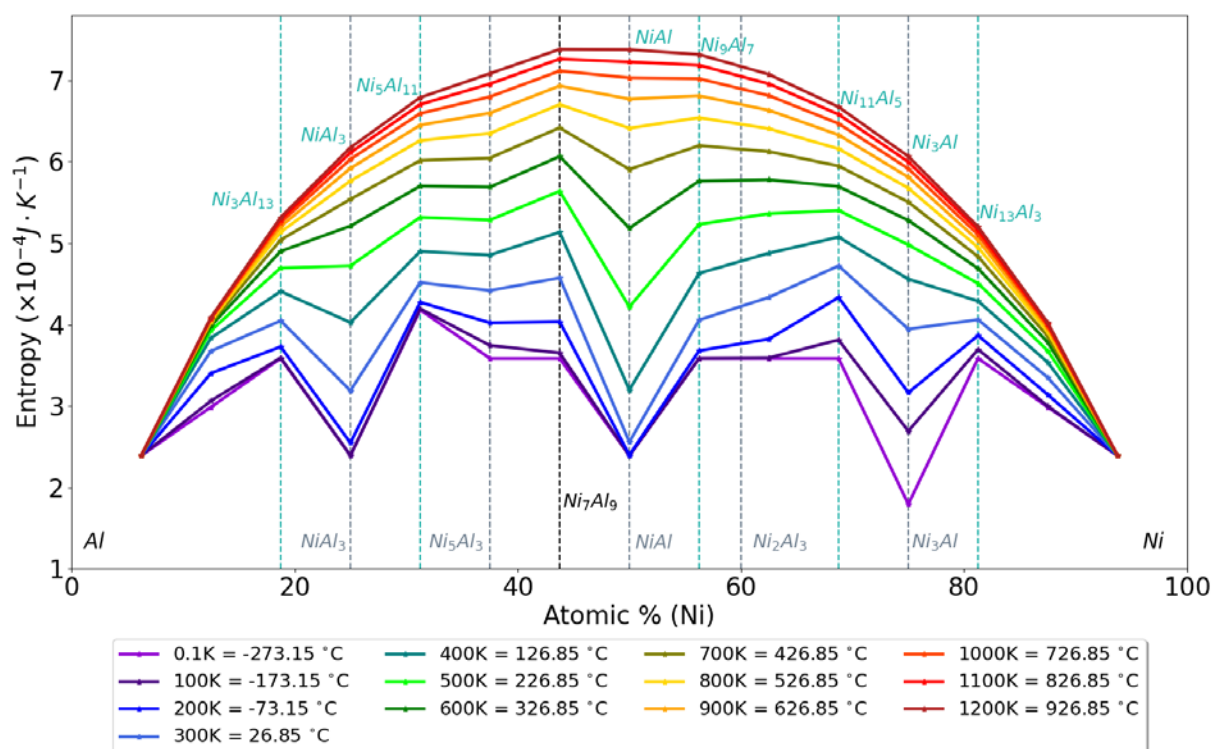


Figure 5-3 Statistical entropy data from SOD calculations in Chapter 4, over a temperature range of 0.1K to 1200K, for the $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases.

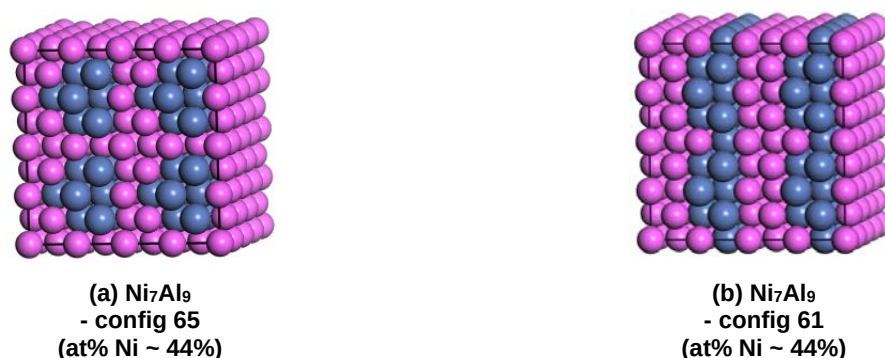


Figure 5-4 (a) – (b) The atomic structure for the most stable unique $\text{Ni}_{1-x}\text{Al}_x$ bimetallic configurations, namely (a) 65 and (b) 61, of Ni_7Al_9 . (Al = magenta atoms and Ni = blue atoms.)

5.2 Computational method

Density Functional Theory (DFT) calculations were performed using the Cambridge Serial Total Energy Package (CASTEP)¹⁰ in the Materials Studio 2020 (MS2020)¹¹ program developed by the BIOVIA software company. Dispersion correction (DFT-D) calculations were considered when optimising the bulk $\text{Ni}_{1-x}\text{Al}_x$ bimetallic structures because the identified surface slab structures will be used later for surface interaction calculations.

The computational model developed in Chapter 3 was applied to the eight most stable unique $\text{Ni}_{1-x}\text{Al}_x$ bimetallic configurations identified in Chapter 4 (reiterated in Figure 5-2) and the additional unique $\text{Ni}_{1-x}\text{Al}_x$ bimetallic configurations identified from entropy (Figure 5-4).

The Computational Method section is divided into three subsections: identifying the optimal $\text{Ni}_{1-x}\text{Al}_x$ bimetallic surface slabs (5.2.1), leaching Al atoms from the identified $\text{Ni}_{1-x}\text{Al}_x$ bimetallic surface slabs (5.2.2), and adsorption of the $\text{OH}\cdot$ diatomic radical species onto the leached $\text{Ni}_{1-x}\text{Al}_x$ bimetallic surface slabs (5.2.3).

5.2.1 Bulk and (111)-surface slab optimisation

5.2.1.1 Bimetallic bulk structures

The $2\times 2\times 1$ bulk structures of the uniquely identified $\text{Ni}_{1-x}\text{Al}_x$ bimetallic configurations were imported from the SOD output. The imported bulk structures were duplicated in the c-direction to give a $2\times 2\times 2$ bimetallic bulk structure. This duplication was done to gain a cubic symmetry for further calculation.

The bimetallic bulk structures were geometrically optimised using the DFT model developed in Chapter 3.

5.2.1.2 Bimetallic (111)-surface slab structures

The optimised $2\times 2\times 2$ bimetallic bulk structures were cleaved at the (111)-Miller plane with a fractional top setting of 2.603 (10.6 Å) and fractional thickness of 1.618 (6.592 Å), and optimised using the DFT model developed in Chapter 3. The (111) surface was chosen because previous XRD data showed that this is the most dominant surface both before and after leaching for Raney nickel.^{12,13}

The surface and electronic properties, including the work functions and surface energies, for the (111)-surface slabs of the bimetallic phases were calculated using the approach in the DFT model developed in Chapter 3. The surface energies were calculated using equation 2-14¹⁴ the work function was calculated automatically and derived from the potentials' files, which plots the averaged electrostatic potential oriented perpendicular to the surface slab's normal; and the d-band centres were calculated as specified in Chapter 3. The surface energy is the energy needed to create a new surface and could be related to the stability of the surface. It can be described as a measurement of the extra energy that surface atoms have because of various reasons, for example, broken bonds leading to lower coordination numbers.¹⁵

The calculated surface properties, along with properties previously found in literature, were used to identify the most suitable surface slabs for simulating leaching.

5.2.2 Leaching behaviour and simulation

5.2.2.1 Leaching behaviour

The leaching of Al from the Ni-Al system is typically done with a base, such as NaOH.^{16–20} Therefore, the interaction between the (111)-surface slab and an $\text{OH}\cdot$ species was investigated. Ni_8Al_8 surface slab was used to determine the interaction between the surface and an $\text{OH}\cdot$

species. Two cases were considered: adding an OH⁻ species in the top site above an Al atom or in the fcc site between two Al atoms and a Ni atom in the surface. These combined structures were optimised using the DFT model developed in Chapter 3. The goal was to obtain a visual representation of the leaching behaviour; therefore, no additional properties were calculated.

5.2.2.2 Leaching simulation

There are various ways to simulate leaching.^{1,21,22} In this study, a manual leaching approach was used. Manual leaching entails the stepwise removal of atoms to be leached from a surface slab. In this study, the atom that would be leached is Al.²³ This removal was verified in the section 5.2.2.1 by studying the leaching behaviour of an OH⁻ species on the Ni₈Al₈ surface for the top and fcc sites.

The optimised Ni_{1-x}Al_x bimetallic phase (111)-surface slabs that were identified in section 5.3.1 were used. The initial Al atoms were chosen after considering the effect of deeper leaching or a Ni-rich area on OH⁻ adsorption. An Al atom was selected and removed; the surface slab was optimised using the DFT model developed in Chapter 3. This process was repeated three consecutively times resulting in a set of four Al atoms being removed. Different variations of second, third, and fourth Al atom removals were investigated. After each removal, the resulting surface slab was optimised using the DFT model developed in Chapter 3. The energy required to remove one Al atom at a time was calculated using equation 5-1 (equation 2-17):

$$E_{Al\ removal} = E_{surface\ slab(b)} - E_{surface\ slab(a)} - E_{Al} \quad (5-1)$$

where $E_{Al\ removal}$ is the energy required to remove an Al atom from the surface slab, $E_{surface\ slab(b)}$ is the optimised energy of the surface slab before removing a specific atom, $E_{surface\ slab(a)}$ is the optimised energy of the surface slab after removing a specific atom, and E_{Al} is the optimised energy of a single Al atom. Finally, the route requiring the least energy to remove sequential Al atoms from a specific Ni_{1-x}Al_x bimetallic phase (111)-surface slab was determined.

Additionally, the atomic electron density difference was calculated for the (111)-surface slabs after each leaching step. The average energy for Al removal was also calculated for each slab. The average energy was calculated by averaging the removal energy over each of the top three layers and then averaging these calculated average energies over the slab.

5.2.3 Simulated adsorption

There are various ways to simulate adsorption.^{24,25} In this study, adsorption was done by identifying several positions by considering the NN environment and bonding of an adsorbate at these positions' atoms. The adsorption was done for a pure Ni (111)-surface slab and the leached Ni_{1-x}Al_x bimetallic phase (111)-surface slab having the route requiring the least energy to remove subsequent Al atoms from a specific area.

The adsorbed species in this study was the diatomic radical OH·, derivative of the widely accepted first adsorbate for the OER^{8,26}, and the adsorption positions were related to Ni atoms. The DFT model developed in Chapter 3 was used to optimise the leached surface slab/OH·-system. The adsorption energy was calculated using equation 5-2²⁵ (equation 2-17):

$$E_{ads} = E_{(OH\cdot/surface\ slab)} - E_{OH\cdot} - E_{surface\ slab} \quad (5-2)$$

E_{ads} is the adsorption energy, $E_{(OH\cdot/surface\ slab)}$ is the optimised energy of the leached OH·/surface slab system, $E_{OH\cdot}$ is the optimised energy of OH· and $E_{surface\ slab}$ is the optimised energy of the leached surface slab before adsorption.

The d-band centres and d-band centre shifts were calculated in addition to the adsorption energy. The adsorption energies of OH· on the pure Ni (111)-surface were compared to the literature. The adsorption energies of OH· onto each final leached (111)-surface slab for each Ni_{1-x}Al_x bimetallic phase were compared to those of pure Ni (111).

5.3 Results and discussions

5.3.1 Bulk and (111)-surface slab optimisation

The property data from the DFT calculations for the Ni_{1-x}Al_x bimetallic phase (111)-surface slabs of the configurations that were previously identified and shown in Figures 5-2 and 5-4, are given in Table 5-1. The configurations of the Ni_{1-x}Al_x bimetallic phases are arranged in ascending order of at% Ni content. The Ni₇Al₉ bimetallic phase (~at% Ni = 44%) has two configurations, namely configuration 65 and configuration 61, with different property data. The table also includes the pure metal surface slab data calculated in Chapter 3 for comparison. For the final bulk structure and surface slab fractional coordinates, refer to Appendix F.

Table 5-1 The calculated spin moment (m_s) and some measured interatomic distances (d_{X-Y}) for (111)-surface slabs are shown.

Bimetallic phase	~at% Ni	m_s (μ_B /atom)	d_{Ni-Ni} (Å)	d_{Al-Al} (Å)	d_{Ni-Al} (Å)
Al	0	0.000	-	2.777	-
Ni ₃ Al ₁₃	19	0.000	2.750	2.844	2.651
Ni ₄ Al ₁₂	25	0.000	2.801	2.736	2.501
Ni ₅ Al ₁₁	31	0.000	2.893	2.690	2.545
Ni ₇ Al ₉	44	0.000	2.432	2.618	2.471
	44	0.000	2.514	2.776	2.436
Ni ₈ Al ₈	50	0.000	2.736	2.666	2.438
Ni ₉ Al ₇	56	0.000	2.469	2.679	2.364
Ni ₁₁ Al ₅	69	-0.042	2.500	2.847	2.379
Ni ₁₂ Al ₄	75	0.089	2.493	2.715	2.415
Ni ₁₃ Al ₃	81	0.202	2.475	2.674	2.513
Ni	100	0.655	2.435	-	-

The calculated spin magnetic moment (m_s) of Ni was 0.655 μ_B , which is in good agreement with the literature value of 0.620 μ_B .^{27,28} This large spin moment is expected for Ni since it is a ferromagnetic material with a high spin. Further, it can be seen in Table 5-1 that the Ni content in the bimetallic surface slab influences the magnetic properties of the slab. Surface slabs with lower Ni content tended to have the magnetic properties of Al; this observation agrees with the literature.²⁹ Surface slabs with higher Ni content above 60%, tended to have the magnetic properties of Ni. The macroscopic magnetic properties of a material are related to the spin properties of the electrons in the material. The magnitude of the spin moment increases gradually from a Ni content of ~69% to ~81%. However, for $Ni_{11}Al_5$, the average spin moment was negative, indicating that the surface slab had an overall negative electron spin. The increase in the magnitude of the spin moment of $Ni_{1-x}Al_x$ bimetallic phase (111)-surface slabs with increasing Ni content is consistent with the literature.³⁰ The spin state of transition metal catalysts can influence the catalytic pathway and, therefore, the catalytic activity.³¹ However, the effect of the spin state on the catalytic activity is outside the scope of this study.

The density of states (DOS), measures quantify how the electrons are packed within a specific energy state. The DOS can be calculated for the whole band or for individual spin states in the band. Figure 5-5 shows the total p-band DOS and total d-band DOS of Ni_5Al_{11} and $Ni_{11}Al_5$, compared to the p-band DOS of pure Al and the d-band DOS of pure Ni. This comparison reveals the influence of the Ni and Al content on the DOS of the $Ni_{1-x}Al_x$ bimetallic phases.

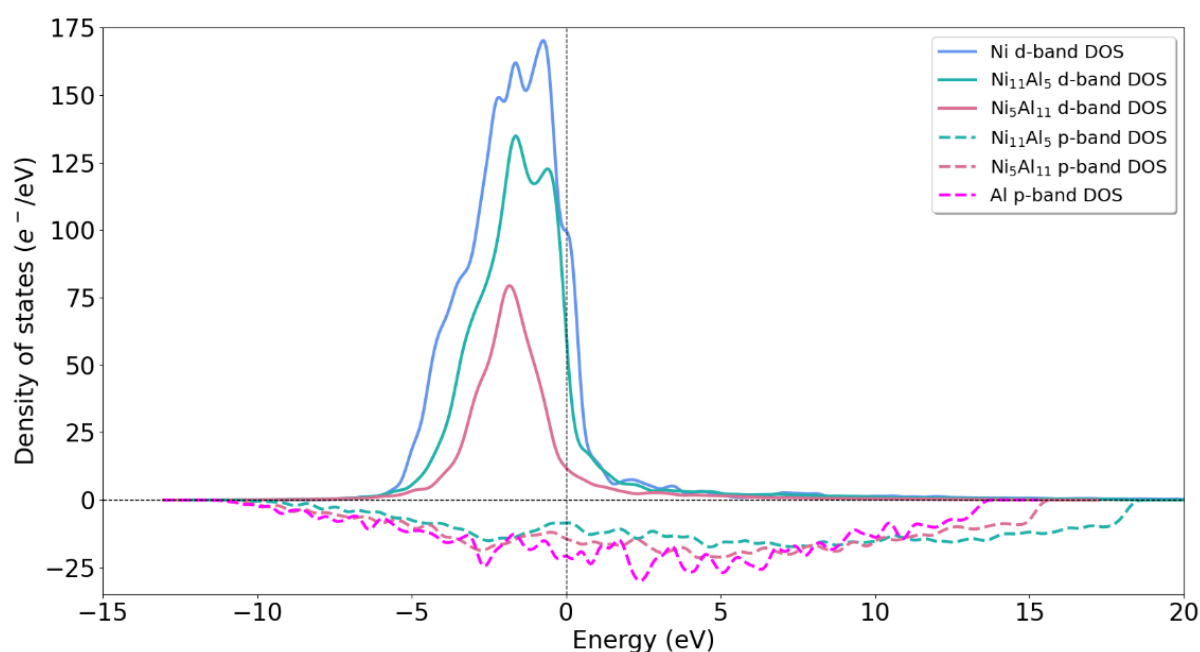


Figure 5-5 Partial density of states for pure Al, Ni_5Al_{11} , $Ni_{11}Al_5$ and pure Ni. The positive y-axis represents the d-band DOS, while the negative y-axis represents the p-band DOS.

For the bimetallic phase $Ni_{11}Al_5$ with higher Ni content (represented by the green solid line), the position of the d-band centre was closer to that of pure Ni compared to the position of the d-band centre of its lower Ni content counterpart Ni_5Al_{11} (represented by the light pink solid line). However

for the bimetallic phase $\text{Ni}_5\text{Al}_{11}$ with higher Al content (represented by the light pink dashed line), the position of the p-band DOS centre was much closer to that of pure Al than that of its lower Al content counterpart $\text{Ni}_{11}\text{Al}_5$ (represented by the green dashed line). This DOS comparison showed that the Ni and Al content highly influenced the surface slabs' electronic and magnetic properties. A comparison of the beta and alpha DOS of these bimetallic phases to pure Ni and Al was also made. This showed that the $\text{Ni}_{11}\text{Al}_5$ bimetallic phase follows the d-band symmetry of pure Ni better than the $\text{Ni}_5\text{Al}_{11}$. The p-band symmetry of the $\text{Ni}_5\text{Al}_{11}$ bimetallic phase is closer to that of pure Al (see Figure A-3).

The interatomic spacing (d_X - d_X , $X = \text{Ni}, \text{Al}$) was measured for one surface pair of each of the Ni-Ni, Al-Al and Ni-Al atomic pairs, as shown in Table 5-1. It was observed that the overall trend of the $d_{\text{Ni}}\text{-}d_{\text{Ni}}$ data was declining, while the $d_{\text{Al}}\text{-}d_{\text{Al}}$ and $d_{\text{Ni}}\text{-}d_{\text{Al}}$ data were decreasing, reaching minimums at Ni_8Al_8 and Ni_9Al_7 , respectively, before increasing again. However, none of these observed trends showed smooth decreases or increases. In these measurements, nearest-neighbour (NN) interactions which could influence the bond lengths were not considered,³² which could explain the lack of smooth trends. Due to the non-homogeneity of the various $\text{Ni}_{1-X}\text{Al}_X$ bimetallic phase (111)-surface slabs taking the NN interactions into account is challenging and further investigation is needed.

Figure 5-6(a) shows the Ni_8Al_8 (111)-surface slab, and Figures 5-6 (b) and (c) show the calculated electron density distribution and atomic electron density difference of this slab, respectively.

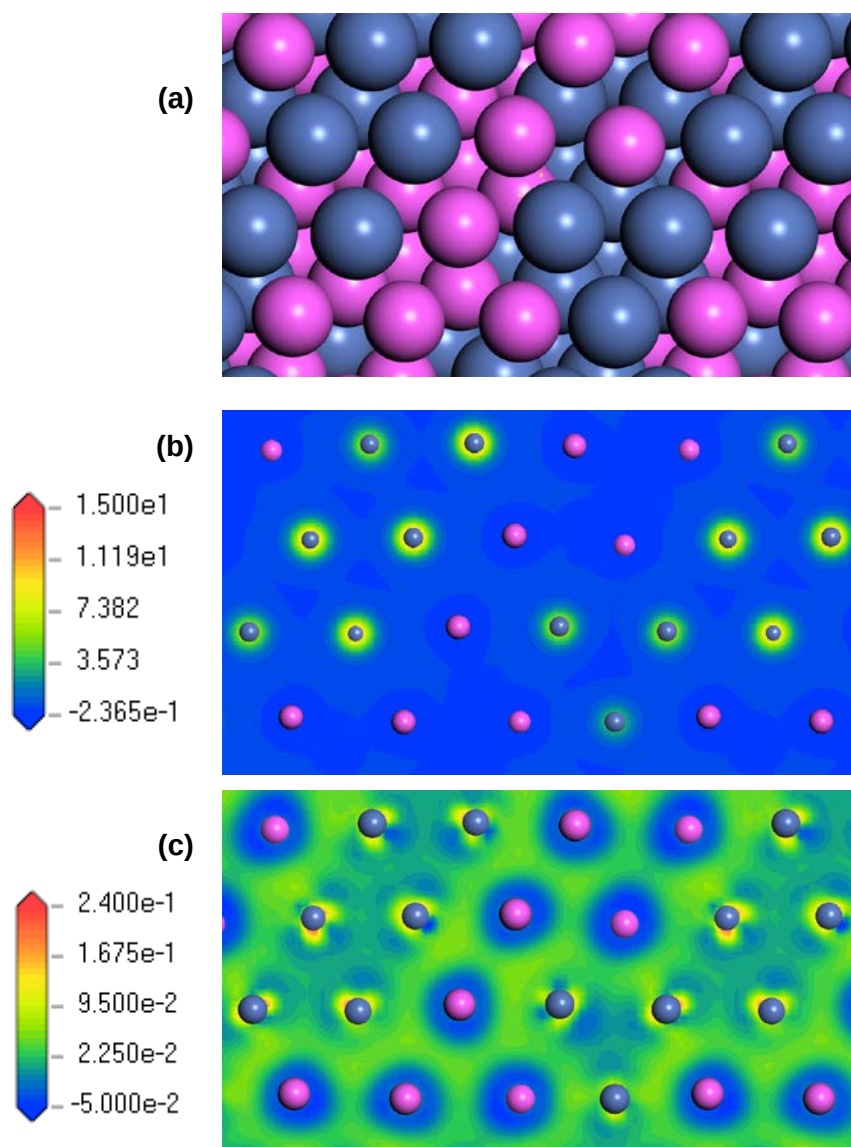


Figure 5-6 (a) The top view of the Ni_8Al_8 (111)-surface slab structure. (b) An isosurface slice of the electron density distribution of the top layer of the Ni_8Al_8 (111)-surface slab structure. The isosurface scale indicates that blue shows low electron density, while red shows high electron density. (c) An isosurface slice of the atomic electron density difference distribution of the top layer of the Ni_8Al_8 (111)-surface slab structure. The isosurface scale indicates that blue shows electron depletion, while red shows electron accumulation. (Al = magenta atoms, and Ni = blue atoms.)

The calculated electron density distribution and atomic electron density difference for the other slab systems are available in Appendix A (Figure A-3 and Figure A-4). The blue regions represent lower electron density (electron depletion), while the red regions represent higher electron density (electron accumulation) in the electron density distribution (Figure 5-6 (b)) and the atomic electron density difference (Figure 5-6 (c)). It is observed that the density of electrons is higher on the Ni atoms at the surface than on the Al atoms. The lower electron density on the Al atoms implies that negative species, such as OH^- , would rather coordinate with the Al atoms.

Finally, the work function and surface energy of the $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase (111)-surface slabs were compared in Figure 5-7. The work function and surface energy both showed an overall upward fluctuating trend. A similar trend for the Ni-Al alloy system was observed by Franken *et al.*²⁹ However, at a Ni content of ~44%, a shift in the data was observed (going from

configuration 65 to configuration 61, shown in Figure 5-4), with a downward shift for the work function and an upward shift for the surface energy. This shift in the data coincided with the overall change in the atomic arrangement within the structures, as seen in Figures 5-2 and 5-4. In these structures, a more grouping (clustering) pattern was observed for Ni before the shift, while the atoms were seen to be in a layered pattern after the shift.

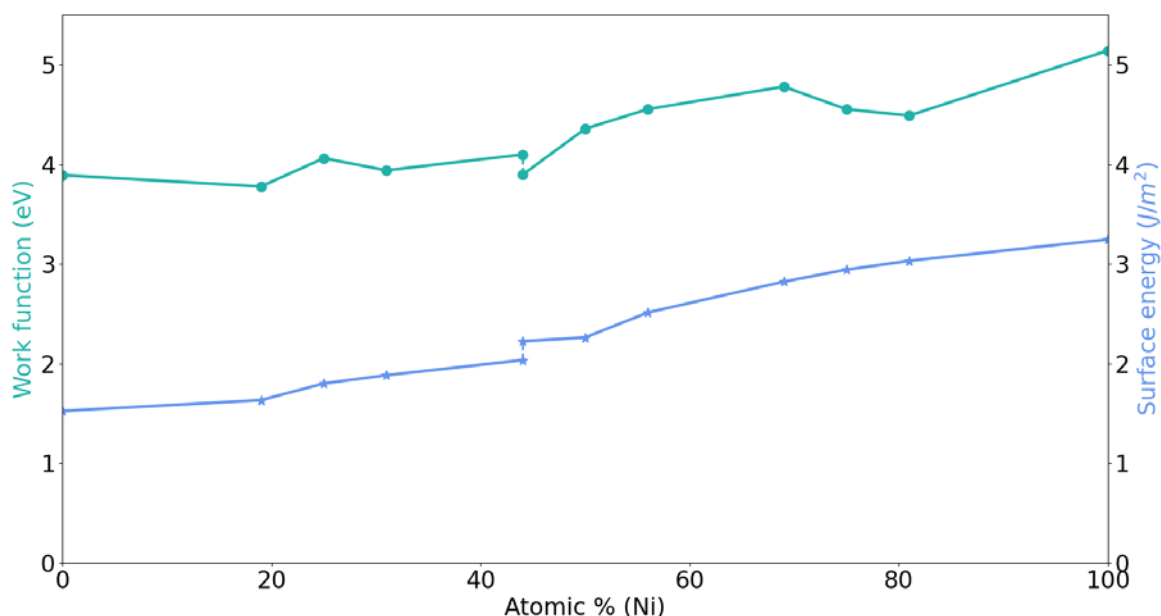


Figure 5-7 Work function (green) and surface energy (blue) for the $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase (111)-surface slabs in order of ascending Ni content from the left.

Considering the work function data seen in Figure 5-7 (green line), the observed upward trend in the data was not smooth and was observed to fluctuate around an imaginary linear increase line. Two different maximum values were observed for the bimetallic regions in the two sections of the data (namely, before and after a Ni content of ~44%). The first was at ~25% Ni content, and the second was at ~69% Ni content. In both cases, the number of atoms surrounded by like atoms in the top layer changed (see Appendix A, Figure A-3). A previous study showed that electrons tend to flow (typically 1-2 electrons per 100 surface atoms in the surface) from a metal with a smaller work function to one with a larger work function.³⁰ This observed tendency could explain the electron distributions depicted in Figures 5-6 (b) and (c). These electron distributions could be attributed to the surface slab atoms' influence on the work function and the possible influence of the NN on the electron distribution. From the surface representations in Appendix A (see Figure A-3), it could be concluded that the surface slabs with greater Al NN-groups showed lower work functions than those with predominantly Ni NN-groups. Lower work functions have been shown to increase the leachability of surfaces.³³ Higher leachability would imply lower leaching energies.

A smooth upward trend was observed for the surface energy seen in Figure 5-7 (blue line). The data shows a slight decrease at 50% Ni content. This slight decrease could be due to the influence of equal amounts of each element in the surface slab; the NN of the sub-surface layer

atoms also seem to be distributed equally. From the surface energy data, it could be deduced that the higher the Ni content, the higher the energy of the less coordinated surface atoms. The higher energy is due to the stronger bonds of Ni atoms to the bulk compared to Al atoms. Higher less-coordinated-atom energies could lead to the surface being less stable configurationally. Less stable surfaces are more prone to surface reconstruction to instil stability.³⁴ The surface energy of the Ni_8Al_8 surface was calculated to be 2.26 J/m^2 which is comparable to a literature value of 2.20 J/m^2 for the ordered body-centred cubic (bcc) structure of NiAl .³⁵ In contrast, the surface energy of the ordered fcc structure of Ni_3Al surface was calculated to be 2.944 J/m^2 , in this work, which does not agree with the literature value of 1.966 J/m^2 ³⁵ (deviation of 33%). However, Purja *et al.*³⁵ indicated that the literature values of (embedded atom model) EAM studies for NiAl and Ni_3Al surface energies are severely underestimated. For this reason, the values calculated in this study were more accurate since they were larger and compared with the surface energy of other phases. Additionally, earlier studies have found that surface energy calculations can differ by approximately 30% depending on whether the surface slab atoms were allowed to relax or left unrelaxed.³⁶ The surface slab atoms in this study were allowed to relax within the constrained lattice.

An additional property that needs to be considered when identifying a surface for leaching is the atomic composition of the surface, or, in other words, the ratio of Ni to Al atoms in the surface. The $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases on the left-hand side of the Ni content range in Figure 5-7 could contain too much Al. The sequential leaching of these high Al-content surfaces could lead to a structural collapse of the pores within the catalyst at a certain point. At the same time, those $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases on the right-hand side of the Ni content range in Figure 5-7 could contain too much Ni. This Ni content could lead to unsatisfactory pore sizes being formed when the Al is leached out. This observation coincides with previously identified suitable Raney nickel precursors, such as NiAl bimetals with a Ni content between 40% - 60%.^{1,4-6}

To summarise, the most suitable $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases for further investigation in this study were identified by considering the surface slab's work function, surface energy, and atomic composition. Lower work functions could improve leachability, thus the $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases to the left of the graph in Figure 5-7 were preferred. However, leaching from surfaces with high surface energy could reduce surface stability and cause surface reconstruction. Additionally, the atomic arrangement of the surface slabs could affect the structural integrity and pore size of the final structure. Therefore, the phases after the shift at ~44% up to just before ~70% in Figure 5-7 were considered. These surface slabs have a range of atomic ratios that may lead to structural integrity and useful pore sizes. These surface slabs span a range of work functions and surface energies from both the higher and lower sides of the spectrum, which could result in favourable properties. The selected surface slabs are shown in Figure 5-8.

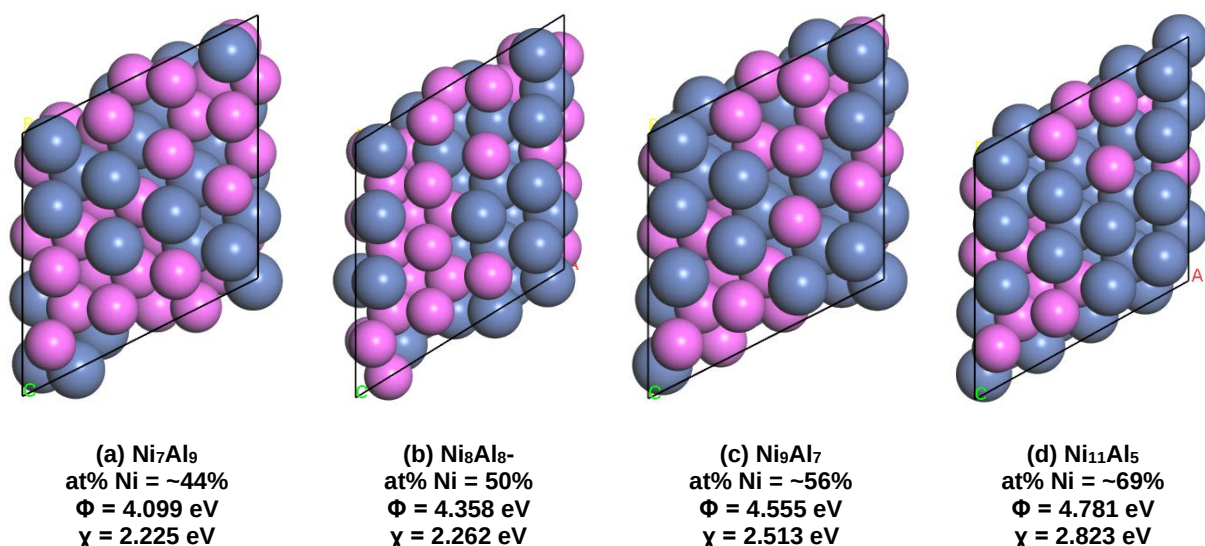


Figure 5-8 (a) – (d) Surface structures of configurations identified using DFT calculated properties for the subsequent leaching of Al. The work functions (Φ) and surface energies (γ) are also given.

5.3.2 Leaching behaviour and simulation

5.3.2.1 Leaching behaviour

Although there are various coordination sites for fcc (111)-surfaces,³⁷ only two possible coordination sites, namely top and fcc sites, were selected to evaluate the behaviour of an $\text{OH}\cdot$ species within the NiAl system. These positions were chosen so that the target atom was surrounded by different types of NN atoms in the surface and subsurface layers. The $\text{OH}\cdot$ species was added above the bimetallic surface at these two sites, and the combined NiAl- $\text{OH}\cdot$ system was optimised.

For the first coordination site, the $\text{OH}\cdot$ species was placed directly over an Al atom (top site). Figure 5-9 shows the side and top views of the surface before and after the geometric optimisation. The top site targeted Al atom and NN atoms were numbered as shown in Figure 5-9(b), with the targeted Al atom as atom number 7, located directly beneath the $\text{OH}\cdot$ species. It was observed that the $\text{OH}\cdot$ species pulled the Al atom from the surface (Figure 5-9(c)), indicating that the Al atom would be removed. Additionally, the H atom was pulled toward a Ni atom. This observation was reflected in Table 5-2 by the change in the measured bond lengths and interatomic distances of the $\text{OH}\cdot$ species and the surrounding atoms.

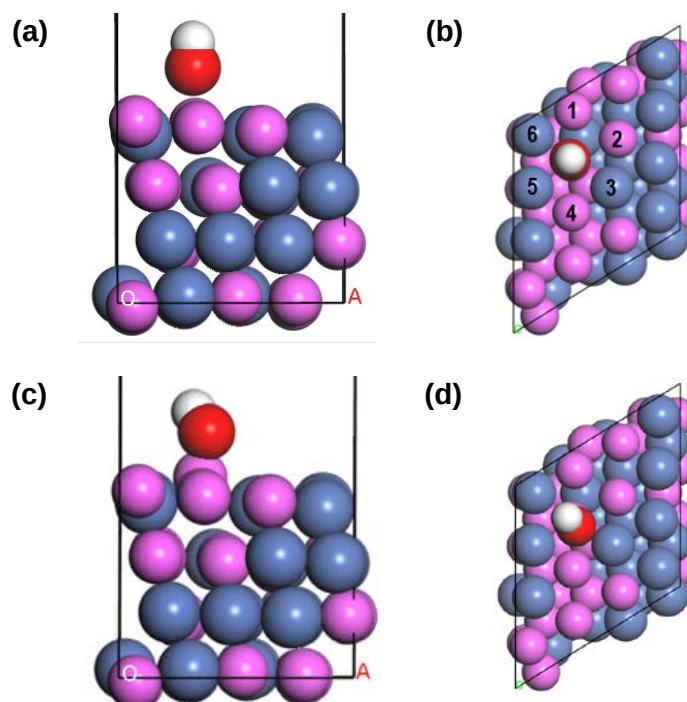


Figure 5-9 The leaching behaviour of an OH^- species, before and after optimisation, where OH^- was placed directly over an Al atom (top site). (a) Side view before optimisation, (b) top view before optimisation, (c) side view after optimisation and (d) top view after optimisation.

Table 5-2 Bond length of OH^- and interatomic distances and bond lengths of the atoms surrounding the initial top position of the OH^- species, before and after optimisation.

Bond pair	Bond length / interatomic distance (Å)	
	Before optimisation	After optimisation
$\text{Al}_7 - \text{Al}_1$	2.628	2.727
$\text{Al}_7 - \text{Al}_2$	2.711	2.875
$\text{Al}_7 - \text{Ni}_3$	2.513	2.728
$\text{Al}_7 - \text{Al}_4$	2.608	2.646
$\text{Al}_7 - \text{Ni}_5$	2.475	2.552
$\text{Al}_7 - \text{Ni}_6$	2.471	2.565
$\text{Al}_7 - \text{O}$	2.157	1.732
O-H	0.941	0.970
$\text{Ni}_6 - \text{H}$	4.097	3.927

All the bond lengths between Al_7 and its NNs increased, while the $\text{Al}_7 - \text{O}$ bond length decreased to 1.732 Å (shown in Table 5-2) during optimisation. These changes in bond lengths indicate that the Al atom would be removed from the NiAl surface in the process of leaching. However, the Al-O bond length was longer than the Al-O bond length in an $\text{Al}(\text{OH})_3$ molecule, which is in the 1.681 Å – 1.702 Å range,^{38–40} and it was shorter than the Al-O bond length within an Al_2O_3 molecule, which is in the 1.76 Å – 1.87 Å range.^{41–43}

Additionally, the bond length of O-H, within the OH^- - Al_7 interaction, was measured to be 0.970 Å after optimisation, which agreed with the bond length of 0.988 Å²⁵ for the isolated OH^- molecule, rather than the O-H bond length in the $\text{Al}(\text{OH})_3$ molecule which is in the 0.878 Å – 0.944 Å

range.^{38–40} The interatomic distance between Ni₆ and the H atom also decreased, indicating that the H atom would be attracted to the Ni atoms on the surface. These results imply that the OH[•] species would remove the Al atom from the surface. However, during the leaching process, the OH[•] species could dissociate and possibly form hydrogen gas.⁴⁴ This dissociation is, however, beyond the scope of this study.

The second coordination site considered was an fcc site. At this site, the OH[•] species was centred between two Al atoms and a Ni atom. Figure 5-10 shows the side and top views of the surface slab before and after the geometric optimisation. The fcc targeted Al atoms and NN atoms were labelled as seen in Figure 5-10 (b).

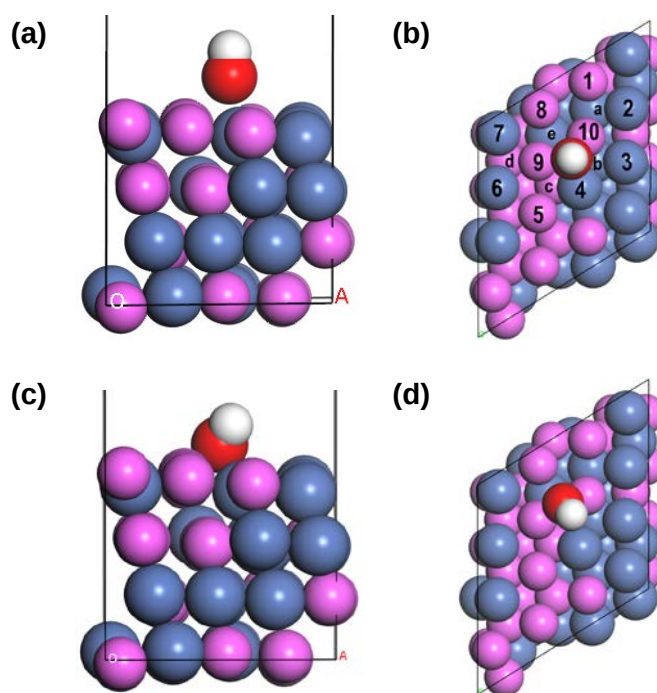


Figure 5-10 The leaching behaviour of an OH[•] species, before and after optimisation, where OH[•] was placed in a position between two Al atoms and a Ni atom (fcc site). (a) Side view before optimisation, (b) top view before optimisation, (c) side view after optimisation and (d) top view after optimisation.

The OH[•] species moved from the fcc site towards a bridge site between the Al atoms of the fcc coordination site rather than towards the Ni atom (Figure 5-10 (c) – (d)). This movement indicates a preference of the OH[•] species to coordinate with the Al atoms, implying that an Al atom is more likely to be removed from the surface than a Ni atom. This conclusion is supported by the observation that the bond lengths (Table 5-3) between most of the surrounding atoms increased after optimisation, except for the bond between Ni_e and Al atoms of the fcc site where OH[•] adsorbed (Al₉ and Al₁₀), which decreased. This decrease may indicate that Ni pulls the Al atoms closer to maintain the stable electronic structure that would be disrupted by the bond breaking.

The measured bond lengths of Al₉ – O and Al₁₀ – O decreased during optimisation, 1.914 Å and 1.943 Å, respectively. These measured values are ~15% larger than the Al-O bond length in an AlOH molecule, which is in the 1.681 Å – 1.702 Å range,^{38–40} and is ~6.5% larger than the Al-O bond length within the Al₂O₃ molecule, which is in the range of 1.76 Å – 1.87 Å.^{41–43}

However, the bond length of O-H, within the $\text{Al}_9\text{-OH}\cdots\text{Al}_{10}$ interaction, increased to 0.984 Å during optimisation. This measured OH $\cdot$ bond length agreed with the bond length of an isolated OH $\cdot$ molecule, 0.988 Å,²⁵ rather than the O-H bond length within the AlOH molecule with a range of 0.878 Å – 0.944 Å.^{38–40} The larger bond length could indicate that the bond would break and lead to the formation of hydrogen gas during the leaching process.⁴⁴ Additionally, the H atom would be pulled toward a Ni atom. This behaviour is, however, outside the scope of this study.

Table 5-3 Bond lengths of OH $\cdot$ and interatomic distances and bond lengths of the atoms surrounding the initial fcc position of the OH $\cdot$ species, before and after optimisation.

Bond pair	Bond length / interatomic distance (Å)		Bond pair	Bond length / interatomic distance (Å)	
	Before optimisation	After optimisation		Before optimisation	After optimisation
$\text{Al}_9 - \text{Al}_8$	2.628	2.773	$\text{Al}_{10} - \text{Al}_1$	2.801	2.823
$\text{Al}_9 - \text{Al}_{10}$	2.711	2.792	$\text{Al}_{10} - \text{Ni}_2$	2.518	2.467
$\text{Al}_9 - \text{Ni}_4$	2.513	2.661	$\text{Al}_{10} - \text{Ni}_3$	2.345	2.322
$\text{Al}_9 - \text{Al}_5$	2.608	2.597	$\text{Al}_{10} - \text{Ni}_4$	2.540	2.683
$\text{Al}_9 - \text{Ni}_6$	2.475	2.443	$\text{Al}_{10} - \text{Al}_8$	2.720	2.870
$\text{Al}_9 - \text{Ni}_7$	2.471	2.444	$\text{Al}_{10} - \text{Ni}_a$	2.478	2.501
$\text{Al}_9 - \text{Al}_c$	2.852	2.904	$\text{Al}_{10} - \text{Ni}_b$	2.474	2.490
$\text{Al}_9 - \text{Al}_d$	2.783	2.851	$\text{Al}_{10} - \text{Ni}_e$	2.774	2.748
$\text{Al}_9 - \text{Ni}_e$	2.759	2.666	$\text{Al}_{10} - \text{O}$	2.556	1.943
$\text{Al}_9 - \text{O}$	2.489	1.914	O-H	0.941	0.984
$\text{Ni}_4 - \text{H}$	3.531	3.003			

It can be concluded that the coordination position of the OH $\cdot$ species on the slab surfaces, whether top or fcc, does not affect the leaching behaviour. The OH $\cdot$ species bond with the Al atoms, and then remove the Al atoms from the surface. The final fractional coordinates for the leaching behaviour are given in Appendix I.

5.3.2.2 Leaching simulation

The manual leaching data for each of the previously identified surface slabs are given in this section. For each surface slab, four sets of atoms were identified to be removed. Each subsequent set of atoms was identified after identifying the previous sets' lowest energy removal. This energy was calculated using equation 5-1.

5.3.2.2.1 (111)-surface slab of Ni_7Al_9

For Ni_7Al_9 , the Al atoms identified for removal are shown in Figure 5-11. Figure 5-11 (a) shows the first and second sets of Al atoms that were removed. These atoms were all located in the top layer of the surface slab. Figures 5-11 (b) and (c) show the third set of Al atoms that were removed; these atoms were located in the top and second layers, respectively. Finally,

Figure 5-11 (d) shows the fourth set of Al atoms that were removed; these atoms were in the third layer of the surface slab.

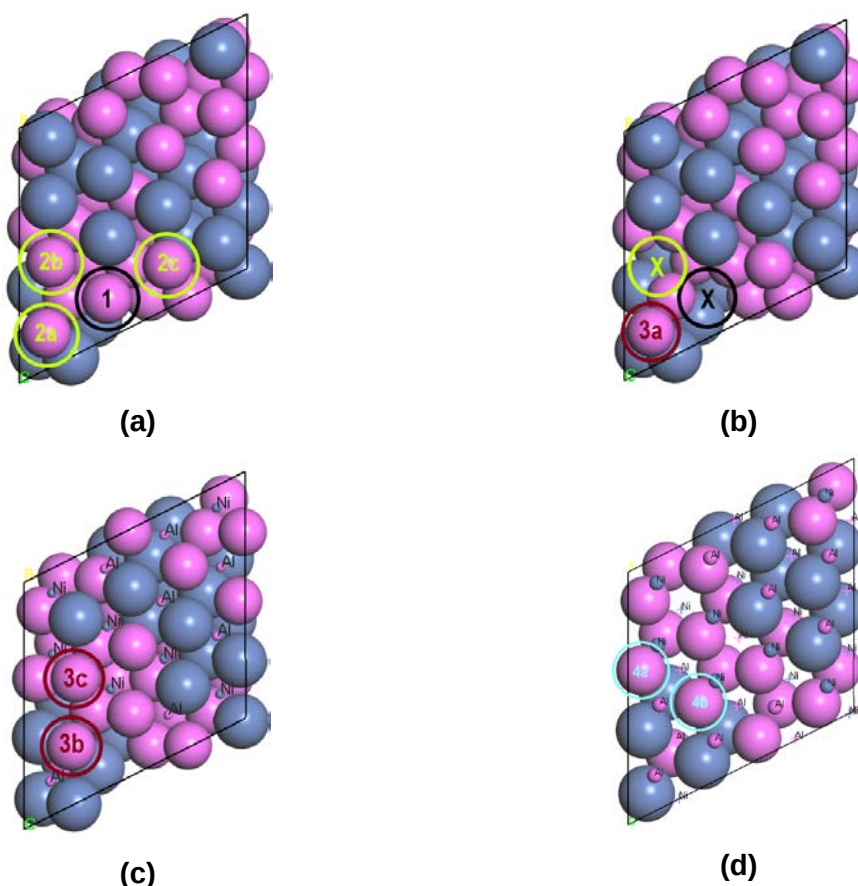


Figure 5-11 (a) - (e) Al atoms identified to be removed from the Ni_7Al_9 surface. (a) The first and second atoms to be removed. (b) and (c) The third atoms to be removed. (d) The fourth atoms to be removed. (The smaller spheres represent the top layer atoms, while the crosshairs represent the second layer atoms. Al = magenta atoms and Ni = blue atoms.)

The energy required to remove Al atoms from the Ni_7Al_9 surface is listed in Table 5-4. The energy required to remove the first Al atom from the Ni_7Al_9 surface was calculated to be -5.019 eV. The lowest energy required to remove the second Al atom was calculated to be -5.423 eV and corresponded to position 2b. Next, the lowest energy needed to remove the third Al atom was calculated to be -4.375 eV, which corresponded to the removal of the atom at position 3c. Finally, the lowest energy needed to remove the fourth and final Al atom was calculated as -3.499 eV, corresponding to position 4a. The average energy calculated for this Al atom removal path was -4.579 eV.

The atomic electron density difference of the different stages of Al atom removal for Ni_7Al_9 is shown in Figure 5-12. The isosurface scale shows electron accumulation on the red side, while electron depletion is on the blue side.

Figures 5-12 (a), (d), and (f) show the first, second and third layers before Al removal, respectively. For the top layer, the overall colour was green, indicating a neutral/even electron distribution between the different atomic species. With Al atom removal (Figures 5-12 (b), (c), (e) and (g)), the electron distribution did not change too much; rather, the cavity created had a smaller electron

deficit than the regions surrounding the remaining Al atoms. This electron deficit surrounding the remaining Al atoms could lead to more-negative adsorption species coordinating within these cavities. With the removal of the Al atom, it was observed that the electron accumulation surrounding the adjacent Ni atom would be drawn towards the newly created cavity. This tendency was, however, only observed for the top layer, with little change in the deeper layers. The Al atoms showed a stronger electron depletion on the side of the cavity. This electron depletion could lead to leaching species (OH^-) coordinating with cavity-adjacent Al atoms when further leaching is applied. In Figure 5-12 (f) and (g), it was seen that the atoms underwent a significant shift in position during the geometric optimisation. This observed restructuring could indicate that the surface slab was unstable.

Table 5-4 The calculated Al removal energy (eV) for the Ni_7Al_9 bimetallic phase.

# Al atoms removed	Atom position (Figure 5-11)	Energy to remove Al (eV)
0	-	-
1	-	-5.019
2	2a	-5.823
2	2b	-5.423
2	2c	-5.442
3	3a	-5.426
3	3b	-5.752
3	3c	-4.375
4	4a	-3.499
4	4b	-5.217

The change in the surface slab structure with each leaching step is shown in Figure 5-13. Figure 5-13 (a) shows the surface slab structure before leaching. In Figure 5-13 (b) – (d), it was observed that the surface slab structure stayed relatively stable when one, two, and three atoms were removed (leached). This first set of atoms was all located in the first two layers of the surface slab. However, once the fourth atom was removed from the third layer of the slab, the surface slab experienced significant atom rearrangement (reconstruction) (Figure 5-13 (e)). This restructuring could be attributed to excessive leaching into a four-layer slab surface leading to instability, which was restored through surface restructuring.

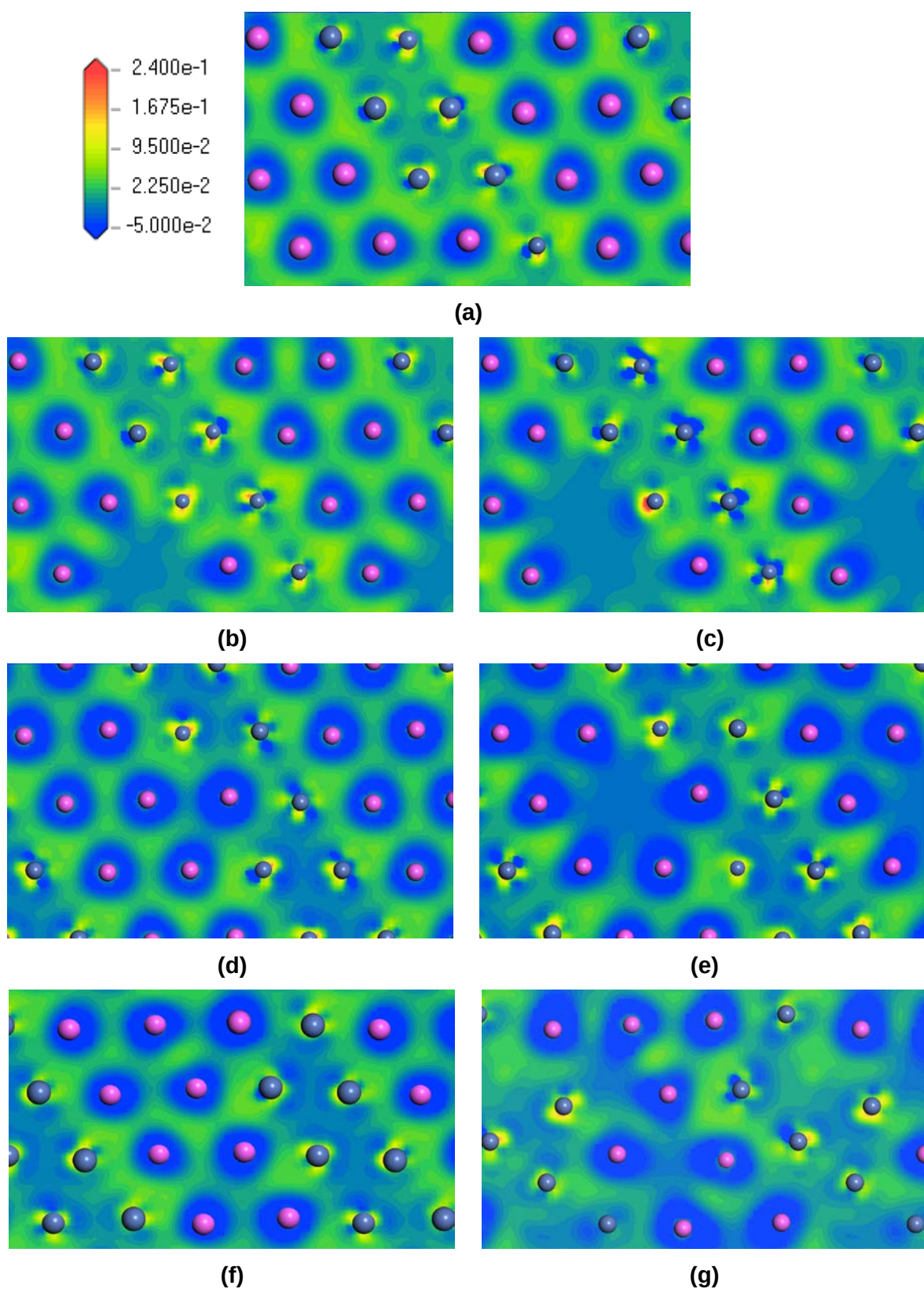


Figure 5-12 Atomic electron density difference slices for the manual leaching of Ni_7Al_9 . (a) Top layer before Al atoms were leached. (b) Top layer after one atom has been removed. (c) Top layer after two atoms have been removed. (d) The second layer before Al atoms were leached. (e) The second layer after Al atoms were leached. (f) The third layer before Al atoms were leached. (g) The third layer after Al atoms were leached. (Al = magenta atoms and Ni = blue atoms.)

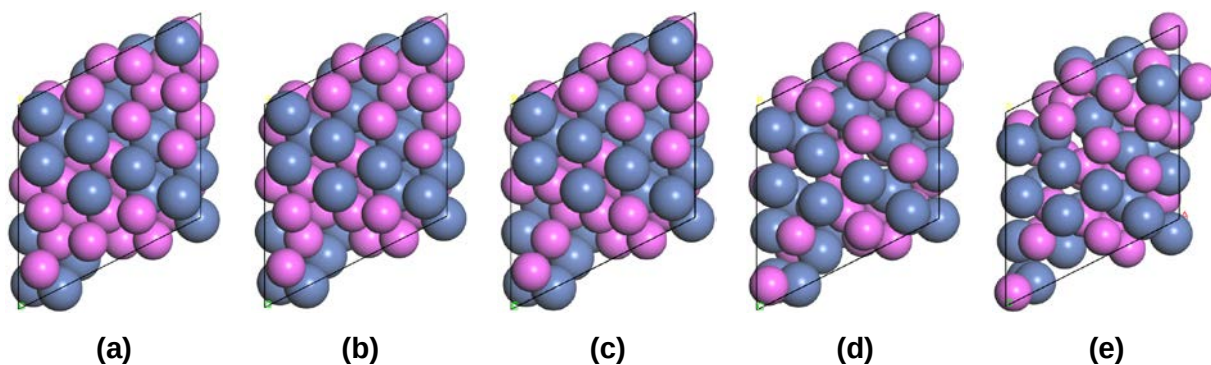


Figure 5-13 (a) – (e) The structure changes of the surface slab for Ni_7Al_9 during leaching. (a) The surface slab structure before leaching. (b) - (e) The results of each sequential leaching step, from one to four Al atoms being removed. (Al = magenta atoms and Ni = blue atoms.)

5.3.2.2.2 (111)-surface slab of Ni_8Al_8

For Ni_8Al_8 , the Al atoms identified for removal are shown in Figure 5-14.

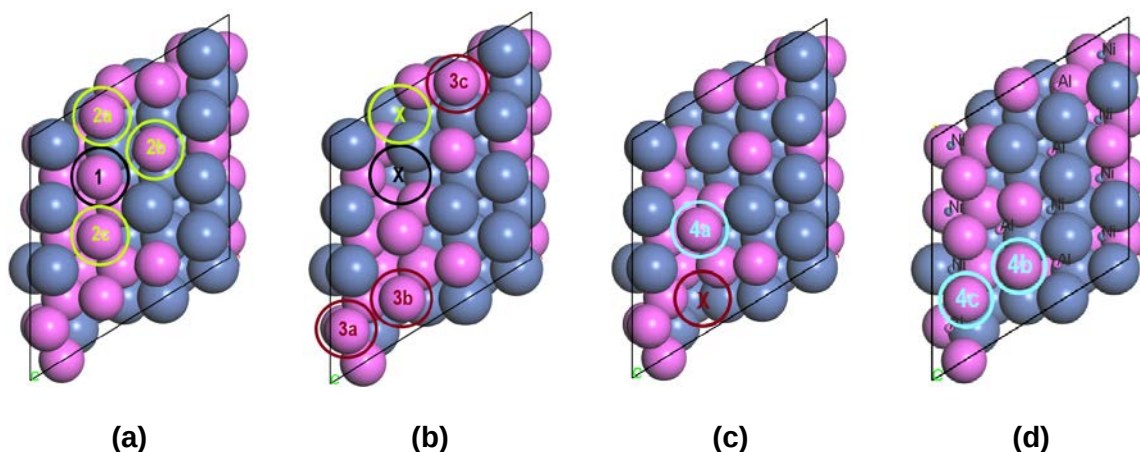


Figure 5-14 (a) – (d) Al atoms identified to be removed from the Ni_8Al_8 surface slab. (a) The first and second atoms to be removed. (b) The third atoms to be removed. (c) The fourth atoms to be removed (top layer). (d) The fourth atoms to be removed (second layer). The smaller spheres represent the top layer atoms. (Al = magenta atoms and Ni = blue atoms.)

Figure 5-14 (a) shows the first and second sets of Al atoms that were removed. These atoms were all located in the top layer of the surface slab. Figure 5-14 (b) shows the third set of Al atoms that were removed. These atoms were all located in the top layer of the surface slab. Finally, Figure 5-14 (c) and (d) show the fourth set of Al atoms that were removed. These atoms were located in the top and second layers, respectively.

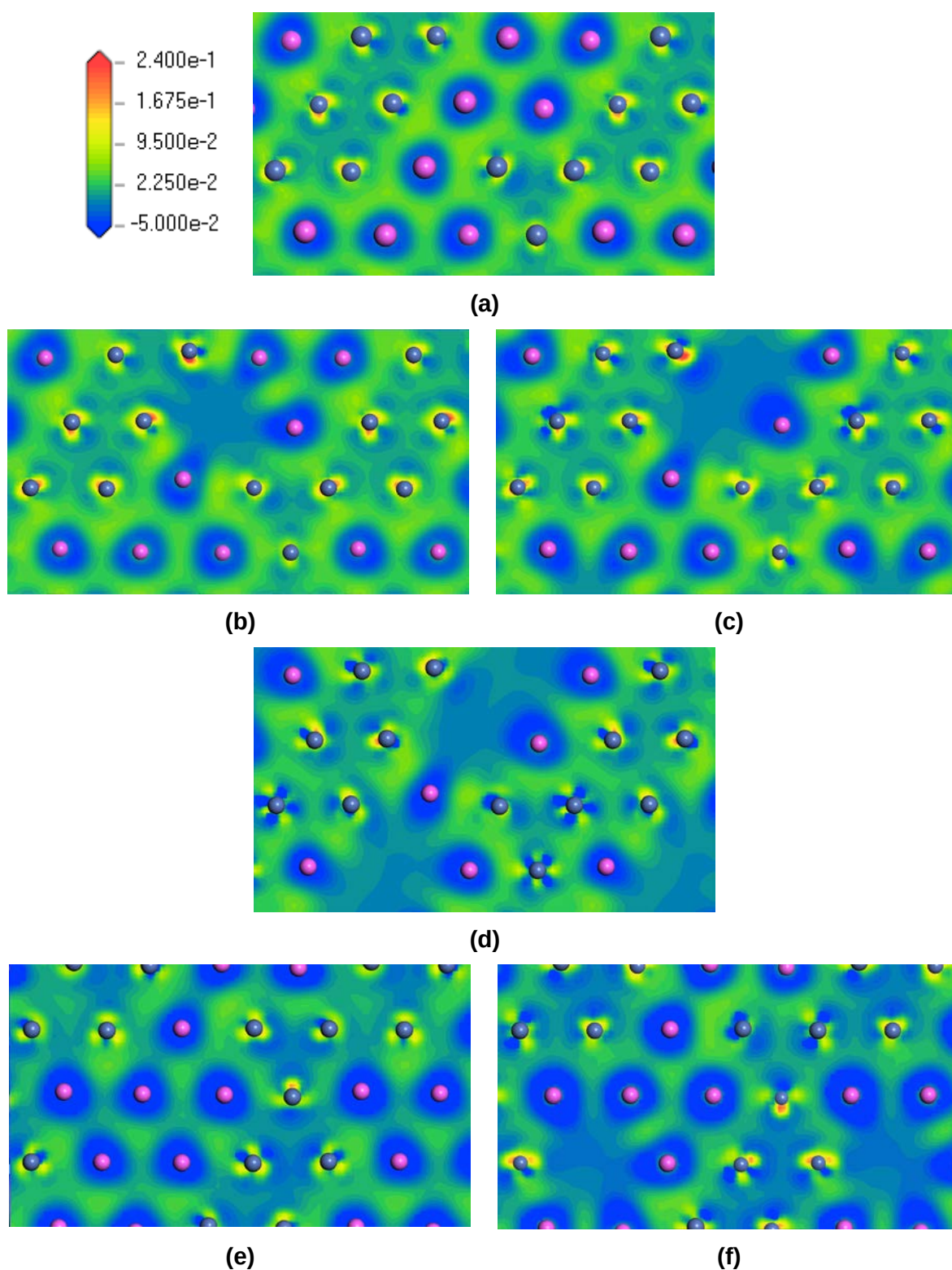
The energy required to remove Al atoms from the Ni_8Al_8 surface is listed in Table 5-5. The energy required to remove the first Al atom from the Ni_8Al_8 surface was calculated to be -5.860 eV. The lowest energy required to remove the second Al atom was calculated to be -5.336 eV and corresponded to position 2a. The lowest energy needed to remove the third Al atom was calculated to be -5.205 eV, which corresponded to the removal of the atom at position 3b. Finally, the lowest energy needed to remove the fourth and final Al atom was calculated as -5.519 eV, corresponding to position 4c. The average energy calculated for this Al atom removal path was -5.480 eV.

Table 5-5 The calculated Al removal energy (eV) for the Ni₈Al₈ bimetallic phase.

# Al atoms removed	Atom position (Figure 5-14)	Energy to remove Al (eV)
0	-	-
1	1	-5.860
2	2a	-5.336
2	2b	-6.439
2	2c	-5.849
3	3a	-5.563
3	3b	-5.205
3	3c	-5.891
4	4a	-5.657
4	4b	-5.689
4	4c	-5.519

The atomic electron density difference of the different stages of Al atom removal for Ni₈Al₈ is shown in Figure 5-15. The isosurface scale shows electron accumulation on the red side, while electron depletion is on the blue side. Figure 5-15 (a) and (e) show the first and second layers before Al removal, respectively. For the top layer, the overall colour was green, indicating a neutral/even electron distribution between the different atom species. The deeper layer had a bluer hue in the isosurface, indicating that the interatomic regions were more electron depleted. With Al atom removal (Figure 5-15 (b) - (e)), the electron distribution did not change too much, but rather the cavity created tended to have a larger electron deficit than the interatomic regions. It was, however, observed that the newly created cavity drew the electron accumulation surrounding the adjacent Ni atom towards it. The deeper layer did not show this effect. The Al atoms next to the newly created cavity showed a stronger electron deficit on the cavity side. This electron deficit could lead to the coordination preference of leaching species (OH⁻) with cavity adjacent Al atoms when further leaching is applied.

The change in the surface slab structure with each leaching step is shown in Figure 5-16. Figure 5-16 (a) shows the surface slab structure before leaching. In Figure 5-16 (b) – (e), it could be seen that the surface slab structure stayed relatively stable when one, two, three, and four atoms were removed (Figure 5-16 (b) – (e)).



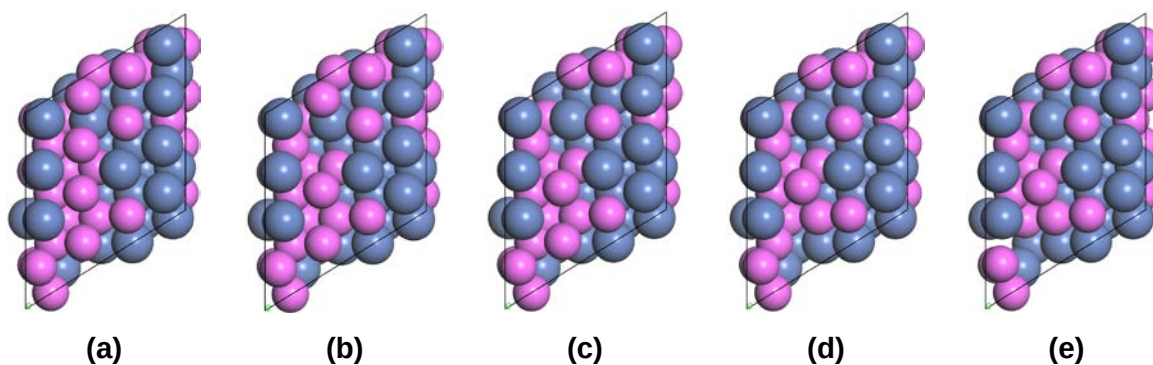


Figure 5-16 (a) – (e) The structure changes of the surface slab for Ni_8Al_8 during leaching. (a) The surface slab structure before leaching. (b) - (e) The results of each sequential leaching step, from one to four Al atoms removed. (Al = magenta atoms and Ni = blue atoms.)

5.3.2.2.3 (111)-surface slab of Ni_9Al_7

For Ni_9Al_7 , the Al atoms identified for removal are shown in Figure 5-17. Figure 5-17 (a) shows the first and second sets of Al atoms that were removed. These atoms were all located in the top layer of the surface slab. Figure 5-17 (b) and (c) show the third set of Al atoms that were removed; these were located in the top and second layers, respectively. Finally, Figure 5-17 (d) and (e) show the fourth set of Al atoms that were removed; these atoms were located in the top layer and second layer of the surface slab.

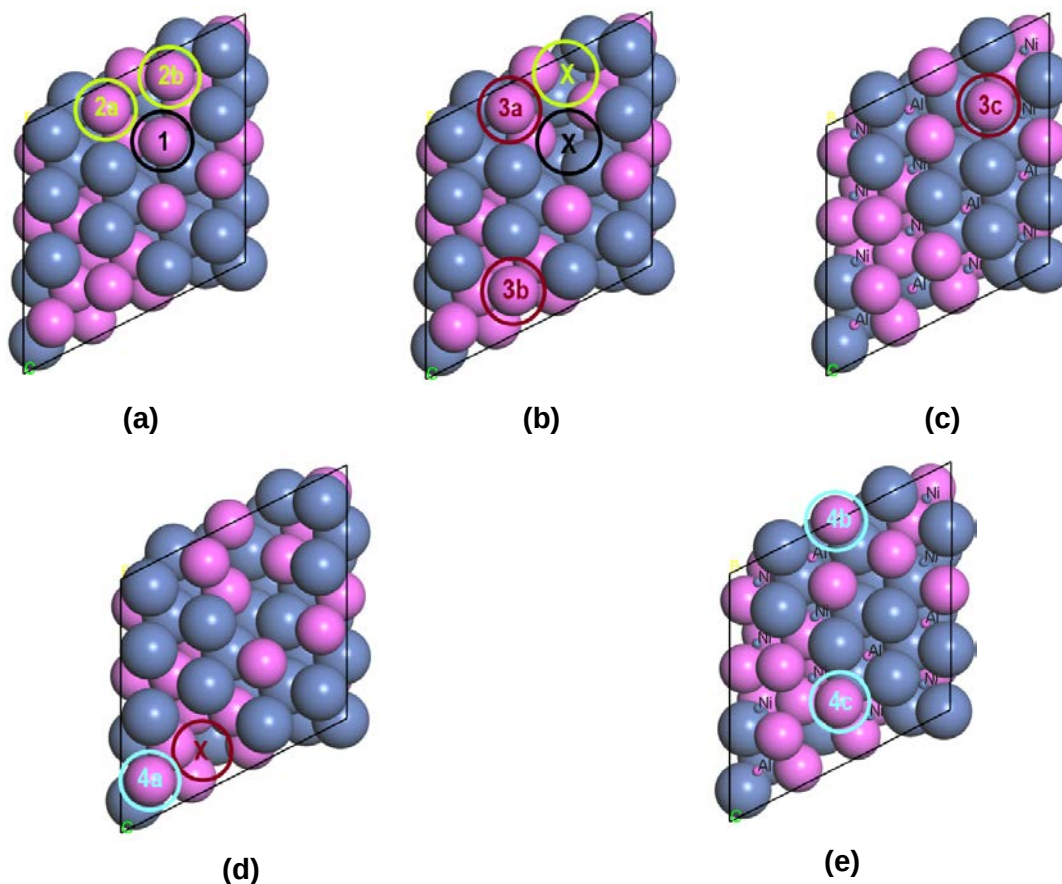


Figure 5-17 (a) - (e) Al atoms identified to be removed from the Ni_9Al_7 surface. The first and second atoms to be removed are shown in (a), while (b) and (c) show the third atoms to be removed. (d) and (e) The fourth atoms to be removed. The smaller spheres represent the top layer atoms. (Al = magenta atoms and Ni = blue atoms.)

The energy required to remove Al atoms from the Ni_9Al_7 surface is listed in Table 5-6. The energy required to remove the first Al atom from the Ni_9Al_7 surface was calculated to be -5.786 eV. The lowest energy to remove the second Al atom was calculated to be -5.632 eV and corresponded to position 2b. Next, the lowest energy to remove the third Al atom was calculated to be -5.068 eV; this corresponded to the removal of the atom at position 3b. Finally, the lowest energy needed to remove the fourth and final Al atom was calculated as -5.828 eV, corresponding to position 4b. The average energy calculated for this Al atom removal path was -5.578 eV.

Table 5-6 The calculated Al removal energy (eV) for the Ni_9Al_7 bimetallic phase

# Al atoms removed	Atom position (Figure 5-17)	Energy to remove Al (eV)
0	-	-
1	-	-5.786
2	2a	-5.812
2	2b	-5.632
3	3a	-5.441
3	3b	-5.068
3	3c	-6.359
4	4a	-5.834
4	4b	-5.828
4	4c	-5.984

The atomic electron density difference of the different stages of Al atom removal for Ni_9Al_7 is shown in Figure 5-18. The isosurface scale shows electron accumulation on the red side, while the blue side shows electron depletion.

Figure 5-18 (a) and (e) show the first and second layers before Al removal, respectively. The top layer was green overall, indicating a neutral/even electron distribution between the different atom species. However, before the removal of the Al atoms, the region between the hexagonal Ni formation showed a more electron-depleted distribution than previous structures. The deeper layer showed a bluer hue in the isosurface, indicating that the interatomic regions tended to be more electron depleted. With Al atom removal, the Ni atoms experienced the surrounding electron accumulation being pulled towards the newly created cavity. The cavity adjacent Al atom experienced a stronger electron depletion at the side of the cavity. This electron depletion could indicate that the leaching species (OH^-) would coordinate stronger with the Al atoms adjacent to the cavity.

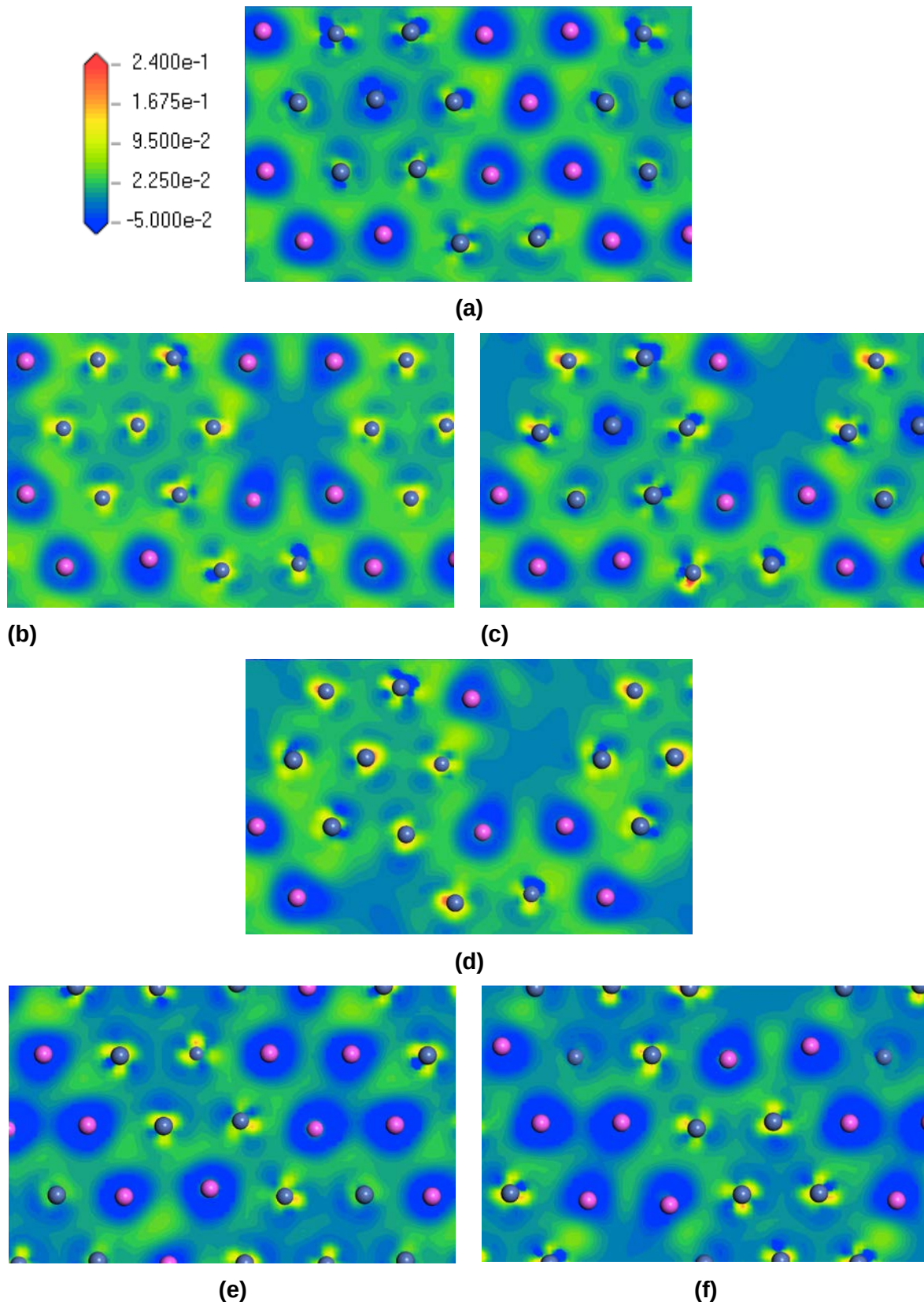


Figure 5-18 (a) - (f) Atomic electron density difference slices for the manual leaching of Ni_9Al_7 . (a) Top layer before Al atoms were leached. (b) Top layer after one atom has been removed. (c) Top layer after two atoms have been removed. (d) Top layer after three atoms have been removed. (e) The second layer before Al atoms were leached. (f) The second layer after one atom has been removed. (Al = magenta atoms and Ni = blue atoms.)

Figure 5-19 shows how the surface slab structure changed with each leaching step. The surface slab structure before leaching is shown in Figure 5-19(a). When one, two, three, and four atoms

were removed, it was observed that the surface slab structure remained largely stable (Figure 5-19 (b) – (e)).

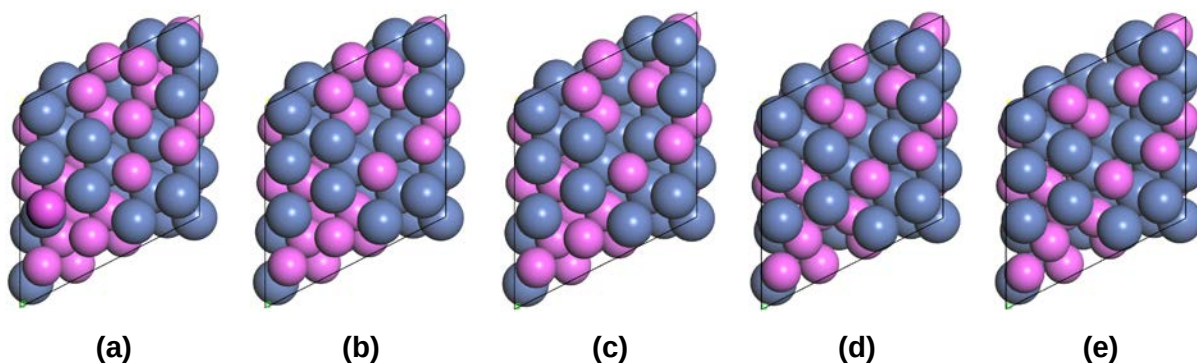


Figure 5-19 (a) – (e) The structure changes of the surface slab for Ni_9Al_7 during leaching. (a) The unleached surface slab structure. (b) - (e) The results of each sequential leaching step, from one to four Al atoms removed. (Al = magenta atoms and Ni = blue atoms.)

5.3.2.2.4 (111)-surface slab of $\text{Ni}_{11}\text{Al}_5$

For $\text{Ni}_{11}\text{Al}_5$, the Al atoms identified for removal are shown in Figure 5-20. Figure 5-20 (a) and (b) show the first, second and third sets of Al atoms which were removed; these atoms were in the top layer of the surface slab. While Figure 5-20 (c) shows the fourth set of Al atoms that were removed, from the second layer.

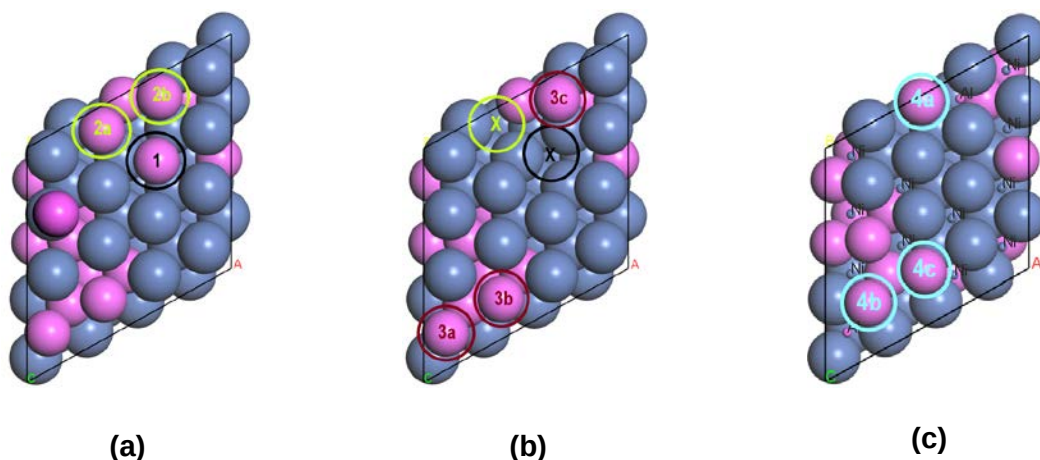


Figure 5-20 (a) - (c) Al atoms identified to be removed from the $\text{Ni}_{11}\text{Al}_5$ surface. (a) The first and second atoms to be removed, while (b) shows the third atoms to be removed. The smaller spheres represent the top layer atoms. (Al = magenta atoms and Ni = blue atoms.)

The energy required to remove Al atoms from the $\text{Ni}_{11}\text{Al}_5$ surface is listed in Table 5-7. The energy required to remove the first Al atom from the $\text{Ni}_{11}\text{Al}_5$ surface was calculated to be -6.834 eV. The lowest energy to remove the second Al atom was calculated to be -6.182 eV and corresponded to position 2a. Next, the lowest energy to remove the third Al atom was calculated to be -5.800 eV; this corresponded to the removal of the atom at position 3b. Finally, the least energy required to remove the fourth and final Al atom was calculated as -6.043 eV, corresponding to position 4b. The average energy calculated for this Al atom removal path was -6.215 eV.

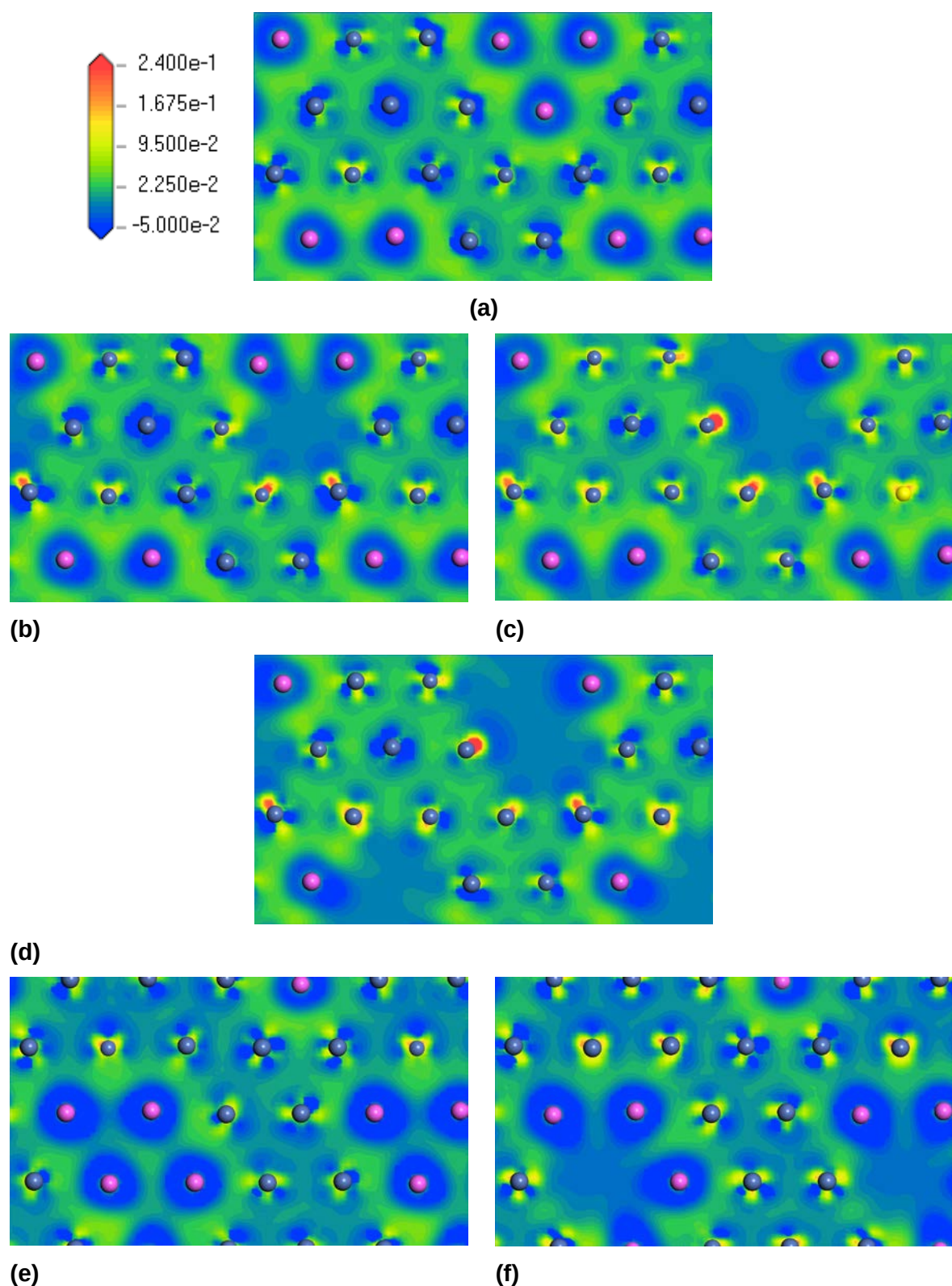
Table 5-7 The calculated Al removal energy (eV) for the Ni₁₁Al₅ bimetallic phase

# Al atoms removed	Atom position (Figure 5-20)	Energy to remove Al (eV)
0	-	-
1	1	-6.834
2	2a	-6.182
2	2b	-6.340
3	3a	-6.437
3	3b	-5.800
3	3c	-6.220
4	4a	-6.618
4	4b	-6.043
4	4c	-6.549

The atomic electron density difference of the different stages of Al atom removal for Ni₁₁Al₅ is shown in Figure 5-21. The isosurface scale shows electron accumulation on the red side, while electron depletion is on the blue side.

Figure 5-21 (a) and (e) show the first and second layers before Al removal, respectively. The top layer was overall green, indicating a neutral/even electron distribution between the different atom species. However, before the removal of the Al atoms, the region between the Ni atoms showed a more electron deficient distribution than previous structures. The deeper layer showed a bluer hue in the isosurface, indicating that the interatomic regions tended to be more electron depleted. With Al atom removal, the electron distribution did not change too much; rather the cavity created tended to have a larger electron deficit than the interatomic regions. However, it showed that the newly formed cavity attracted the electron accumulation surrounding the nearby Ni atom. In contrast, the Al atoms adjacent to the newly created cavity experienced a higher electron depletion in the direction of the cavity. This electron depletion could show that leaching species (OH⁻) would coordinate with the Al atoms in the cavity site.

Figure 5-22 shows how the surface slab structure changed with each leaching step. Figure 5-22 (a) shows the surface slab structure before leaching. The surface slab structure remained largely stable (Figure 5-22 (b) – (e)) throughout the consecutive atom removals.



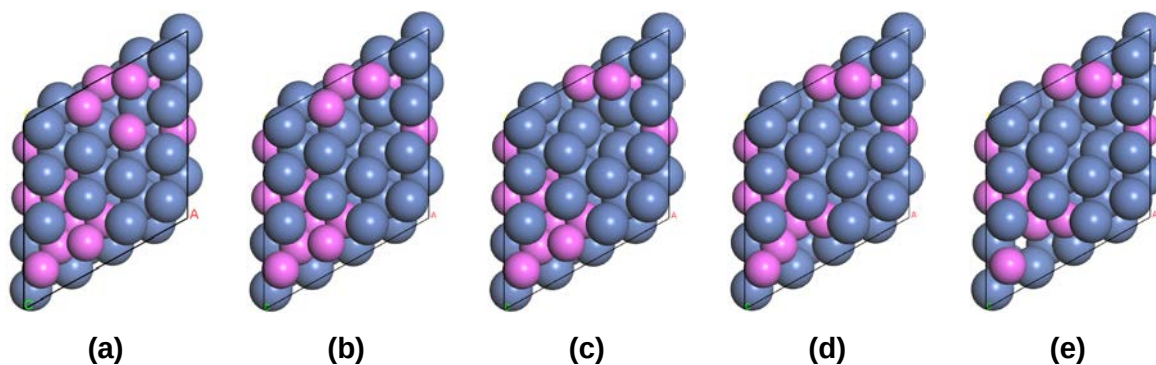


Figure 5-22 The structure changes of the surface slab for $\text{Ni}_{11}\text{Al}_5$, during leaching. (a) The surface slab structure before leaching. (b) - (e) The results of each sequential leaching step, from one to four Al atoms removed. (Al = magenta atoms and Ni = blue atoms.)

In conclusion, the atomic electron density difference showed that the top layer for all surface slabs had an evenly spread electron distribution before Al removal. Deeper layers tended toward a bluer hue, indicating a deficit in electron distribution, especially between Ni atoms, with electron accumulation observed in the immediate lattice space. With Al atom removal, it was observed that the electron accumulation surrounding the Ni atoms tended to be drawn towards the newly created cavity. The same was observed for the depletion of electrons surrounding the Al atoms. This electron depletion could cause leaching species (OH^-) to coordinate with the Al atoms around and within the cavities. The removal energies were compared to cohesive energies for the Ni-Al systems, namely NiAl (4.46 eV) and Ni_3Al (4.61 eV),⁴⁵ and was found to be higher. These higher removal energies could be explained by the fact that cohesive energies are energies averaged over the whole system, while a specific removal pathway was followed in this study. Finally, the average energy to remove an Al atom from the surface slab increased with an increase in Ni content, which is in agreement with the trend observed in literature for cohesive energy.⁴⁵ This observation with regard to Ni content agrees with what the work functions predicted: that surfaces with lower work functions would have increased leachability, leading to lower leaching energies.³³ For the final fractional coordinates after each Al atom removal from the surface slab structures, refer to Appendix G.

5.3.3 Simulated adsorption

The simulated adsorption was done by identifying five Ni atoms at different positions on the final leached $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase (111)-surface slabs and adsorbing an $\text{OH}^\cdot$ species to these Ni atoms. The adsorption is considered on top of Ni and not Al for the leached surfaces, because as seen in section 5.3.2.1 such adsorption would cause Al leaching. The positions identified for adsorption are shown in Figure 5-23, and the surface slab layer in which the identified adsorption position is located is shown in Table 5-8. For comparison, an $\text{OH}^\cdot$ species was adsorbed onto a pure Ni (111)-surface slab at the top (P1), the bridge (P2) and the fcc (P3) sites on the first (top) layer of the surface slab.

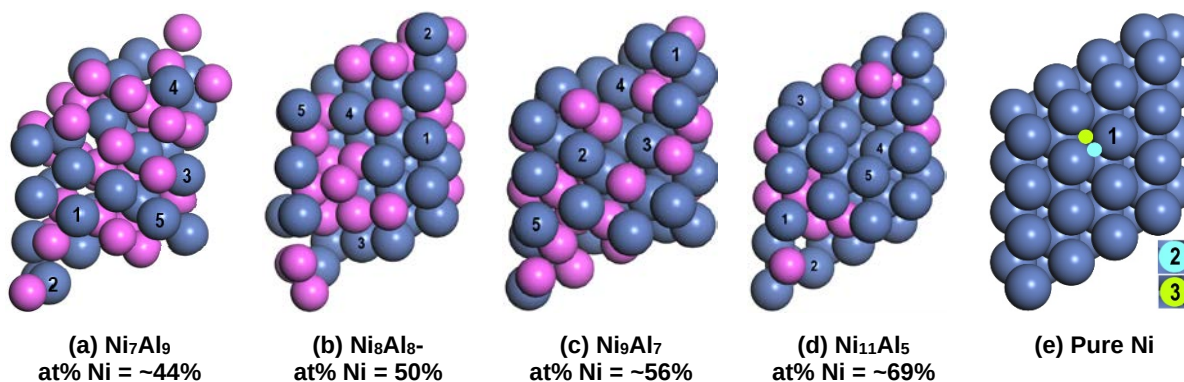


Figure 5-23 Adsorption positions of OH· onto final leached Ni_{1-x}Al_x bimetallic phase (111)-surface slab structures, as well as the pure Ni (111)-surface slab. (Al = magenta atoms and Ni = blue atoms.)

Table 5-8 Adsorption position depths from Figure 5-23

	Ni ₇ Al ₉	Ni ₈ Al ₈	Ni ₉ Al ₇	Ni ₁₁ Al ₅
P1	1 st	1 st	1 st	1 st
P2	2 nd	1 st	1 st	3 rd
P3	2 nd	3 rd	2 nd	2 nd
P4	1 st	2 nd	3 rd	2 nd
P5	1 st	1 st	1 st	1 st

The combined Ni_{1-x}Al_x-OH· system was optimised, and the d-band centre (ϵ_d) was calculated. The d-band centre (ϵ_d) indicates the binding properties of the species to the surface slab and could be used as a descriptor of catalytic activity toward adsorbing species.^{46,47} An upward shift of the d-band centre towards the Fermi level indicates stronger surface-adsorbate binding. In contrast a downward shift in the d-band centre is known to correlate with weaker surface-adsorbate binding.^{46,47}

In this study, the d-band centre data for the Ni_{1-x}Al_x bimetallic surfaces surrounds the d-band centre of pure Ni. This data is shown in Table 5-9 in the first row. Due to Pauli repulsion, it was previously discovered that OH⁻ will adsorb less strongly to surfaces with higher (less negative) d-band centres.⁴⁸ The d-band centres' data in Table 5-9 shows an overall downward shift, towards lower d-band centres, after adsorption.

For pure Ni (111), an upward and downward d-band centre shift was observed. The upward shift corresponded to higher (less negative) adsorption energies, while the downward shift corresponded to lower (more negative) and more optimal adsorption energies. For the bimetallic phases, the d-band was observed to shift to lower energies (larger negative energies) in 90% of the adsorption cases. This shift to lower energies represented a downward shift of the d-band centre (as seen in Figure 5-24). This downward shift, therefore, showed that these surface slabs experience weaker adsorption at these positions. The adsorption positions (10%) that experience an upward shift in the d-band centres are related to the Ni₉Al₇ surface slab. The upward and downward shifts were seen to correspond to the adsorption positions and proximity of stronger-binding Al atoms and possibly smaller pore sizes.

Table 5-9 Calculated d-band centres for each $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase and pure Ni (111)-surface slab before and after adsorption at the different positions.

	Ni_7Al_9	Ni_8Al_8	Ni_9Al_7	$\text{Ni}_{11}\text{Al}_5$	Ni
before	-1.610	-1.491	-1.453	-1.402	-1.597
P1	-1.677	-1.521	-1.466	-1.418	-1.596
P2	-1.651	-1.541	-1.452	-1.406	-1.601
P3	-1.641	-1.535	-1.452	-1.403	-1.603
P4	-1.712	-1.522	-1.458	-1.405	-
P5	-1.654	-1.546	-1.463	-1.411	-

The adsorption energies of the $\text{OH}^\cdot$ species were seen to vary between -6.000 eV and -2.500 eV in this study. The more negative values are very large; this is due to $\text{OH}^\cdot$ species' tendency to adsorb more strongly to surfaces than OH^- species.⁴⁹ Considering the first row of Table 5-9 and adsorption energy data in Table 5-10, the behaviour of $\text{OH}^\cdot$ adsorbing less strongly to surfaces with higher (less negative) d-band centres was observed for Ni_7Al_9 , Ni_8Al_8 , Ni_9Al_7 , and $\text{Ni}_{11}\text{Al}_5$, but not for pure Ni.

The adsorption of the $\text{OH}^\cdot$ species on the top layer of the surface slab showed overall the highest (less negative) adsorption energies, which showed that weaker adsorbate-surface interactions were present. In contrast, deeper layered adsorption positions had lower (more negative) adsorption energies, indicating stronger adsorbate-surface interactions. One of the reasons for this variation in adsorption energy could be the NN environment of the target Ni atom. Another possible reason for these stronger adsorbate-surface interactions could be that the leaching done in this study did not give large enough cavities for the neighbouring atoms to not play a role and bind the $\text{OH}^\cdot$ species stronger to the surface slab. Comparing the adsorption energies per position and the layer-averaged adsorption energies (Table 5-11), it is clear that the surface slab of Ni_7Al_9 showed lower overall adsorption energies. These lower adsorption energies could be attributed to the significant rearrangement of atoms seen during the optimisation of the leached surface slab.

Mohsenzadeh *et al.*²⁵ determined the adsorption energy of the $\text{OH}^\cdot$ species onto the Ni (111)-surface to be -3.41 eV, while Seenivasan *et al.*⁵⁰ calculated the adsorption energy of the $\text{OH}^\cdot$ species onto the Ni (111)-surface to be -3.31 eV. Xiang *et al.*⁵¹ found that an adsorption energy of -3.18 eV was more optimal than an adsorption energy of -1.86 eV for a OH^- species with respect to the OER. An adsorption energy of -3.20 eV can be seen as optimal for any of the adsorbed OER species. This value is based on the scaling relation of the free energies of $^*\text{OH}$ to $^*\text{OOH}$.⁹ The adsorption energy for the pure Ni top adsorption site (P1) was calculated to be -2.547 eV, which is less than the observed literature values.²⁵ However, the adsorption energy for the pure Ni bridge (P2) and fcc (P3) adsorption sites were calculated to be -3.149 eV and

-3.208 eV, respectively, which agreed well with more optimal adsorption energies for OER species. The average adsorption energies for each of the surface slabs listed in Table 5-11 were calculated to be -4.759 eV, -3.968 eV, -4.101 eV, and -3.806 eV, respectively.

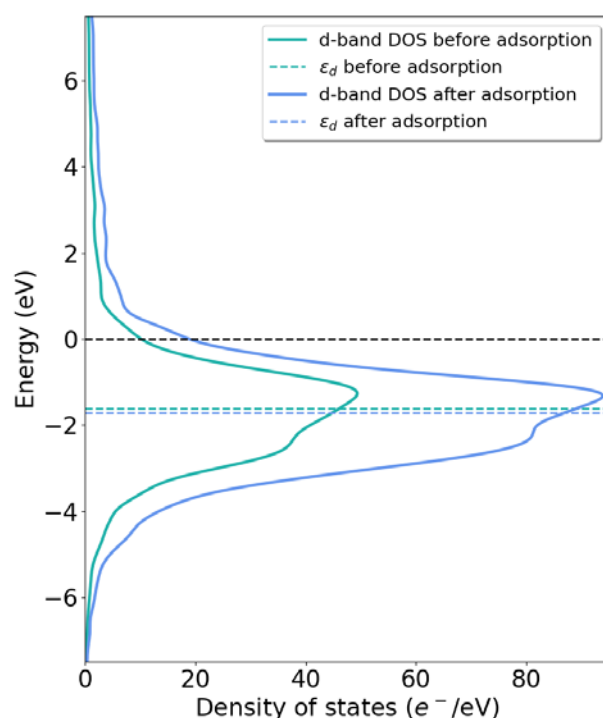


Figure 5-24 Representation of a positive (downward) d-band shift by using Ni_7Al_9 data.

Table 5-10 Calculated adsorption energies in eV for each $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase and pure Ni (111)-surface slab at the different positions.

	Ni_7Al_9	Ni_8Al_8	Ni_9Al_7	$\text{Ni}_{11}\text{Al}_5$	Ni
P1	-6.053	-4.062	-3.403	-3.568	-2.547
P2	-4.009	-3.194	-3.974	-3.679	-3.149
P3	-4.571	-4.298	-4.145	-4.203	-3.208
P4	-5.677	-4.152	-4.607	-4.140	-
P5	-3.953	-3.106	-3.279	-3.564	-

Table 5-11 Calculated average adsorption energies in eV per layer for each $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase and pure Ni (111)-surface slab.

	Ni_7Al_9	Ni_8Al_8	Ni_9Al_7	$\text{Ni}_{11}\text{Al}_5$	Ni
Layer 1 (top)	-5.228	-3.454	-3.552	-3.566	-2.968
Layer 2	-4.290	-4.152	-4.145	-4.172	-
Layer 3	-	-4.298	-4.607	-3.679	-

In conclusion, both upward and downward d-band centre shifts were observed for the adsorption of $\text{OH}^\cdot$ onto the pure Ni (111) and $\text{Ni}_{1-x}\text{Al}_x$ bimetallic (111)-surface-slabs. The overall adsorption

energy of OH $\cdot$ was weaker for less negative d-band centres materials in all Ni $_{1-x}$ Al $_x$ bimetallic (111)-surface-slabs. None of the average surface slab energies was related to the literature values. The top layer adsorption energies for Ni $_8$ Al $_8$ and Ni $_9$ Al $_7$, as well as the top and third layers of Ni $_{11}$ Al $_5$, were in better agreement with the literature values for optimal OER adsorption energies.⁹ These higher (less negative) adsorption energies could be due to less NN interaction experienced on the top layer compared to the deeper layers. The Ni $_{1-x}$ Al $_x$ bimetallic phases, Ni $_8$ Al $_8$, Ni $_9$ Al $_7$, and Ni $_{11}$ Al $_5$, could be used to produce active OER catalysts. For the final fractional coordinates for each adsorption position for the Ni $_{1-x}$ Al $_x$ bimetallic (111)-surface-slabs and pure Ni (111), refer to Appendix H and Appendix I.

5.4 Conclusion

In this chapter, the pure metal DFT model developed in Chapter 3 was applied to several Ni $_{1-x}$ Al $_x$ bimetallic phase bulks and their (111)-surface slabs. Eight of the Ni $_{1-x}$ Al $_x$ bimetallic phase bulks were identified in Chapter 4. Two additional Ni $_{1-x}$ Al $_x$ bimetallic phase bulks were identified using statistical data and applying the same identification method as the previously mentioned eight. These optimised bulks were used to identify four surface slabs for simulated leaching, which was done manually. This manual leaching was done by identifying several Al atoms, removing them by hand, and optimising the structure, whereafter the energy to remove the Al atom was calculated. It was found that the average energy needed to remove an Al atom increased with an increase in Ni content, which agrees with the literature.⁵² Adsorption of OH $\cdot$ species onto the pure Ni (111)-surface and the final leached (111)-surface slabs was evaluated; for the pure Ni (111) the top, bridge, and fcc sites were considered. For the final leached (111)-surface slabs, five positions were identified at varying depths. The calculated d-band centre shifts showed that for 90% of the adsorption positions, comparatively weaker adsorbate-surface interactions were observed, while the other 10% showed comparatively stronger adsorbate-surface interactions. Both upward and downward shifts were observed for the d-band centre shift of pure Ni (111). The adsorption of the OH $\cdot$ species onto the bridge and fcc sites of the Ni (111)-surface agreed with the literature and was close to the optimal adsorption energy for the OER.⁹ Therefore, pure Ni (111)-surface could be considered a good OER catalyst when the bridged site was considered. The adsorption energies for the top layer of the surface slabs of Ni $_8$ Al $_8$ and Ni $_9$ Al $_7$, as well as the third layer of Ni $_{11}$ Al $_5$, were in relative agreement with the literature values and tended towards more optimal adsorption energies for the OER. By comparison, the leached bimetallic phases identified in this study, especially Ni $_8$ Al $_8$, Ni $_9$ Al $_7$, and Ni $_{11}$ Al $_5$, could lead to active catalysts towards the OER.

References

- (1) Schweizer, S.; Chaudret, R.; Low, J.; Subramanian, L. Molecular Modeling and Simulation of Raney Nickel: From Alloy Precursor to the Final Porous Catalyst. *Comput Mater Sci* **2015**, *99*, 336–342.
- (2) Luong, V.; Philipsen, V.; Hendrickx, E.; Opsomer, K.; Detavernier, C.; Laubis, C.; Scholze, F.; Heyns, M. Ni-Al Alloys as Alternative EUV Mask Absorber. *Applied Sciences* **2018**, *8* (4), 521. <https://doi.org/10.3390/app8040521>.
- (3) Grau-Crespo, R.; Hamad, S.; Catlow, C. R. A.; De Leeuw, N. H. Symmetry-Adapted Configurational Modelling of Fractional Site Occupancy in Solids. *Journal of Physics: Condensed Matter* **2007**, *19* (25), 256201. <https://doi.org/10.1088/0953-8984/19/25/256201>.
- (4) Barnard, N. C.; Brown, S. G. R. Kinetic Monte Carlo Modelling the Leaching of Raney Ni-Al Alloys. In *WIT Transactions on Engineering Sciences*; 2007; Vol. 54, pp 53–62. <https://doi.org/10.2495/ECOR070061>.
- (5) Lee, G. D.; Suh, C. S.; Park, J. H.; Park, S. S.; Hong, S. S. Raney Ni Catalysts Derived from Different Alloy Precursors (I) Morphology and Characterization. *Korean Journal of Chemical Engineering* **2005**, *22* (3), 375–381. <https://doi.org/10.1007/BF02719414>.
- (6) Fultz, B. Vibrational Thermodynamics of Materials. *Progress in Materials Science*. Pergamon May 1, 2010, pp 247–352. <https://doi.org/10.1016/j.pmatsci.2009.05.002>.
- (7) Thesner, C.; Falch, A.; Cornelia, G.; Van Sittert, C. Using Site Occupation Disorder to Build Bulk Structures of Ni_{1-x}Al_x. *Suid-Afrikaanse Tydskrif vir Natuurwetenskap en Tegnologie* **2022**, *40* (1), 174–179. <https://doi.org/10.36303/SATNT.2021cosaami.33>.
- (8) Liang, Q.; Brocks, G.; Bieberle-Hütter, A. Oxygen Evolution Reaction (OER) Mechanism under Alkaline and Acidic Conditions. *JPhys Energy* **2021**, *3* (2), 26001. <https://doi.org/10.1088/2515-7655/abdc85>.
- (9) Li, J. Oxygen Evolution Reaction in Energy Conversion and Storage: Design Strategies Under and Beyond the Energy Scaling Relationship. *Nano-Micro Letters*. Springer Science and Business Media B.V. December 1, 2022. <https://doi.org/10.1007/s40820-022-00857-x>.
- (10) Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. I. J.; Refson, K.; Payne, M. C. First Principles Methods Using CASTEP. *Zeitschrift für Kristallographie-Crystalline Materials* **2005**, *220* (5/6), 567–570.
- (11) Dassault Systèmes BIOVIA, Materials Studio, 20.1.0.5, San Diego: Dassault Systèmes, 2020. Dassault Systèmes: San Diego 2020.
- (12) Yang, Y.; Luo, M.; Zhang, W.; Sun, Y.; Chen, X.; Guo, S. Metal Surface and Interface Energy Electrocatalysis: Fundamentals, Performance Engineering, and Opportunities. *Chem* **2018**, *4* (9), 2054–2083. <https://doi.org/10.1016/J.CHEMPR.2018.05.019>.
- (13) Oura, K.; Lifshits, V. G.; Saranin, A. A.; Zotov, A. V.; Katayama, M. *Surface Science: An Introduction*; Springer Berlin Heidelberg, 2013.
- (14) Wang, J.; Wang, S. Q. Surface Energy and Work Function of Fcc and Bcc Crystals: Density Functional Study. *Surf Sci* **2014**, *630*, 216–224. <https://doi.org/10.1016/j.susc.2014.08.017>.
- (15) Tran, R.; Xu, Z.; Radhakrishnan, B.; Winston, D.; Sun, W.; Persson, K. A.; Ong, S. P. Data Descriptor: Surface Energies of Elemental Crystals. *Sci Data* **2016**, *3*. <https://doi.org/10.1038/sdata.2016.80>.

- (16) Raney, M. Catalysts from Alloys: Nickel Catalysts. *Ind Eng Chem* **1940**, 32 (9), 1199–1203. <https://doi.org/10.1021/ie50369a030>.
- (17) Lee, Y. J.; Lee, Y. S.; Cha, J. Y.; Jo, Y. S.; Jeong, H.; Sohn, H.; Yoon, C. W.; Kim, Y.; Kim, K. B.; Nam, S. W. Development of Porous Nickel Catalysts by Low-Temperature Ni–Al Chemical Alloying and Post Selective Al Leaching, and Their Application for Ammonia Decomposition. *Int J Hydrogen Energy* **2020**, 45 (38), 19181–19191. <https://doi.org/10.1016/j.ijhydene.2020.05.025>.
- (18) Devred, F.; Gieske, A. H.; Adkins, N.; Dahlborg, U.; Bao, C. M.; Calvo-Dahlborg, M.; Bakker, J. W.; Nieuwenhuys, B. E. Influence of Phase Composition and Particle Size of Atomised Ni–Al Alloy Samples on the Catalytic Performance of Raney-Type Nickel Catalysts. *Appl Catal A Gen* **2009**, 356 (2), 154–161. <https://doi.org/10.1016/j.apcata.2008.12.039>.
- (19) Jarvis, D. J.; Voss, D. IMPRESS Integrated Project—An Overview Paper. *Materials Science and Engineering: A* **2005**, 413–414. <https://doi.org/10.1016/j.msea.2005.09.066>.
- (20) Lee, Y. J.; Lee, B. Y.; Yoon, C. W.; Lee, Y. S.; Jeong, H.; Choi, S. H.; Kim, D. H.; Kim, Y.; Kim, K. B.; Nam, S. W. Facile Synthesis of Micro-Sized Ni–Al Alloy Powders through Low-Temperature Chemical Alloying. *J Alloys Compd* **2020**, 815, 152392. <https://doi.org/10.1016/j.jallcom.2019.152392>.
- (21) Barnard, N. C.; Brown, S. G. R.; Devred, F.; Bakker, J. W.; Nieuwenhuys, B. E.; Adkins, N. J. A Quantitative Investigation of the Structure of Raney-Ni Catalyst Material Using Both Computer Simulation and Experimental Measurements. *J Catal* **2011**, 281 (2), 300–308. <https://doi.org/10.1016/j.jcat.2011.05.010>.
- (22) Sadjadi, S.; Koohestani, F.; Bahri-Laleh, N. Pd Immobilization on the Multi-Amine Functionalized Halloysite as an Efficient Catalyst for Hydrogenation Reaction: An Experimental and Computational Study. *Appl Clay Sci* **2020**, 192. <https://doi.org/10.1016/j.clay.2020.105645>.
- (23) Smith, A. J.; Trimm, D. L. The Preparation of Skeletal Catalysts. *Annual Review of Materials Research*. 2005, pp 127–142. <https://doi.org/10.1146/annurev.matsci.35.102303.140758>.
- (24) Bai, Y.; Kirvassilis, D.; Xu, L.; Mavrikakis, M. Atomic and Molecular Adsorption on Ni(111). *Surf Sci* **2019**, 679, 240–253. <https://doi.org/10.1016/j.susc.2018.08.004>.
- (25) Mohsenzadeh, A.; Bolton, K.; Richards, T. DFT Study of the Adsorption and Dissociation of Water on Ni(111), Ni(110) and Ni(100) Surfaces. *Surf Sci* **2014**, 627, 1–10. <https://doi.org/10.1016/j.susc.2014.04.006>.
- (26) Xie, X.; Du, L.; Yan, L.; Park, S.; Qiu, Y.; Sokolowski, J.; Wang, W.; Shao, Y. Oxygen Evolution Reaction in Alkaline Environment: Material Challenges and Solutions. *Advanced Functional Materials*. John Wiley and Sons Inc May 1, 2022. <https://doi.org/10.1002/adfm.202110036>.
- (27) Botha, L. M.; Santos-Carballal, D.; Terranova, U.; Quesne, M. G.; Ungerer, M. J.; Van Sittert, C. G. C. E.; De Leeuw, N. H. Mixing Thermodynamics and Electronic Structure of the Pt_{1-x}Ni_x (0 ≤ x ≤ 1) Bimetallic Alloy. *RSC Adv* **2019**, 9 (30), 16948–16954. <https://doi.org/10.1039/c9ra02320h>.
- (28) Doll, K. Density Functional Study of Ni Bulk, Surfaces and the Adsorbate Systems Ni(1 1 1) ($\sqrt{3} \times \sqrt{3}$)R30°-Cl, and Ni(1 1 1)(2 × 2)-K. *Surf Sci* **2003**, 544 (1), 103–120. <https://doi.org/10.1016/j.susc.2003.07.008>.
- (29) Franken, P. E. C.; Ponec, V. *Photoelectric Work Functions of Ni–Al Alloys: Clean Surfaces and Adsorption of CO*; 1974; Vol. 35.

- (30) Chapter 3 The Electronic Structure of Alloys; Experimental Results; 1995; pp 143–174. [https://doi.org/10.1016/S0167-2991\(06\)80475-1](https://doi.org/10.1016/S0167-2991(06)80475-1).
- (31) Zhong, W.; Qiu, Y.; Shen, H.; Wang, X.; Yuan, J.; Jia, C.; Bi, S.; Jiang, J. Electronic Spin Moment As a Catalytic Descriptor for Fe Single-Atom Catalysts Supported on C₂N. *J Am Chem Soc* **2021**, *143* (11), 4405–4413. <https://doi.org/10.1021/jacs.1c00889>.
- (32) Wang, L. L.; Khare, S. V.; Chirita, V.; Johnson, D. D.; Rockett, A. A.; Frenkel, A. I.; Mack, N. H.; Nuzzo, R. G. Origin of Bulklike Structure and Bond Length Disorder of Pt₃₇ and Pt₆Ru₃₁ Clusters on Carbon: Comparison of Theory and Experiment. *J Am Chem Soc* **2006**, *128* (1), 131–142. <https://doi.org/10.1021/ja053896m>.
- (33) Nie, Y.; Yang, L.; Sun, W.; Gao, Z.; Wang, Q. Increase in Gold Dissolution in Copper Ammonia Thiosulfate Solution via Cobalt Surface Modification. *Hydrometallurgy* **2020**, *197*. <https://doi.org/10.1016/j.hydromet.2020.105473>.
- (34) Ramezani-Dakheel, H.; Mirau, P. A.; Naik, R. R.; Knecht, M. R.; Heinz, H. Stability, Surface Features, and Atom Leaching of Palladium Nanoparticles: Toward Prediction of Catalytic Functionality. *Physical Chemistry Chemical Physics* **2013**, *15* (15), 5488–5492. <https://doi.org/10.1039/c3cp00135k>.
- (35) Purja Pun, G. P.; Mishin, Y. Development of an Interatomic Potential for the Ni–Al System. *Philosophical Magazine* **2009**, *89* (34–36), 3245–3267. <https://doi.org/10.1080/14786430903258184>.
- (36) Sun, W.; Ceder, G. Efficient Creation and Convergence of Surface Slabs. *Surf Sci* **2013**, *617*, 53–59. <https://doi.org/10.1016/j.susc.2013.05.016>.
- (37) Lazo, C.; Keil, F. J. Phase Diagram of Oxygen Adsorbed on Ni(111) and Thermodynamic Properties from First-Principles. *Phys Rev B Condens Matter Mater Phys* **2009**, *79* (24). <https://doi.org/10.1103/PhysRevB.79.245418>.
- (38) Fortenberry, R. C.; Trabelsi, T.; Francisco, J. S. Anharmonic Frequencies and Spectroscopic Constants of OAlOH and AlOH: Strong Bonding but Unhindered Motion. *Journal of Physical Chemistry A* **2020**, *124* (42), 8834–8841. <https://doi.org/10.1021/acs.jpca.0c07945>.
- (39) Apponi, A. J.; Barclay, W. L., Jr.; Ziurys, L. M. The Millimeter-Wave Spectrum of AlOH. *Astrophys J* **1993**, *414*, L129. <https://doi.org/10.1086/187013>.
- (40) Trabelsi, T.; Francisco, J. S. Is AlOH the Astrochemical Reservoir Molecule of AlO?: Insights from Excited Electronic States. *Astrophys J* **2018**, *863* (2), 139. <https://doi.org/10.3847/1538-4357/aad5e0>.
- (41) The Materials Project. *Materials Data on Al₂O₃ by Materials Project*. <https://doi.org/10.17188/1279805>.
- (42) Young, M. J.; Bedford, N. M.; Yanguas-Gil, A.; Letourneau, S.; Coile, M.; Mandia, D. J.; Aoun, B.; Cavanagh, A. S.; George, S. M.; Elam, J. W. Probing the Atomic-Scale Structure of Amorphous Aluminum Oxide Grown by Atomic Layer Deposition. *ACS Appl Mater Interfaces* **2020**, *12* (20), 22804–22814. <https://doi.org/10.1021/acsami.0c01905>.
- (43) Rahane, A. B.; Deshpande, M. D.; Kumar, V. Structural and Electronic Properties of (Al₂O₃)_n Clusters with n = 1–10 from First Principles Calculations. *Journal of Physical Chemistry C* **2011**, *115* (37), 18111–18121. <https://doi.org/10.1021/jp2050614>.
- (44) Hu, H.; Qiao, M.; Pei, Y.; Fan, K.; Li, H.; Zong, B.; Zhang, X. Kinetics of Hydrogen Evolution in Alkali Leaching of Rapidly Quenched Ni–Al Alloy. *Appl Catal A Gen* **2003**, *252* (1), 173–183. [https://doi.org/10.1016/S0926-860X\(03\)00416-2](https://doi.org/10.1016/S0926-860X(03)00416-2).

- (45) Wang, G.; Xu, Y. Embedded-Atom Potential for Ni-Al Alloy. In *IOP Conference Series: Materials Science and Engineering*; Institute of Physics Publishing, 2018; Vol. 452. <https://doi.org/10.1088/1757-899X/452/2/022025>.
- (46) Bhattacharjee, S.; Waghmare, U. V.; Lee, S. C. An Improved D-Band Model of the Catalytic Activity of Magnetic Transition Metal Surfaces. *Sci Rep* **2016**, *6*. <https://doi.org/10.1038/srep35916>.
- (47) Peck, M. A.; Santos-Carballal, D.; de Leeuw, N. H.; Claeys, M. Density Functional Theory Study of the Adsorption of Oxygen and Hydrogen on 3d Transition Metal Surfaces with Varying Magnetic Ordering. *South African Journal of Chemistry* **2021**, *74*, 69–72. <https://doi.org/10.17159/0379-4350/2021/V74A11>.
- (48) Xin, H.; Linic, S. Communications: Exceptions to the d -Band Model of Chemisorption on Metal Surfaces: The Dominant Role of Repulsion between Adsorbate States and Metal d -States. *Journal of Chemical Physics* **2010**, *132* (22). <https://doi.org/10.1063/1.3437609>.
- (49) Zhang, W.; Zou, G.; Choi, J. H. Adsorption Behavior of the Hydroxyl Radical and Its Effects on Monolayer MoS₂. *ACS Omega* **2020**, *5* (4), 1982–1986. <https://doi.org/10.1021/acsomega.9b03837>.
- (50) Seenivasan, H.; Tiwari, A. K. Water Dissociation on Ni(100) and Ni(111): Effect of Surface Temperature on Reactivity. *Journal of Chemical Physics* **2013**, *139* (17). <https://doi.org/10.1063/1.4827641>.
- (51) Xiang, Q.; Li, F.; Chen, W.; Ma, Y.; Wu, Y.; Gu, X.; Qin, Y.; Tao, P.; Song, C.; Shang, W.; Zhu, H.; Deng, T.; Wu, J. In Situ Vertical Growth of Fe-Ni Layered Double-Hydroxide Arrays on Fe-Ni Alloy Foil: Interfacial Layer Enhanced Electrocatalyst with Small Overpotential for Oxygen Evolution Reaction. *ACS Energy Lett* **2018**, *3* (10), 2357–2365. <https://doi.org/10.1021/acsenergylett.8b01466>.
- (52) Bailey, M. S.; Wilson, N. T.; Roberts, C.; Johnston, R. L. Structures, Stabilities and Ordering in Ni-Al Nanoalloy Clusters. *European Physical Journal D* **2003**, *25* (1), 41–55. <https://doi.org/10.1140/epjd/e2003-00218-2>.

CHAPTER 6 Conclusions and Future work

This chapter serves to reiterate the problem statement and aim. It gives an overview of the dissertation, summarises the most important findings of each part of the research, and gives a summative conclusion. Recommendations for future work are listed at the end of the chapter.

6.1 Reiteration of the problem statement, aim and objectives	94
6.2 Achievement of study objectives	95
6.3 Recommendations for future work	99

6.1 Reiteration of the problem statement, aim and objectives

Water electrolysis, consisting of two half-reactions, requires inexpensive and sustainable materials for electrocatalysts to be commercially viable. However, the choice of materials to be used as electrocatalysts is also influenced by the pH of the electrocatalytic environment.^{1,2} In an acidic environment, more inert materials, such as noble metals, are typically used.³ These metals, usually Ir and Ru, are costly due to their natural scarcity.³ In contrast, in an alkaline environment, more earth-abundant base metals can be used.^{1,2}

Raney nickel, a porous Ni structure formed from NiAl nanoparticle clusters from which Al has been leached, is one such material for the alkaline oxygen evolution reaction (OER) at 30°C.¹ Leaching of the Al is, however, not always accurately reproducible⁴ due to the varying segregation of Al to the surface and within the bulk of the NiAl bimetals.^{5–7} The amount of Al present in the Raney nickel after leaching influences the structural stability and performance of the final Raney nickel catalyst.^{8,9} To understand the leaching process and the impact of external factors on the final catalyst's structure, composition, and activity towards the alkaline OER, it is beneficial to develop and evaluate a model for Raney nickel from precursor to final catalyst. Previous computational and experimental studies on Raney nickel were limited to three bimetallic phases, namely Ni₂Al₃, NiAl, and NiAl₃. Thus, a more comprehensive computational approach that includes a large spectrum of NiAl bimetallic phases (not just selecting the commonly used phases) will result in a more holistic and in-depth understanding of the characteristics of Raney nickel and its potential as an OER electrocatalyst.

As stated in Chapter 1, this study aimed to develop and evaluate a model for the simulation of Raney nickel-type electrocatalysts and to test the activity of the resulting catalyst towards the OER in alkaline media. The following objectives were set as a way of achieving this goal:

- Scrutinise the available literature on hydrogen energy, water electrolysis as a hydrogen production method, oxygen evolution reaction (OER) in alkaline media, and Raney nickel catalyst systems (experimental and computational) to assist with the model development.
- Develop a density functional theory (DFT) model by creating and optimising pure metal bulks for Ni and Al and their (111)-surface slabs with the CAMbridge Serial Total Energy Package (CASTEP).¹⁰ Validate the model by comparing the results to existing experimental and computational literature values.
- Construct several Ni_{1-x}Al_x bimetal bulk configurations with the Site-Occupancy Disorder (SOD)¹¹ program. Optimise the constructed bimetal configurations using the General Utility Lattice Program (GULP)¹² and determine the most stable configurations with thermodynamic calculations.
- Optimise the most stable bimetallic bulk configurations with the CASTEP¹⁰ model developed with pure metals. Using the most stable optimised bimetallic bulk configurations, create and

optimise (111)-surface slabs with CASTEP.¹⁰ Investigate the electronic and magnetic properties of the most stable bimetal bulks and the (111)-surfaces. Identify the most suitable (111)-surface slabs using surface energy and surface properties. Leaching of Al was simulated by manually removing Al from the (111)-surface slabs and the subsequent adsorption of the OER species (OH[•]) onto the leached surfaces.

- Compare the findings of this study with available experimental and computational results found in the literature.

The following sections will demonstrate how the objectives of the study were achieved. Recommendations will also be made for future studies.

6.2 Achievement of study objectives

An understanding of the field of research, namely the electrochemistry of water electrolysis,^{13–17} Raney nickel^{18,19} and related computational models^{11,12,20}, was needed before the aim of the study could be addressed. This necessary background understanding was accomplished by conducting a literature study summarised in Chapter 2.

The knowledge gained in Chapter 2 was then applied to develop a density functional theory (DFT) model using pure metals to investigate bulk and surface slab structures as well as surface and electronic properties. The software of choice for the computational model development was the CAMbridge Serial Total Energy Package (CASTEP),¹⁰ a module of the Materials Studio 2020 (MS2020)²¹ software developed by the BIOVIA software company. This software package was chosen due to the use of robust pseudopotentials and plane-wave basis for periodic systems.^{10,22}

The computational model was developed and validated in Chapter 3. To find the best computational settings for the NiAl system, the k-point grid, dispersion correction scheme, and pseudopotential were varied for the pure bulk metal structures, namely Ni and Al, and their (111)-surface slabs. The (111)-surface slabs used consisted of four atomic layers, with a surface area of $9.488 \times 10^{-19} \text{ m}^2$ for Ni and $12.339 \times 10^{-19} \text{ m}^2$ for Al. The rest of the settings were kept constant, as indicated in Table 6-1.

Table 6-1 DFT settings used during computational model development

Setting name	Setting value
Setup	
DFT functional	GGA PBE
Spin polarisation	Collinear
Use formal spin as initial	Checked/selected
Cell optimisation	Full (for bulks) and none (for slabs)
Basis set for variable cell	Fixed Basis Quality
Compressibility	Medium
Optimisation algorithm	TPSD
Electronic properties	
Energy cut-off	570 eV
Density	Standard
Finite basis correction	Never
SCF Tolerance	2.0×10^{-6} eV/atom
Electronic minimiser	Density mixing
Apply dipole correction	None
Potentials representation	Reciprocal space
Relativistic treatment	Koelling-Harmon

The developed computational model was validated by comparing the calculated structures and electronic properties of pure bulk structures of Ni and Al and the (111)-surface slabs of these pure metals to literature values.^{3,23–30} This validation led to the identification of the 9×9×9 k-point grid as the optimal choice for bulk optimisation and the 9×9×1 k-point grid for surface slab optimisation. However, the same computational level was used for the bulk and surface slab optimisation calculations. Additionally, the TS dispersion correction scheme and ultrasoft pseudopotential were identified as the optimal dispersion scheme and pseudopotential for bulk and surface slab optimisations. Surface and electronic properties, which include the surface energy (γ),³¹ the work function (Φ),³¹ the d-band centres (ε_d), the interatomic spacing (d_x - d_x) for Ni-Ni and Al-Al, and the magnetic spin moment (m_s), were used to validate the surface calculations.

In Chapter 4, the Site-Occupancy Disorder (SOD)¹¹ program was used to systematically build and determine the unique configurations of several $\text{Ni}_{1-x}\text{Al}_x$ bimetallic structure mixtures (bimetallic phases). The unique configurations identified by the SOD¹¹ program using symmetry operators were geometrically optimised using the General Utility Lattice Program (GULP)¹². These optimised configurations were used to calculate the thermodynamic and statistical properties. The most stable configurations were identified by comparing the entropy of the individual configurations with a probability of existence $\geq 10\%$. From this comparison ten configurations were identified. However, two configurations were eliminated because those identified under the same bimetallic phase had similar atomic arrangements (only the position of one or two atoms differed). The final eight configurations were within the following $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases, namely: $\text{Ni}_3\text{Al}_{13}$, $\text{Ni}_4\text{Al}_{12}$, $\text{Ni}_5\text{Al}_{11}$, Ni_6Al_8 , Ni_9Al_7 , $\text{Ni}_{11}\text{Al}_5$, $\text{Ni}_{12}\text{Al}_4$, and $\text{Ni}_{13}\text{Al}_3$.

The findings of Chapter 4 were published as a manuscript in the Suid-Afrikaanse Tydskrif vir Natuurwetenskap en Tegnologie / South African Journal of Science and Technology³² and presented at the virtual Conference of the South African Advanced Materials Initiative (CoSAAMI) 2021, which took place in October 2021. The findings of Chapter 4 were also presented as a poster at the Chem4Energy Annual Conference – Sustainable Energy 2023, which took place in March 2023.

In Chapter 5, an additional $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase, namely, Ni_7Al_9 , was identified from the statistical SOD¹¹ data and the entropy of the configurations. Two configurations of Ni_7Al_9 were identified as the most stable. The bulk structures of these two configurations, along with the eight configurations identified in Chapter 4, were geometrically optimised with CASTEP¹⁰ using the same settings identified in Chapter 3. The optimised bulk structures were then cleaved at a (111)-Miller plane to create a (111)-surface slab with four atomic layers and surface areas, as given in Table 6-2. These surface areas were used in surface energy calculations. These (111)-surface slabs were then optimised using the same settings as in Chapter 3.

Table 6-2 The surface areas of the cleaved $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase (111)-surface slabs

$\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase	Area ($\times 10^{-19} \text{ m}^2$)
$\text{Ni}_3\text{Al}_{13}$	11.60
$\text{Ni}_4\text{Al}_{12}$	11.30
$\text{Ni}_5\text{Al}_{11}$	11.08
Ni_7Al_9 (Config 65)	10.66
Ni_7Al_9 (Config 61)	10.39
Ni_8Al_8	10.74
Ni_9Al_7	9.99
$\text{Ni}_{11}\text{Al}_5$	9.96
$\text{Ni}_{12}\text{Al}_4$	9.68
$\text{Ni}_{13}\text{Al}_3$	9.64

Additionally, surface and electronic properties, which included the d-band centres (ϵ_d), the magnetic spin moment (m_s), the surface energies (γ),³¹ and the work functions (Φ),³¹ were calculated and the interatomic spacing (d_x - d_x) for Ni-Ni, Al-Al, and Ni-Al were measured. The surface compositions, along with literature recommendations,^{6,8,33,34} were used to identify surface slabs for simulated leaching. The surface slabs identified for the simulated leaching were the Ni_7Al_9 , Ni_8Al_8 , Ni_9Al_7 , and $\text{Ni}_{11}\text{Al}_5$ (111)-surface slabs.

For each identified surface slab, a series of manually simulated leaching was done on four sets of Al atoms. The manually simulated leaching was done by identifying and removing an initial Al atom, whereafter the new surface slab was optimised in CASTEP²⁰ using the same settings identified in Chapter 3. The initial Al atom was identified by considering its position on the surface slab and the surrounding nearest-neighbour (NN) environment. Hereafter, for the second, third, and fourth Al atoms to be removed, a set of three Al atoms was identified as the next step in Al

atom removal by considering the NN atoms to the previously removed Al atom. From this set, the Al atom with the lowest energy to be removed was then used to determine the sequential set of atoms to be removed. The average Al atom removal energy was calculated for the leaching path followed. This energy was observed to increase with an increase in Ni content, which agreed with what was seen in the literature.³⁵

Finally, adsorption of an OH⁻ species on leached Ni_{1-x}Al_x-surface slabs and on pure Ni (111)-surface slabs was undertaken. For each leached Ni_{1-x}Al_x surface slab, five Ni-centred adsorption positions were identified by considering the NN environment of the Ni atom and the depth within the leached surface slab. For the pure Ni (111) surface slab, the top and bridged adsorption sites were used. The d-band centres of the surface slabs, before and after the five adsorption positions, were used to calculate the d-band centre shifts. The d-band centre shifts for pure Ni (111) showed upward and downward shifts. The upward shift coincided with the top site, while the downward shifts coincided with the bridge and fcc sites. The d-band centre shifts for each of the five adsorption positions were calculated and found to show a positive (downward) shift for 90% of the chosen positions. A downward shift indicates weaker adsorbate-surface interactions. While the other 10% of the selected positions had a negative (upward) shift in the d-band centre, indicating stronger adsorbate-surface interactions. The upward and downward shifts were seen to correspond to the adsorption positions and proximity of stronger-binding Al atoms and possibly smaller pore sizes. It was found that the bridged and fcc sites of pure Ni (111) agreed with more optimal adsorption energies for OER.³⁶ The averaged adsorption energies of the top layers of Ni₈Al₈ and Ni₉Al₇, as well as the top and third layers of Ni₁₁Al₅, were in better agreement with the literature values and optimal adsorption energies for OER.^{36,37} Due to the agreement of the pure Ni (111) adsorption energy to more optimal adsorption energies for OER, pure Ni (111) is considered an effective catalyst for the OER. By comparison, the bimetallic (111)-surface slabs of Ni₈Al₈, Ni₉Al₇, and Ni₁₁Al₅ could be leached and be active catalysts for the OER. Although Ni₈Al₈ (NiAl) has previously been studied as a Raney nickel precursor, the Ni₉Al₇ and Ni₁₁Al₅ bimetallic phases were newly identified in this study.

To conclude, all the objectives in Chapter 1 were successfully achieved. The developed DFT model can be employed for further study into Ni_{1-x}Al_x bimetallic phases. Furthermore, a manual approach to leaching and adsorption is a practical alternative to molecular dynamics methods. From the manual adsorption, it was observed that the novel Ni₉Al₇ and Ni₁₁Al₅ bimetallic phases could lead to active Raney nickel catalysts for OER. The following section contains recommendations for future work.

6.3 Recommendations for future work

Although the objectives of this study were achieved, some methods could afford a more in-depth approach to further the research. Therefore, the recommendations for future work are the following:

- Utilise the bulk and surface slab structures of the pure metals (Ni and Al) from this study to extract data such as the lattice constants, Bulk moduli, and cohesive energies and compare these values to the available literature (computational and experimental). Additionally, build thicker surface slab structures with a portion of the layers kept frozen during optimisation to represent the bulk material and compare the results to the available literature.
- Molecular-dynamic simulation of the leaching of Al from the $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases identified in Chapter 5 using 20% NaOH and 40% NaOH leaching cells. Additionally, larger systems with thicker slabs can be used. This investigation will lead to a better understanding of the leaching dynamics of the $\text{Ni}_{1-x}\text{Al}_x$ and NaOH systems. The variation of the NaOH concentration could also lead to the identification of the optimum NaOH concentration regarding morphological properties, including pore size and stability.
- Evaluate the reconstruction related to leaching and the effect this could have on the pore stability and activity.
- Simulate adsorption of H_2O , OH^- , O^{2-} , OOH^- and O_2 onto the (111)-surfaces of the pure metals and the bimetallics identified in Chapter 5, as well as onto bimetal surfaces after the molecular dynamic simulated leaching. This investigation will lead to understanding of the reactivity of the bimetallics and developed Raney nickel catalysts towards the alkaline OER.

References

- (1) Colli, A. N.; Girault, H. H.; Battistel, A. Non-Precious Electrodes for Practical Alkaline Water Electrolysis. *Materials* **2019**, *12* (8), 1336. <https://doi.org/10.3390/ma12081336>.
- (2) Fabbri, E.; Haberer, A.; Waltar, K.; Kötter, R.; Schmidt, T. J. Developments and Perspectives of Oxide-Based Catalysts for the Oxygen Evolution Reaction. *Catal Sci Technol* **2014**, *4* (11), 3800–3821. <https://doi.org/10.1039/c4cy00669k>.
- (3) Botha, L. M.; Santos-Carballal, D.; Terranova, U.; Quesne, M. G.; Ungerer, M. J.; van Sittert, C. G. C. E.; de Leeuw, N. H. Mixing Thermodynamics and Electronic Structure of the $\text{Pt}_{1-x}\text{Ni}_x$ ($0 \leq x \leq 1$) Bimetallic Alloy. *RSC Adv* **2019**, *9* (30), 16948–16954. <https://doi.org/10.1039/c9ra02320h>.
- (4) Klein, J. C.; Hercules, D. M. Surface Analysis of Raney Nickel Alloys. *Anal Chem* **1981**, *53* (6), 754–758.

- (5) Manzoor, A.; Pandey, S.; Chakraborty, D.; Phillpot, S. R.; Aidhy, D. S. Entropy Contributions to Phase Stability in Binary Random Solid Solutions. *NPJ Comput Mater* **2018**, *4* (1). <https://doi.org/10.1038/s41524-018-0102-y>.
- (6) Fultz, B. Vibrational Thermodynamics of Materials. *Progress in Materials Science*. Pergamon May 1, 2010, pp 247–352. <https://doi.org/10.1016/j.pmatsci.2009.05.002>.
- (7) MA, E. Alloys Created between Immiscible Elements. *Prog Mater Sci* **2005**, *50* (4). <https://doi.org/10.1016/j.pmatsci.2004.07.001>.
- (8) Schweizer, S.; Chaudret, R.; Low, J.; Subramanian, L. Molecular Modeling and Simulation of Raney Nickel: From Alloy Precursor to the Final Porous Catalyst. *Comput Mater Sci* **2015**, *99*, 336–342.
- (9) Schweizer, S.; Chaudret, R.; Spyriouni, T.; Low, J.; Subramanian, L. Influence of the Precursor Composition and Reaction Conditions on Raney-Nickel Catalytic System. In *Foundations of Molecular Modeling and Simulation: Select Papers from FOMMS 2015*; Snurr, R. Q., Adjiman, C. S., Kofke, D. A., Eds.; Springer Singapore: Singapore, 2016; pp 125–135. https://doi.org/10.1007/978-981-10-1128-3_8.
- (10) Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. I. J.; Refson, K.; Payne, M. C. First Principles Methods Using CASTEP. *Zeitschrift für Kristallographie-Crystalline Materials* **2005**, *220* (5/6), 567–570.
- (11) Grau-Crespo, R.; Hamad, S.; Catlow, C. R. A.; de Leeuw, N. H. Symmetry-Adapted Configurational Modelling of Fractional Site Occupancy in Solids. *Journal of Physics: Condensed Matter* **2007**, *19* (25), 256201. <https://doi.org/10.1088/0953-8984/19/25/256201>.
- (12) Gale, J. D.; Rohl, A. L. The General Utility Lattice Program (GULP). *Mol Simul* **2003**, *29* (5), 291–341. <https://doi.org/10.1080/0892702031000104887>.
- (13) Doyle, R. L.; Lyons, M. E. G. The Oxygen Evolution Reaction: Mechanistic Concepts and Catalyst Design. In *Photoelectrochemical solar fuel production*; Springer, 2016; pp 41–104.
- (14) Khan, M. A.; Zhao, H.; Zou, W.; Chen, Z.; Cao, W.; Fang, J.; Xu, J.; Zhang, L.; Zhang, J. Recent Progresses in Electrocatalysts for Water Electrolysis. *Electrochemical Energy Reviews* **2018**, *1* (4), 483–530.
- (15) Brauns, J.; Turek, T. Alkaline Water Electrolysis Powered by Renewable Energy: A Review. *Processes*. MDPI AG February 1, 2020. <https://doi.org/10.3390/pr8020248>.
- (16) Mallouk, T. E. Water Electrolysis: Divide and Conquer. *Nat Chem* **2013**, *5* (5), 362–363.

- (17) Zeng, K.; Zhang, D. Recent Progress in Alkaline Water Electrolysis for Hydrogen Production and Applications. *Prog Energy Combust Sci* **2010**, 36 (3), 307–326. <https://doi.org/10.1016/j.pecs.2009.11.002>.
- (18) Raney, M. *Method of Producing Finely-Divided Nickel*; 1926.
- (19) Raney, M. Catalysts from Alloys: Nickel Catalysts. *Ind Eng Chem* **1940**, 32 (9), 1199–1203. <https://doi.org/10.1021/ie50369a030>.
- (20) Hasnip, P. J.; Refson, K.; Probert, M. I. J.; Yates, J. R.; Clark, S. J.; Pickard, C. J. Density Functional Theory in the Solid State. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*. The Royal Society Publishing March 13, 2014. <https://doi.org/10.1098/rsta.2013.0270>.
- (21) Dassault Systèmes BIOVIA, Materials Studio, 20.1.0.5, San Diego: Dassault Systèmes, 2020. Dassault Systèmes: San Diego 2020.
- (22) CASTEP/About CASTEP. <http://www.castep.org/CASTEP/CASTEP> (accessed 2023-04-12).
- (23) Zhukovskii, Y. F.; Mastrikov, Y.; Shunin, Y.; Jacobs, P. W. M.; Zhukovskii, Y. F.; Mastrikov, Y.; Shunin, Y. N. Bulk and Surface Properties of Metallic Aluminium: DFT Simulations. *Computer Modelling & New Technologies* **2002**, 6 (1), 7–28.
- (24) Mittendorfer, F.; Eichler, A.; Hafner, J. *Structural, Electronic and Magnetic Properties of Nickel Surfaces*; 1999; Vol. 423.
- (25) Michaelson, H. B. The Work Function of the Elements and Its Periodicity. *J Appl Phys* **1977**, 48 (11), 4729–4733. <https://doi.org/10.1063/1.323539>.
- (26) Kitchin, J. R.; Khan, N. A.; Barteau, M. A.; Chen, J. G.; Yakshinskiy, B.; Madey, T. E. Elucidation of the Active Surface and Origin of the Weak Metal-Hydrogen Bond on Ni/Pt (1 1 1) Bimetallic Surfaces: A Surface Science and Density Functional Theory Study. *Surf Sci* **2003**, 544 (2–3), 295–308. <https://doi.org/10.1016/j.susc.2003.09.007>.
- (27) Greeley, J.; Mavrikakis, M. Surface and Subsurface Hydrogen: Adsorption Properties on Transition Metals and near-Surface Alloys. *Journal of Physical Chemistry B* **2005**, 109 (8), 3460–3471. <https://doi.org/10.1021/jp046540q>.
- (28) Tyson, W. R.; Miller, W. A. Surface Free Energies of Solid Metals: Estimation from Liquid Surface Tension Measurements. *Surf Sci* **1977**, 62 (1), 267–276. [https://doi.org/10.1016/0039-6028\(77\)90442-3](https://doi.org/10.1016/0039-6028(77)90442-3).
- (29) Lee, J. Y.; Punkkinen, M. P. J.; Schönecker, S.; Nabi, Z.; Kádas, K.; Zólyomi, V.; Koo, Y. M.; Hu, Q. M.; Ahuja, R.; Johansson, B.; Kollár, J.; Vitos, L.; Kwon, S. K. The Surface Energy

- and Stress of Metals. *Surf Sci* **2018**, 674, 51–68. <https://doi.org/10.1016/J.SUSC.2018.03.008>.
- (30) Singh-Miller, N. E.; Marzari, N. Surface Energies, Work Functions, and Surface Relaxations of Low-Index Metallic Surfaces from First Principles. *Phys Rev B* **2009**, 80 (23), 235407. <https://doi.org/10.1103/PhysRevB.80.235407>.
 - (31) Wang, J.; Wang, S. Q. Surface Energy and Work Function of Fcc and Bcc Crystals: Density Functional Study. *Surf Sci* **2014**, 630, 216–224. <https://doi.org/10.1016/j.susc.2014.08.017>.
 - (32) Thesner, C.; Falch, A.; Van Sittert, C. G. C. E. Using Site Occupation Disorder to Build Bulk Structures of $\text{Ni}_{1-x}\text{Al}_x$. *Suid-Afrikaanse Tydskrif vir Natuurwetenskap en Tegnologie / South African Journal of Science and Technology* **2022**, 40 (1), 174–179. <https://doi.org/10.36303/SATNT.2021cosaami.33>.
 - (33) Barnard, N. C.; Brown, S. G. R. Kinetic Monte Carlo Modelling the Leaching of Raney Ni-Al Alloys. In *WIT Transactions on Engineering Sciences*; 2007; Vol. 54, pp 53–62. <https://doi.org/10.2495/ECOR070061>.
 - (34) Lee, G. D.; Suh, C. S.; Park, J. H.; Park, S. S.; Hong, S. S. Raney Ni Catalysts Derived from Different Alloy Precursors (I) Morphology and Characterization. *Korean Journal of Chemical Engineering* **2005**, 22 (3), 375–381. <https://doi.org/10.1007/BF02719414>.
 - (35) Bailey, M. S.; Wilson, N. T.; Roberts, C.; Johnston, R. L. Structures, Stabilities and Ordering in Ni-Al Nanoalloy Clusters. *European Physical Journal D* **2003**, 25 (1), 41–55. <https://doi.org/10.1140/epjd/e2003-00218-2>.
 - (36) Li, J. Oxygen Evolution Reaction in Energy Conversion and Storage: Design Strategies Under and Beyond the Energy Scaling Relationship. *Nano-Micro Letters*. Springer Science and Business Media B.V. December 1, 2022. <https://doi.org/10.1007/s40820-022-00857-x>.
 - (37) Mohsenzadeh, A.; Bolton, K.; Richards, T. DFT Study of the Adsorption and Dissociation of Water on Ni(111), Ni(110) and Ni(100) Surfaces. *Surf Sci* **2014**, 627, 1–10. <https://doi.org/10.1016/j.susc.2014.04.006>.

Figure A-1 Continued

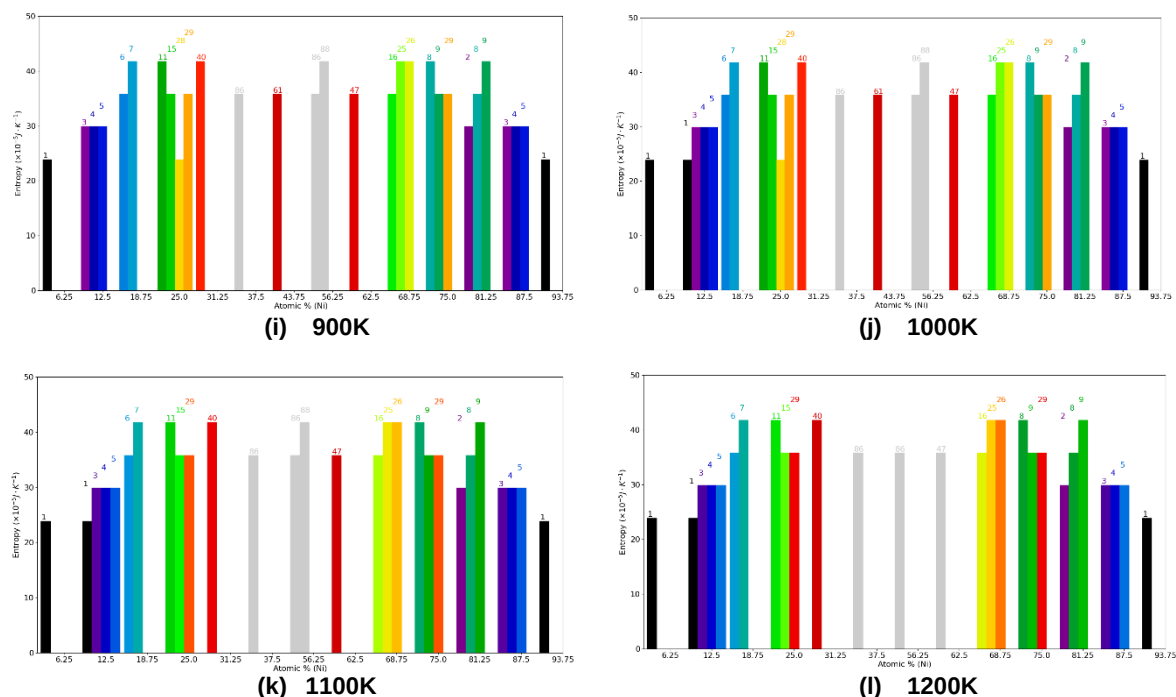
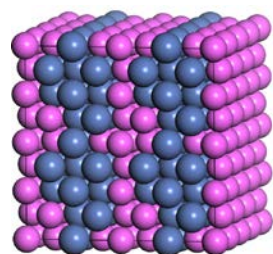


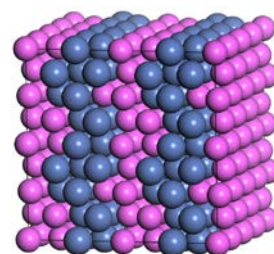
Figure A-1 continued (a) –(l)The entropy of the different configurations (the identifying number shown above the bar), with probabilities $\geq 10\%$ relative to Ni content at all temperatures 0.1K -1200K, excluding 700K

A.2 Chapter 5 supplementary information

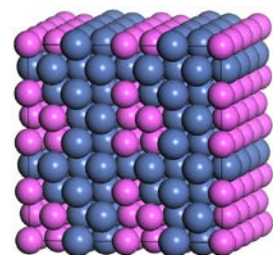
This section contains the additional images referred to in Chapter 5.



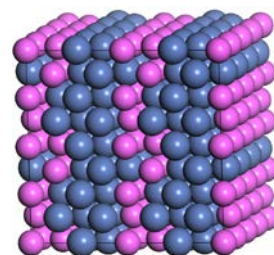
(a) Ni_9Al_7
– config 88 (Ni = 56%)



(b) Ni_9Al_7
– config 89 (Ni = 56%)



(c) $\text{Ni}_{11}\text{Al}_5$
–config 25 (Ni = 69%)



(d) $\text{Ni}_{11}\text{Al}_5$
–config 26 (Ni = 69%)

Figure A-2 (a) - (d) Different configurations under the same $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase showing a configurational difference of only one or two atoms. (a) - (b) Configurations 88 and 89 under Ni_9Al_7 . (c) - (d) Configurations 25 and 26 under $\text{Ni}_{11}\text{Al}_5$.

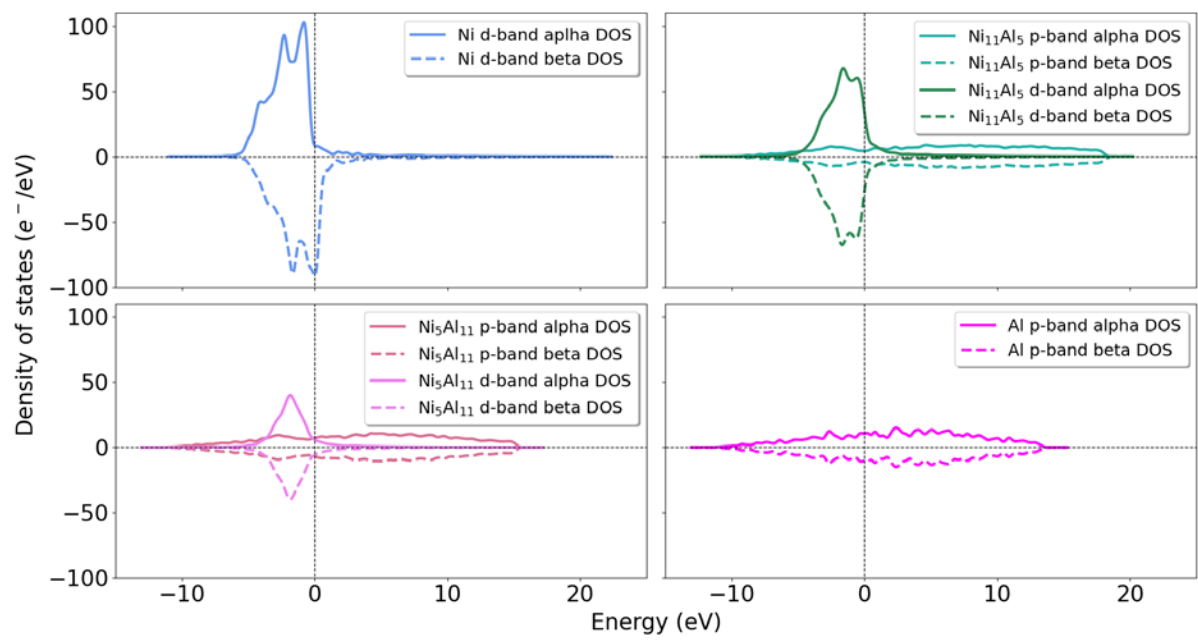


Figure A-3 Alpha and beta DOS for the pure Ni d-band, $\text{Ni}_{11}\text{Al}_5$ and $\text{Ni}_5\text{Al}_{11}$ d- and p-bands and the pure Al p-band.

Appendix B Published article(s)/manuscript(s)

B.1 Published manuscript from Chapter 4

Available online at <https://doi.org/10.36303/SATNT.2021cosaami.33>
Conference of the South African Advanced Materials Initiative

Using site occupation disorder to build bulk structures of $\text{Ni}_{1-x}\text{Al}_x$

CJ Thesner¹, A Falch², CGCE van Sittert^{1*}

¹ Applied Molecular Modelling Group, Research Focus Area: Chemical Resource Beneficiation (CRB), North-West University, Private Bag X6001, Potchefstroom 2520, South Africa

² Electrochemistry for Energy & Environment Group, Research Focus Area: Chemical Resource Beneficiation (CRB), North-West University, Private Bag X6001, Potchefstroom 2520, South Africa
Email: Cornie.VanSittert@nwu.ac.za

Abstract

Raney nickel shows potential as an electrocatalyst for the oxygen evolution reaction (OER). However, the catalytic activity of Raney nickel varies with its properties. These properties are related to the composition of the bimetallic precursor used to synthesise Raney nickel. The bimetallic precursor consists of a combination of bimetallic phases. Various studies have been done on the well-known bimetallic phases, namely, Ni_2Al_3 , NiAl and NiAl_3 . However, to get a more comprehensive understanding of the influence of the bimetallic precursor on the properties of Raney nickel, a larger spectrum of bimetallic phases needs to be evaluated. In this study, the Site Occupation Disorder (SOD) program was used to build solid-state structures (bimetallic phases) with various $\text{Ni}_{1-x}\text{Al}_x$ bimetallic ratios. These $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases were evaluated, and unique configurations for each $\text{Ni}_{1-x}\text{Al}_x$ bimetallic ratio were obtained. The unique configurations were geometrically optimised using the General Utility Lattice Program (GULP) at 0K. These optimised unique configurations were thermodynamically evaluated over a range of 0.1K – 1200K, and the most stable configurations with a probability higher than 10% were identified. This study found that the stable non-homogeneous configurations fall within a range of 20% - 80% Ni content. A weight average combination of these configurations of the bimetallic phases will produce a non-homogeneous precursor with an average Ni content of 20% - 80%, which is in close agreement with experimental results. The approach in this study enables researchers to obtain a larger, repeatable spectrum of bimetallic phases for the investigation of Raney nickel precursors.

Keywords: Site Occupation Disorder, General Utility Lattice Program, nickel, aluminium, bimetallic phases, Raney nickel

1. Introduction

The world is facing an energy and environmental crisis, which has led to a need to develop various alternative forms of energy production.^{1,2,3} Hydrogen gas (H_2) has been identified as a clean, sustainable and highly energy-dense energy source. However, H_2 is not found naturally.⁴ There are several methods to produce H_2 . The most prominent methods include reforming natural gas, gasification of coal, and water electrolysis.^{5,6} Water electrolysis is considered a highly sustainable and clean way to produce H_2 of high purity with only oxygen gas (O_2) as a by-product.^{5,8}

Water electrolysis consists of two half-cell reactions: the OER and the hydrogen evolution reaction (HER).^{8,9} Of these two reactions, the OER is the rate-determining reaction and therefore requires an efficient electrocatalyst.⁷ Studies have shown that Raney nickel, a porous Ni structure, is a possible electrocatalyst for the OER in an alkaline environment.⁹

However, the activity and selectivity of Raney nickel vary with the morphological properties of the final synthesised Raney nickel. The morphological properties of Raney nickel are dependent on the synthesis method,¹⁰⁻¹³ which is influenced by the composition of the bimetallic precursor and the final porous structure.¹³⁻¹⁵ During the synthesis of Raney nickel, the primary metal (Ni) is combined with a secondary metal (usually zinc (Zn) or aluminium (Al)) to form a bimetallic precursor containing various bimetallic phases.^{16,17} The secondary metal in the bimetallic precursor is more active

towards the leaching than the Ni. Of the two secondary metals mentioned above, Al produced the best results in leachability without influencing Ni's integrity.^{17,18}

The most studied $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases, both experimentally and computationally, are Ni_2Al_3 , NiAl and NiAl_3 . These studies usually started with a specific bimetallic phase within an alloy or a bimetallic precursor.^{11,14,17,19,20} However, to get a more comprehensive understanding of the influence of the bimetallic precursor on the morphological properties of Raney nickel, a larger spectrum of bimetallic phases needs to be evaluated. The bimetallic phases could be evaluated separately or combined in one bimetallic precursor structure.

The SOD²¹ program can be used for a more systematic approach to build and model a spectrum of $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases. This program utilises the site occupancy disorder phenomenon seen in solid-state chemistry.²¹ In the SOD program, atoms of the secondary metal (Al) are systematically substituted into each of the available lattice spaces of the bulk structure of the pure primary metal (Ni), according to a pre-defined $\text{Ni}_{1-x}\text{Al}_x$ bimetallic ratio at 0K. This substitution leads to several configurations that are directly proportional to the size of the bulk structure. In order to reduce the number of configurations obtained, only the unique configurations are identified by applying a set of geometric operators (translation, rotation, and reflection) that work in conjunction with the symmetry of the crystal structure of the primary metal.

Each unique configuration is accompanied by a degeneracy value, Ω_m , which is the number of symmetry-bound configurations identified in the larger bulk structure. These symmetry-bound configurations have the same energy due to similar atomic arrangements within the larger bulk structure. Only one of these symmetry-bound configurations is listed as output for the SOD program, namely the unique configuration.

The unique configurations were geometrically optimised at 0K using GULP to find the most stable geometric orientation for the configurations.^{22,23} These optimised structures were submitted to thermodynamic calculations with statistical SOD. These calculations require an input file of temperatures at which the data should be calculated. The thermodynamic calculations include the Boltzmann probability distributions, the configurational entropy, and the enthalpy of mixing.

In this study, a larger spectrum of potential $Ni_{1-x}Al_x$ bimetallic phases that may influence the morphology and thus the synthesis and properties of Raney nickel were built using SOD.

2. Computational method

2.1 Configurations built with SOD

The face-centred cubic (fcc) unit cell for Ni, within the space group Fm-3m, was constructed using the following lattice parameters: a , b , and c of 3.524 Å, and cell angles of 90.0°.²⁴ The unit cell was expanded into a $2 \times 2 \times 1$ supercell. The $2 \times 2 \times 1$ cell contains 16 atoms, where each atom represents 6.25% of the cell. Using the SOD program at 0K resulted in numerous symmetry-bound configurations for a specific $Ni_{1-x}Al_x$ bimetallic phase. Symmetry operations reduced these symmetry-bound configurations to unique configurations, which were geometrically optimised using GULP²³ with the interatomic many-body potentials from the Sutton-Chen library.²² The Boltzmann probability distributions, the configurational entropy and enthalpy of mixing were calculated for a temperature range of 0.1K - 1200K, in steps of 100K.

2.2 Boltzmann probability distributions

The Boltzmann probability distribution was calculated using the following equation:²¹

$$P_m = \frac{1}{Z} \Omega_m e^{(-E_m/k_B T)} \quad (1)$$

where m is the specific configuration, E_m is the configuration energy, Ω_m the configuration degeneracy showing the number of times the unique configuration is observed, k_B is Boltzmann's constant ($8.6173 \times 10^{-5} \text{ eV} \cdot \text{K}^{-1}$), and Z is the partition function in the following equation:

$$Z = \sum_{m=1}^N e^{(-E_m/k_B T)} \quad (2)$$

2.3 Stability of configurations

The stability of the configurations was determined by studying the entropy, which is calculated using the following equation:²¹

$$S_m = k_B T \ln \Omega_m \quad (3)$$

where T is temperature, and the rest of the terms are as defined earlier.

The morphology of the various bimetallic phases could be explained by the enthalpy of mixing.²⁵

$$\Delta H_{mix} = H[Ni_{1-x}Al_x] - (1-x)H[Ni] - xH[Al] \quad (4)$$

where $H[Ni_{1-x}Al_x]$ is the enthalpy of a specific $Ni_{1-x}Al_x$ bimetallic phase, and $H[Ni]$ and $H[Al]$ are the enthalpies of the pure metals. The $H[Ni_{1-x}Al_x]$ can be calculated as a weight average from the configuration enthalpy:²¹

$$H[Ni_{1-x}Al_x] = \sum_{m=1}^N P_m H_m[Ni_{1-x}Al_x] \quad (5)$$

where $H_m[Ni_{1-x}Al_x]$ is the configuration enthalpy, and the rest of the terms are as defined earlier.

Table 1: The configurations for various $Ni_{1-x}Al_x$ bimetallic phases

Bimetallic phase	Total number of symmetry-bound configurations	Unique configurations	Unique configurations probable at 0K
$Ni_{15}Al_1$	16	1	1
$Ni_{14}Al_2$	120	5	1
$Ni_{13}Al_3$	560	10	1
$Ni_{12}Al_4$	1820	33	1
$Ni_{11}Al_5$	4368	53	1
$Ni_{10}Al_6$	8008	101	1
Ni_9Al_7	11440	122	1
Ni_8Al_8	12870	153	2
Ni_7Al_9	11440	122	1
Ni_6Al_{10}	8008	101	1
Ni_5Al_{11}	4368	53	1
Ni_4Al_{12}	1820	33	1
Ni_3Al_{13}	560	10	1
Ni_2Al_{14}	120	5	1
Ni_1Al_{15}	16	1	1

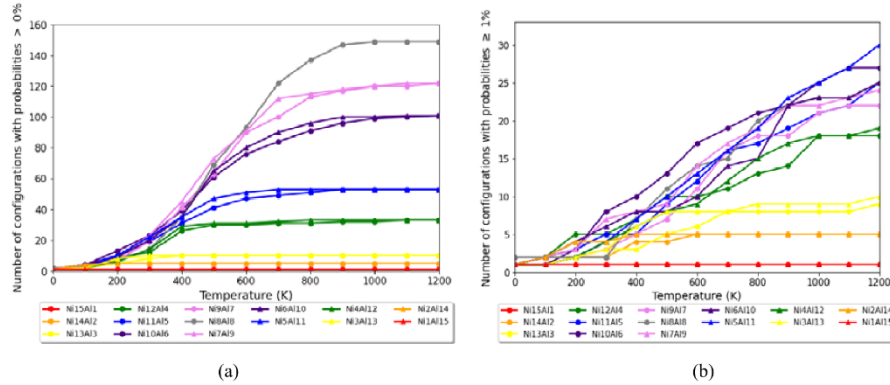


Figure 1: The number of configurations for the $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases over a temperature range of 0.1K – 1200K for (a) existence probabilities $> 0\%$, and (b) existence probabilities $\geq 1\%$. (Circle markers represent ratios where the Ni content is the highest, and triangle markers represent ratios where Al content is the highest.)

3. Results and Discussion

3.1 Configurations built with SOD

The total number of symmetry-bound configurations and the unique configurations for various $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases are listed in Table 1. For example, in the case of the 1:1 atomic ratio (bimetallic phase Ni_8Al_8), the total number of symmetry-bound configurations is 12870, of which only 153 configurations are unique. The number of configurations for all the bimetallic phases investigated is distributed symmetrically around the Ni_8Al_8 bimetallic phase. This distribution is observed since little or no influence outside the bulk structure (periodic supercell) was considered.

Initially, the various symmetry-bound configurations were built at 0K. However, Raney nickel is prepared at higher temperatures. Therefore, the temperature influence on the probability distribution was considered, and it was observed that the number of unique configurations increases as temperature increases.

3.2 Boltzmann probability distributions

Figure 1 shows the number of unique configurations for the various $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases over a temperature range of 0.1K – 1200K. Figure 1(a) shows the number of unique configurations with a probability of existence higher than 0%. The number of unique configurations increases in a sigmoidal trend as the temperature increases and reaches a plateau when the maximum number of unique configurations above 0% existence probability is reached. In Figure 1(a), the data can be divided into three temperature ranges. The first is from 0K – 200K; in this temperature range for most $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases, there is a gradual increase in the number of configurations. At 200K, the bimetallic phases outside the $\text{Ni}_{12}\text{Al}_4$ to $\text{Ni}_4\text{Al}_{12}$ (with a Ni content of 81.25% to 18.75%) range reach their maximum number of unique configurations. The second temperature range is from 200K – 900K; there is a linear increase in the number of unique configurations in this temperature range. The final temperature range is from 900K – 1200K. In this temperature range, all the bimetallic phases in the $\text{Ni}_{12}\text{Al}_4$ to $\text{Ni}_4\text{Al}_{12}$ range reach a plateau for the unique configurations.

plateaus indicate that at 900K, the maximum number of unique configurations is no longer influenced by temperature. It should also be noted that a high percentage of the unique configurations above 200K has a probability of existence of less than 1%.

Figure 1(b) shows the number of unique configurations with probabilities of existence $\geq 1\%$ as the temperature increases. The bimetallic phases outside the $\text{Ni}_{12}\text{Al}_4$ to $\text{Ni}_4\text{Al}_{12}$ range, reach their maximum number of unique configurations at much lower temperatures than the bimetallic phases in the $\text{Ni}_{12}\text{Al}_4$ to $\text{Ni}_4\text{Al}_{12}$ range, as seen in Figure 1(a). None of the bimetallic phases in the $\text{Ni}_{12}\text{Al}_4$ to $\text{Ni}_4\text{Al}_{12}$ range reach their maximum number of unique configurations in Figure 1(b). However, the bimetallic phases in the $\text{Ni}_{12}\text{Al}_4$ to $\text{Ni}_4\text{Al}_{12}$ range have a higher number of unique configurations over the 600K - 1200K temperature range, than the bimetallic phases outside of this range. Since there are fewer unique configurations for all the $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases, the influence of temperature on the number of unique configurations could be seen more clearly. Additionally, the influence of temperature on the existence probability of the two inverse ratio $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases, namely $\text{Ni}_2\text{Al}_{14}$ and $\text{Ni}_{14}\text{Al}_2$ or $\text{Ni}_3\text{Al}_{13}$ and $\text{Ni}_{13}\text{Al}_3$, is seen in Figure 1(b).

The number of unique configurations could be further reduced by increasing the probability of existence cut-off. Therefore, unique configurations with probabilities $\geq 10\%$ will be considered in the rest of the paper.

3.3 Stability of configurations

Studies on high entropy alloys show that the larger the entropy of the substance, the greater the stability thereof.²⁶ This observation follows from the fact that higher entropies lead to lower Gibbs-free energies. Figure 2 shows the entropy for the unique configurations with a probability of existence cut-off of $\geq 10\%$ relative to the Ni content at 700K. The unique configuration data shows a parabolic trend across the Ni content range, centred around the 1:1 atomic ratio. The entropy for the unique configurations over this range of temperatures shows the same parabolic relationship

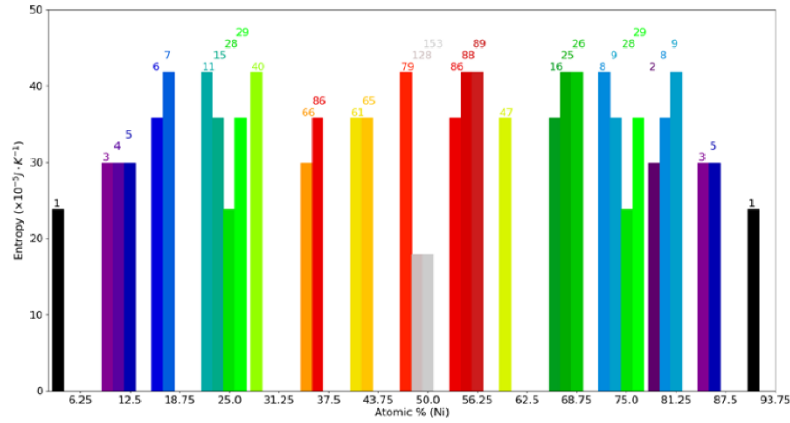


Figure 2: The entropy of the different configurations (the identifying number shown above the bar), with probabilities $\geq 10\%$ relative to Ni content at 700K

with Ni content in the unique configurations as in Figure 2. The unique configurations with the highest entropy are in the 18.75% to 81.25% Ni content range for 700K. The ten configurations showing the highest entropies at 700K in Figure 2 are also seen at 800K. Additionally, 80% of these highest entropy configurations at 700K are also observed in the 600K – 1100K range. Entropy graphs for other temperatures over the entire 0.1K – 1200K range are available in the Supplementary Information.

The unique configurations of the bimetallic phases observed at 700K have an average Ni content of 20% - 80%. This range agrees with experimental studies showing the effective Raney nickel precursors to contain bimetallic phases in the 40% to 60% Ni range.^{16,27}

Although ten unique configurations with the highest entropy were identified in Figure 2, the atomic arrangement of only eight of these configurations is shown in Figure 3 because the atomic arrangement in configurations 88 and 89 under Ni_9Al_7 and configurations 25 and 26 under $Ni_{11}Al_5$ are very similar, for each respective $Ni_{1-x}Al_x$ bimetallic phase. It is observed in Figure 3 (a) – (h) that there is a tendency of like-atoms to form clusters. This clustering tendency leads to patterns of non-homogeneous mixtures within the unique configurations.

The expectation is that the combination of non-homogeneous bimetallic phases will form a non-homogeneous bimetallic precursor. This non-homogeneity agrees with previous observations in literature.²⁸ The non-homogeneity of the bimetallic phases could be further investigated by calculating the enthalpy of mixing of

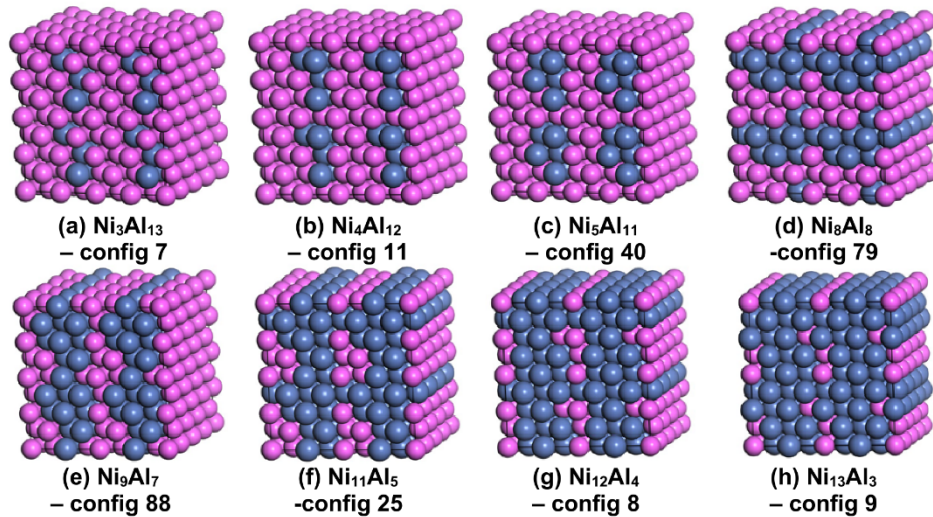


Figure 3: (a) – (h) The atomic structure of the unique configurations identified as most stable from entropy. (Al = magenta atoms and Ni = blue atoms.)

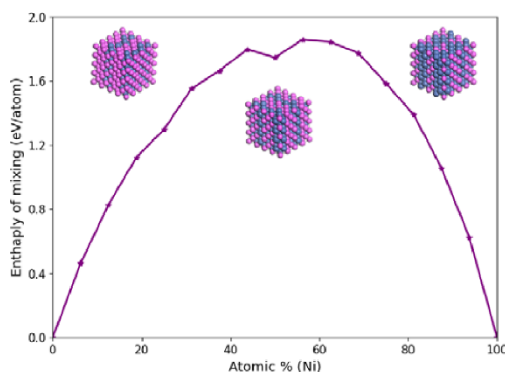


Figure 4: The enthalpy of mixing for $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases. The most stable configuration images of $\text{Ni}_5\text{Al}_{11}$, Ni_8Al_8 and $\text{Ni}_{11}\text{Al}_5$ are included

the bimetallic phases, as shown in equation (4). The enthalpy of mixing for the bimetallic phases is positive, as shown in Figure 4.

The positive enthalpy of mixing indicates that the bimetallic phases are chemically unmixed.^{27,29} Chemical unmixing refers to the segregation of Ni and Al. This segregation leads to the formation of short-to-medium range chemical and topological order or clustering.³⁰ This observation supports the clustering observed in Figure 3. However, in the case of the 1:1 atomic ratio (bimetallic phase Ni_8Al_8), a slight decrease in the enthalpy of mixing is observed. While all the configurations of ratios surrounding the 1:1 atomic ratio show non-homogeneity, the configuration corresponding to the 1:1 ratio show a slightly more homogenous atomic arrangement (see inclusions in Figure 4), leading to a lower enthalpy of mixing.

4. Conclusion

In this study, a full spectrum of $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases was built using SOD. From the results, it can be concluded that using SOD to build the $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases led to the identifications of configurations that include the Ni content (40% - 60%) and agree with the non-homogeneity of Raney nickel precursors that have been used successfully in previous experimental and computational studies of OER.^{14,19,28,29} Therefore, the SOD program provides a reliable spectrum of configurations that could be used for a more in-depth study of the influence of the precursor (containing various $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases) on the properties of Raney nickel. The next step in the study of Raney nickel will be to investigate the leaching of Al from the separate $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases or from a bimetallic precursor structure constructed by combining these $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phases.

Supplementary information

Supplementary Information could be found at <https://doi.org/10.25388/nwu.14626044>

Acknowledgements

The financial assistance of the North-West University (NWU) and the National Research Foundation (NRF), under grant UID 117978,

towards this research is hereby acknowledged. Opinions expressed and conclusions arrived at, are those of the authors and are not necessarily to be attributed to the NRF. Additionally, the authors would like to thank Jabus van den Berg for his technical support. This work was performed using the computational facilities of the Centre for High-Performance Computing (CHPC) of South Africa.

References

- Coyle D. E and Simmons A. R 2014 *Understanding the Global Energy Crisis*
- Demirbas A 2009 Global renewable energy projections *Energy Sources, Part B: Economics, Planning and Policy* **4** 212–24
- Dresselhaus M S and Thomas I L 2001 Alternative energy technologies *Nature* **414** 332–7
- Cheng Y and Jiang S P 2015 Advances in electrocatalysts for oxygen evolution reaction of water electrolysis-from metal oxides to carbon nanotubes *Progress in Natural Science: Materials International* **25** 545–53
- Doyle R L and Lyons M E G 2016 The oxygen evolution reaction: mechanistic concepts and catalyst design *Photoelectrochemical solar fuel production* (Springer) pp 41–104
- Santos D M F, Sequeira C A C and Figueiredo J L 2013 Hydrogen production by alkaline water electrolysis *Química Nova* **36** 1176–93
- Lyu F, Wang Q, Choi S M and Yin Y 2019 Noble-Metal-Free Electrocatalysts for Oxygen Evolution *Small* **15** 1804201
- Khan M A, Zhao H, Zou W, Chen Z, Cao W, Fang J, Xu J, Zhang L and Zhang J 2018 Recent progresses in electrocatalysts for water electrolysis *Electrochemical Energy Reviews* **1** 483–530
- Colli A N, Girault H H and Battistel A 2019 Non-precious electrodes for practical alkaline water electrolysis *Materials* **12** 1336
- Klein J C and Hercules D M 1981 Surface analysis of Raney nickel alloys *Analytical Chemistry* **53** 754–8
- Zeifert B, Blázquez J S, Moreno J G C and Calderón H A 2008 Raney-nickel catalysts produced by mechanical alloying *Reviews on Advanced Materials Science* **18** 633–9
- Tanaka S, Hirose N and Tanaki T 2000 Evaluation of Raney-nickel cathodes prepared with aluminum powder and tin powder *International Journal of Hydrogen Energy*
- Devred F, Gieske A H, Adkins N, Dahlborg U, Bao C M, Calvo-Dahlborg M, Bakker J W and Nieuwenhuys B E 2009 Influence of phase composition and particle size of atomised Ni-Al alloy samples on the catalytic performance of Raney-type nickel catalysts *Applied Catalysis A: General* **356** 154–61
- Schweizer S, Chaudret R, Low J and Subramanian L 2015 Molecular modeling and simulation of Raney Nickel: From alloy precursor to the final porous catalyst *Computational Materials Science* **99** 336–42
- Schweizer S, Chaudret R, Spyriouni T, Low J and Subramanian L 2016 Influence of the Precursor Composition and Reaction Conditions on Raney-Nickel Catalytic System *Foundations of Molecular Modeling and Simulation: Select Papers from FOMMS 2015* ed R Q Snurr, C S Adjiman and D A Kofke (Singapore: Springer Singapore) pp 125–35
- Divisek J, Mergel J and Schmitz H 1990 Advanced water electrolysis and catalyst stability under discontinuous operation *International Journal of Hydrogen Energy* **15** 105–14
- Raney M 1940 Catalysts from alloys: Nickel Catalysts *Industrial and Engineering Chemistry* **32** 1199–203
- Smith A J and Trimm D L 2005 The preparation of skeletal catalysts *Annual Review of Materials Research* **35** 127–42
- Barnard N C and Brown S G R 2007 Kinetic Monte Carlo modelling the leaching of Raney Ni-Al alloys *WIT Transactions on Engineering Sciences* vol 54 pp 53–62
- Barnard N C, Brown S G R, Devred F, Bakker J W, Nieuwenhuys B E and Adkins N J 2011 A quantitative investigation of the structure of Raney-Ni catalyst material using both computer simulation and experimental measurements *Journal of Catalysis* **281** 300–8
- Grau-Crespo R, Hamad S, Catlow C R A and de Leeuw N H 2007 Symmetry-adapted configurational modelling of fractional site occupancy in solids *Journal of Physics: Condensed Matter* **19** 256201
- Kimura Y, Qi Y, Cagin T and Goddard III W A 1998 *CALTECH ASCII TECHNICAL REPORT 003 The Quantum Sutton-Chen Many-Body Potential for Properties of fcc Metals*
- Gale J D and Rohl A L 2003 The general utility lattice program (GULP) *Molecular Simulation* **29** 291–341
- Anon Technical data for the element Nickel in the Periodic Table <https://periodictable.com/Elements/028/data.html> (accessed Oct 15, 2020)

25. Wang Q, Grau-Crespo R and de Leeuw N H 2011 Mixing thermodynamics of the calcite-structured (Mn,Ca)CO₃ solid solution: A computer simulation study *Journal of Physical Chemistry B* **115** 13854–61
26. Zhang Y 2019 *High-Entropy Materials* (Singapore: Springer Singapore)
27. Manzoor A, Pandey S, Chakraborty D, Phillpot S R and Aidhy D S 2018 Entropy contributions to phase stability in binary random solid solutions *npj Computational Materials* **4**
28. Lee G D, Suh C S, Park J H, Park S S and Hong S S 2005 Raney Ni catalysts derived from different alloy precursors (I) morphology and characterization *Korean Journal of Chemical Engineering* **22** 375–81
29. Fultz B 2010 Vibrational thermodynamics of materials *Progress in Materials Science* **55** 247–352
30. MA E 2005 Alloys created between immiscible elements *Progress in Materials Science* **50**

Appendix C Consent by the journal(s)

C.1 Permission for the use of Published manuscript (Chapter 4)

The following is the permission of use for the manuscript published from Chapter 4

Cherise Thesner

From: AJCD Manuscripts <submissions@ajcd.africa>
Sent: 14 September 2022 16:19
To: Cherise Thesner
Cc: Kobus Maree; Hannelie Diedericks; Joleta van Wyk
Subject: Re: Publication of article in dissertation

Dear Cherise Thesner

I trust you are well.

All articles published in this journal are licensed under the Creative Commons Attribution 4.0 International (CC BY 4.0) license, unless otherwise stated.

This therefore means the author is free to:

Share — copy and redistribute the material in any medium or format
I trust you are well.

Adapt — remix, transform, and build upon the material for any purpose, even commercially.

The licensor cannot revoke these freedoms as long as you follow the license terms.

Please ensure that when sharing or adapting the article it must be cited correctly to give credit to the original publication by using the How to cite this article" available on the first page of the publication.

I hope this answers your questions fully. If not do not hesitate to make.

Kind regards
Andrea Valentine

African Journal of Career Development (AJCD)

ajcd.africa | Follow on Twitter: @AJCDjournal | Receive email press releases and call for papers: Subscribe

Submission and Review Editorial Coordinator: Tracy McOwen, Telephone 514 | submissions@ajcd.africa

Finalisation and Publishing Production Coordinator: Suzanne Taylor, Telephone Ext: 505 | publishing@ajcd.africa

Compliment or complaint: Hannelie Diedericks, Telephone Ext: 502 | publishing@aosis.co.za

Tel: +27 21 975 2602 | Fax to email: 086 685 1577 | Fax: +27 21 975 4635

15 Oxford Street, Durbanville, Cape Town, 7550 | Get directions

Published by AOSIS (Pty) Ltd: www.aosis.co.za, [Facebook](#), [Twitter](#), [Google+](#), [LinkedIn](#), [YouTube](#), [SoundCloud](#), and [mailing list subscription](#)



This email adheres to the email disclaimer on www.aosis.co.za

Figure C-1 Permission granted through personal correspondence to publish manuscript (Chapter 4) in dissertation

C.2 Permission for the use of phase diagram (Figure 5-1)

The following is permission given for the use of Figure 5-1. The article is published on the MDPI space which has an open access policy.

MDPI Open Access Information and Policy

All articles published by MDPI are made immediately available worldwide under an open access license. This means:

- everyone has free and unlimited access to the full-text of *all* articles published in MDPI journals;
- everyone is free to re-use the published material if proper accreditation/citation of the original publication is given;
- open access publication is supported by the authors' institutes or research funding agencies by payment of a comparatively low **Article Processing Charge (APC)** for accepted articles.

Permissions

No special permission is required to reuse all or part of article published by MDPI, including figures and tables. For articles published under an open access Creative Common CC BY license, any part of the article may be reused without permission provided that the original article is clearly cited. Reuse of an article does not imply endorsement by the authors or MDPI.

Figure C-2 Open Access permission for the use of phase diagram in Figure 5-1. For full description the following link may be visited: <https://www.mdpi.com/about/openaccess>

Appendix D Additional work

D.1 SOD and GULP Guide

SOD and GULP Guide

Author:
Cherise Thesner

Contact:
23515074@nwu.ac.za
23515074.cj@gmail.com

Working Draft

Contents

1	Getting Started	1
1.1	Linux basics	1
1.1.1	Terminal commands	1
1.1.2	Aliases	2
1.1.3	For loops	3
1.1.4	Scripts	3
1.2	Using the MobaXterm for CHPC	5
1.2.1	CHPC login	5
1.2.2	Upload data	5
1.2.3	Rsync	5
2	Site-Occupancy Disorder (SOD)	7
2.1	SOD input	7
2.2	Steps	11
3	General Utility Lattice Program (GULP)	13
3.1	Steps	15
4	Statistical data	17
4.1	Steps	17
5	Final data from SOD and GULP	19

This guide is an evolving work. If any of the explanations or examples are unclear, or if there is anything you would like more information to be included in the guide feel free to contact the author. Any comments and suggestions are welcome to make this guide as useful as possible for future users and returning users.

1 Getting Started

The clusters that we use are Linux based, so unless your default machine is Linux based you need to install a virtual machine. I would suggest using MobaXterm, which can be downloaded at <https://mobaxterm.mobatek.net/download-home-edition.html>. When setting up MobaXterm, you will be asked to create a master password, **DO NOT LOSE THIS**.

1.1 Linux basics

If you are new to the Linux system, this section will give you some basics on how to navigate the the terminal which is a command line system. This section includes some basic commands, use of aliases, using loop in the command line and how to do scripting. If you already have knowledge of this feel free to skip to the next sections.

1.1.1 Terminal commands

Before jumping into how to setup and run SOD and GULP, there is need to know a few basic terminal commands to properly utilise the system, which is a command line system. These commands are reflected in the table below.

command	Description
ls	- Shows a list of everything in the current directory.
ll	- Similar to the ls command, but this shows the permissions for each object.
pwd	- It shows the full path of the current directory.
cd	- To change directory. • forward: cd /directory_name • Backward: cd ../
mkdir	- Creates a directory • mkdir directory_name
touch	- Creates an empty file. • touch filename • If file has a specific extension(ext) remember to include it in the filename.ext
vi	- This command lets you view a file and commands within this command allow you to edit the file. • vi filename • i - To start editing. • esc - Takes you out of editing mode. • :q - Lets you quit the file being viewed. • :wq! - Quits view and forces a save. (I personally recommend using this every time).
cp	- Copy command. Copy what where. • cp filename destination_directory

- `cp -r directory_name destination_directory` (if `-r` doesn't work just remove it, some versions seem to require it and others not)
 - You need to be in the source directory when you use this command.
 - This command can also be used when you need to create a similar file under a new name. `cp old_file new_file`
- `mv` - Move command. Move what where.
- `mv filename destination_directory`
 - `mv -r directory_name destination_directory` (if `-r` doesn't work just remove it, some versions seem to require it and others not)
 - You need to be in the source directory when you use this command.
 - This command can also be used when you need to rename a file. `mv old_filename new_filename`
- `rm` - Remove command.
- `rm filename`
 - `rm -r directory_name`
- `chmod 777` - Change mode. This is to make a file executable for all users and user groups
- `chmod 777 filename`

When you are using any of the actionable commands such as copy, move, remove and chmod and you would like to do this action for all objects in the current directory use `*` instead of the file or directory name.

1.1.2 Aliases

Another useful thing to know, is how to create an alias so that you don't need to have all your scripts in every directory where you need to use it. One thing I have noticed with aliases is that you can't call it in scripts.

Steps to creating an alias:

1. `vi .bashrc`
2. Press `I` to start editing
3. Type the following:

```
alias x=path (no spaces, alias x is the name of the alias and path is the path you want it to follow)
```

4. Press `esc` to stop editing
5. `:wq!`

A very useful alias to create is `qstat`, which is done in the following manner: `qstat="qstat -u chpc.username"`. This is how you will see the status of work submitted on the chpc cluster.

1.1.3 For loops

For loops are very useful tools when you have to repeat the same action for several objects. These can be done in line in the terminal or can be used in a script. Within this loop you can copy, move, make directories, etc. I will give a quick example of how an inline for loop would look.

Let's use the example of having to copy a file named **file1** to several directories named **f1**, **f2**, ... , **f10**. Simply type the following into the terminal and press enter:

```
for i in {1..10}; do cp file1 f$i; done
```

The **\$i** represents the space where the variable **i** is inserted. For loops can also be used for more complex processes, where you have loops within loops or multiple line loops. An example of a multiple line loop would be one where we would first have to create the directories before being able to copy the files into the directories:

```
for i in {1..10}; do mkdir f$i; cp file1 f$i; done
```

1.1.4 Scripts

Scripting is very useful when you need a series of tasks to be fulfilled. Here I will give one of my scripts as an example. This script (and several others like this one) was written to make the submission of the gulp script (which will be discussed in [chapter 3](#)).

Listing 1: Example of a script

```
1 #!/bin/bash
2 #part1_10
3
4 #script to make the submission of gulp-script to the chpc server
  automated
5 #Please note that if you are using it after using SOD you should
  execute it in th CALCS directory
6
7 mkdir GOUT
8 mkdir originalGIN
9
10 for i in {1..9}
11     do mkdir c0000$i
12         cp c0000$i.gin ./c0000$i
13         mv c0000$i.gin ./originalGIN
14         cp gulp-script_CHPC_PBS.sh ./c0000$i
15         cp sutton-chen_alloy.lib ./c0000$i
16         cd ./c0000$i
```

```

17     qsub gulp-script_CHPC_PBS.sh #Submits gulp script (
        Remember to use your script name if you use this
        example)
18         until [ -f gulp_done ] #The until loop will run
            until the bracket tests positive
19         do echo "Waiting on gulp-output..." #If the test
            is negative it will display the string while
            waiting
20         sleep 30s #Will make the loop wait 30s before
            testing again
21         done
22     cp gulp_output c0000$i.gout
23     mv c0000$i.gout ../GOUT
24     cd ../
25 done
26
27 #Please note that there is a new loop once you reach 10, this will
    be the same in cases of 100, 1000, ... . This is due to the
    way SOD names its output. Note that from 1 – 9 it was c0000$i,
    once you reach 10 it is c000$j and once you reach 100 it will
    be c00$k.
28 for j in 10
29     do mkdir c000$j
30     cp c000$j.gin ./c000$j
31     mv c000$j.gin ./originalGIN
32     cp gulp-script_CHPC_PBS.sh ./c000$j
33     cp sutton-chen_alloy.lib ./c000$j
34     cd ./c000$j
35     qsub gulp-script_CHPC_PBS.sh
36         until [ -f gulp_done ]
37         do echo "Waiting on gulp-output..."
38         sleep 30s
39         done
40     cp gulp_output c000$j.gout
41     mv c000$j.gout ../GOUT
42     cd ../
43 done

```

The first line is of significant importance, a script will not work without this. Note the different colors, they just show a few different components of the script. The green is for comments, blue is for functions, red signifies the begin and end of loops and magenta for strings.

1.2 Using the MobaXterm for CHPC

Before starting to work on the CHPC you need to register as a user (<https://users.chpc.ac.za/>) and take a look at the information on <http://wiki.chpc.ac.za/>. The following section will tell you how to login, upload your data and what the best way is to remove it from the cluster, all using the MobaXterm terminal.

1.2.1 CHPC login

When you open MobaXterm you need to start a local terminal and then from there you log into the CHPC cluster. To log into the CHPC cluster you will need to type in the following: `ssh -x username@lengau.chpc.ac.za`, after pressing enter you will be asked to enter your password (this is the password that you use when you sign into the chpc website: <https://users.chpc.ac.za/>), it will not show the characters as you type. MobaXterm will ask you if it should save your password, it just offers the convenience of not having to enter it each time you login.

Once you are logged in you will see your home directory on the lengau cluster. On the left side of the window you will see a physical representation of the file system (similar to Windows), at the bottom of the window is a checkbox that allows you to keep seeing the directory you are in on the left while navigating via the commands in [section 1.1](#).

1.2.2 Upload data

To upload your work to your home directory you simply drag and drop it into the left side file directory, like you would move them around on a windows machine. **Before doing calculations you need to copy your work to your lustre.** Once you are done with calculations and will not be running calculations for a while you need to clean out your lustre so as to not occupy unnecessary space on the cluster. Before removing your work from your lustre you need to download your data, the best way to do this is discussed in the next section.

1.2.3 Rsync

Rsync is a very useful tool to "download" your data from the cluster. Rsync lets you sync a remote directory to a local directory and will check for updates to all files and directories and only sync new and updated objects (for more information or a different tutorial do to <https://www.digitalocean.com/community/tutorials/how-to-use-rsync-to-sync-local-and-remote-directories-on-a-vps>).

Two very important things to note when you use rsync is 1) you need to be logged into the remote server (lengau cluster) you are pulling the data from and 2) you have to rsync from the local directory you want the data to be downloaded to.

Open two terminals in MobaXterm (it is convenient to have them both open side-by-side via the split option). In the first one you should login to the lengau cluster, in the second one you navigate to the directory where you want to sync you CHPC data. Once you are in the desired directory type the following (depending on which you are syncing, **syncing the lustre is NB!**):

Sync what	Code
lustre	<code>rsync -avz --progress username@scp.chpc.ac.za:lustre/* .</code>
home	<code>rsync -avz --progress username@scp.chpc.ac.za:* .</code>

Please note that the `.` at the end of each line is crucial to the code and not a full stop. And as mentioned in [section 1.1.1](#) the `*` is to select all objects in the current directory. Once the sync is complete you can remove the objects from your lustre, be on the safe side and check that the download was successful, then remove each object **individually**.

2 Site-Occupancy Disorder (SOD)

The Site-Occupancy Disorder (SOD) program is one that builds mixtures. These mixtures are built via substitution of atoms in an existing roster at all possible available positions and then determines the uniqueness of each substitution. To get the latest version of SOD, go to <https://github.com/gcmt-group/sod> and download the entire directory. Here you will find all the necessary scripts and files to run SOD. The authors of SOD would also like the user to reference the article "*Symmetry-adapted configurational modelling of fractional site occupancy in solids*" for the use of SOD, it can be found at <http://iopscience.iop.org/article/10.1088/0953-8984/19/25/256201/meta>

Consider a roster of 9 Ni atoms into which we substitute 2 Al atoms as an illustration what SOD does, do not take values as accurate (Visually shown in Figure 1).

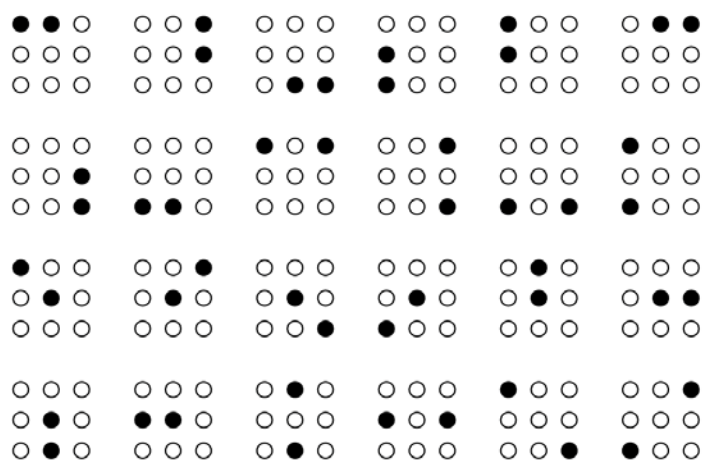


Figure 1: Visual representation of a 9 Ni atom roster with substitutions of 2 Al atoms at different positions.

The unfilled circles represent the Ni atoms and the filled circles represent the Al atoms. As you can see that there is a total of 24 different configurations with this substitution, but only 6 unique configurations. The uniqueness is determined using symmetry operators, so these configurations will be rotated and reflected across diagonals and perpendicular lines and then be compared with one another. This is what SOD does for you.

2.1 SOD input

To use SOD you need top.gulp, INSOD, bottom.gulp and SGO files. The top.gulp and bottom.gulp is used to write the file to completion after running SOD, so that your input for

the General Utility Lattice Program (GULP) is ready for use. The INSOD file is the input that SOD needs to build the structures.

The following three are examples of how the files used should look, feel free to copy and edit them to suit your research.

Listing 2: Example of top.gulp (From sod4.0 example 01-perovskite-gulp)

```

1 #
2 # Keywords:
3 #
4 opti comp
5 #
6 # Options:
7 #
8 title
9 Al/Fe substitutions in LaFeO3 perovskite
10 end
11 cell

```

Please edit the title to suit your research, in both the top.gulp and INSOD.

Listing 3: Example of INSOD (From sod4.0 example 01-perovskite-gulp)

```

1 # Title
2 Al/Fe substitutions in LaFeO3 perovskite
3
4 # a,b,c,alpha,beta,gamma
5 3.7 3.7 3.7 90.000 90.000 90.000
6
7 # nsp: Number of species in the parent structure
8 3
9
10 # symbol(1:nsp): Atom symbols
11 La Fe O
12
13 # natsp0(1:nsp): Number of atoms for each species in the
    assymetric unit
14 1 1 1
15
16 # coords0(1:nat0,1:3): Coordinates of each atom (one line per atom
    )
17 0.0 0.0 0.0
18 0.5 0.5 0.5
19 0.5 0.5 0.0
20

```

```

21 # na,nb,nc (supercell definition)
22 2 2 2
23
24 # sptarget: Species to be substituted
25 1
26
27 # nsubs: Number of substitutions in the supercell
28 4
29
30 # newsymbol(1:2): Symbol of atom to be inserted in the selected
    position ,
31 #           symbol to be inserted in the rest of the
    positions for the same species.
32 Al Fe
33
34 # FILER, MAPPER
35 # FILER: 0 (no calc files generated), 1 (GULP), 2 (METADISE), 11
    (VASP)
36 # MAPPER: 0 (no mapping, use current structure), >0 (map to
    structure in MAPTO file)
37 # (each position in old structure is mapped to MAPPER positions in
    new structure)
38 0 0
39
40 # If FILER=1 then:
41 # ishell(1:nsp) 0 core only / 1 core and shell (for the species
    listed in symbol(1:nsp))
42 1 1 1 1
43 # newshell(1:2) 0 core only / 1 core and shell (for the species
    listed in newsymbol(1:2))
44 1 1

```

Note that SOD is written in a language which is very rigid, please keep the spaces and empty lines the same as the given example (Listing 3) and information table below.

You can find your elemental information needed at <https://periodictable.com/> (choose your element and select technical data at the top of the page). Important information for the execution of SOD and GULP programs are the lattice parameters, lattice angles and what the space group number is.

Note : In the INSOD you need to give the lattice parameters in Å, the above mentioned website gives it in pm.

The following table will give some insight as to how INSOD is laid out.

Line number	Script heading	Description
1	Title	What are you doing in this script
4	a,b,c,alpha,beta,gamma	What is the initial structures spacial properties (lattice paraneters and angles). Double spacing bewteen values
7	nsp: Number of species in the parent structure	How many elements are contained in the initial structure
10	symbol(1:nsp): Atom symbols	Elemental symbols of initial structure, with a space between each element. Single spacing bewteen values
13	natsp0(1:nsp): Number of atoms for each species in the assymetric unit	Number of atoms in the assymetric unit, order of the numbers corresponding to the order of the a elements in line 11. Single spacing between values
16	coords0(1:nat0,1:3): Coordinates of each atom (one line per atom)	The 3D spacial coordinates of the atoms in the asymmetric unit. Each line contains the information for only one atom, the order of the lines corresponds to the order of the elements in line 11. Double spacing bewteen values
21	na,nb,nc (supercell definition)	Specify size of the suppercell. Single spacing bewteen values
24	sptarget: Species to be substituted	How many elements are to be substituted. Single spacing bewteen values
27	nsubs: Number of substitutions in the supercell	How many of the target specie atoms should be substituted.
30 - 31	newsymbol(1:2): Symbol of atom to be inserted in the selected position, symbol to be inserted in the rest of the positions for the same species.	The atom which is added via the substitution is added first and the atom which is being removed removed via the substitution is added last. Single spacing bewteen values

```

34 - 37  FILER, MAPPER
        FILER: 0 (no calc files generated), 1
        (GULP), 2 (METADISE), 11 (VASP)
        MAPPER: 0 (no mapping, use cur-
        rect structure), >0 (map to structure
        in MAPTO file)
        (each position in old structure is
        mapped to MAPPER positions in
        new structure)

40 - 41  If FILER=1 then:
        ishell(1:nsp) 0 core only / 1 core and
        shell (for the species listed in sym-
        bol(1:nsp))

43       newshell(1:2) 0 core only / 1 core and
        shell (for the species listed in newsym-
        bol(1:2))

```

Listing 4: Example of bottom.gulp (Adapted from sod4.0 example 01-perovskite-gulp)

```

1 species      4
2 Fe      core      0.000000
3 Al      core      0.000000
4 La      core      0.000000
5 O       core      0.000000
6
7 library sutton-chen_alloy.lib

```

Please edit the species number and elements to suit your research. If your specific element is not contained within the sutton-chen_alloy.lib file, you need to find an alloy library containing your elements.

2.2 Steps

The steps for each section is given separately, but for convenience sake read through them all before setting up your upload directories. In some cases you need to add files to the existing directories, so doing it before upload is more convenient.

1. First make sure that you have everything ready for upload to your CHPC space.
 - (a) Create a directory called ROOTSOD and copy the downloaded sod directory to this.

- (b) Create your project directories (a separate directory for each combination) containing the correct information for SOD, i.e. top.gulp, bottom.gulp, INSOD and SGO. In the case that you do not have the SGO, you can find it in the downloaded SOD directory under sgo. You then need to copy this data into an empty file named SGO without any extension.
2. These directories can now be uploaded to your CHPC space via the [MobaXterm terminal](#). For log in instructions refer back to [section 1.2.1](#).
3. Once the upload is done, you need to set your executables path, this is done the same as setting up aliases.
 - In the terminal type : `vi .bashrc`
 - Press **I** to start insert and type the following under all other text :
 - `# executable paths`
 - `export PATH=$PATH:/home/username/ROOTSOD/bin`
 - Press `esc` to exist insert mode
 - type `:wq!` and enter, to force a save on exit.
4. Now you need to make all the scripts executable, navigate to ROOTSOD directory and run command **make all**.
5. Now copy the project directories to your lustre (`cp -r ./DIRECTORY_NAME ./lustre`)
6. In each project directory, containing top.gulp, bottom.gulp, INSOD and SGO, run **sod_comb.sh** to build the combination.

Now you have the input needed for GULP.

3 General Utility Lattice Program (GULP)

GULP is an optimisation program, it does geometric optimisations using atomic force-fields and calculates the bulk energies. For more information on the inner workings of GULP you can go to the following link: <http://gulp.curtin.edu.au/gulp/>. The submission script looks as follows :

Listing 5: Example of gulp_script.sh

```
1 #!/ bin/bash --login
2 #PBS -l select=1:ncpus=1:mpiprocs=1:nodetype=haswell_reg
3 #PBS -P CHEM0778
4 #PBS -q test
5 #PBS -l walltime=1:00:00
6 #PBS -m abe
7 #PBS -M your_email
8 #PBS -N GULPtest
9 #PBS -l place=exel
10 #PBS -e /mnt/lustre/users/your_username/LOG/test1.out
11 #PBS -o /mnt/lustre/users/your_username/LOG/test1.err
12
13 # load the vasp module, it loads required compiler, mpi and mkl
   libraries
14   module purge
15   module load chpc/parallel_studio_xe/19.0.4.243/2019.4.070
16   module load chpc/gulp/5.2/parallel_studio/19.0.4.243/2019.4.070
17
18 # submit job from example VASP directory - change for your system
19 MYPATH=$PBS_O_WORKDIR
20 NNODES=$PBS_NUM_NODES
21 NCPUS='cat ${PBS_NODEFILE} | wc -l'
22 PPN='uniq -c ${PBS_NODEFILE} | awk '{print $1}' | uniq'
23
24
25
26 # directory to run the job using /scratch/$USER
27 WDPATH=/mnt/lustre/users/$USER/$SPBS_JOBID
28 #rm -rf ${WDPATH} ; mkdir -p ${WDPATH}
29 pushd ${MYPATH}
30   echo Running on host 'hostname'
31   echo Time is 'date'
32   echo Directory is 'pwd'
33   echo PBS job ID is $PBS_JOBID
34   echo This jobs runs on the following machine: 'echo
     $PBS_NODEFILE | uniq'
35   cat $PBS_NODEFILE
```

```

36     echo Nuber of Processing Elements is $NCPUS
37     echo Number of mpirprocs per node is $PPN
38     #env
39     #cd ${WDPATH}
40
41     # copy input data sets to work area
42     #cp $MYPATH/* .
43
44     # Run the parallel program and once finished copy required files
45     # and delete the unnecessary ones
46     echo GULP Start Time is `date` running NCPUs=$NCPUS
47     start="$(date +%s)"
48     time mpirun -np 1 gulp < *.gin > gulp-output
49
50     touch gulp_done #Once script is done running it will create an
51     # empty file named gulp_done as an indication for an outside
52     # script to continue (for personal use, not incremental to the
53     # working of this script).
54     # Copy output data to home
55     #mv ${WDPATH}/* ${MYPATH}/
56     #rm -rf ${WDPATH}
57
58     # Record Total time for the job
59     stop="$(date +%s)"
60     finish=$(( $stop-$start ))
61     echo GULP $PBS_JOBID Job-Time $finish seconds
62 popd

```

Please change the following data in the script ([Listing 5](#)) before use:

Line number	Script heading	Description
7	PBS -M your_email	Replace your_email with your preferred email address. You will receive 3 emails per submission.
10	PBS -e /mnt/lustre/users/your_username/LOG/test1.out	Replace your_username with the username the CHPC had provided for you. This is an output log.
11	PBS -o /mnt/lustre/users/your_username/LOG/test1.err	Replace your_username with the username the CHPC had provided for you. This is an error log.

3.1 Steps

These are the steps followed for the execution of GULP.

1. Set up your gulp-script. **Note : Need to add your email in the script and your username.**
2. You will need to make this script executable and copy it to the CALCS directory that is created after running SOD.
3. To run the gulp script you need the following files in the CALCS directory
 - gulp_script.sh (copy [Listing 5](#) and edit the necessary information)
 - sutton-chen_alloy.lib (This contains information needed about the elements you use)
4. Within the CALCS directory, do the following (Let's say SOD gave 5 configurations called c00001.gin - c00005.gin):
 - mkdir originalGin
 - mkdir GOUT
 - for i in {1..5}; do mkdir c0000\$i; cp c0000\$i.gin ./c0000\$i; mv c0000\$i.gin ./originalGin; done
 - Now copy all necessary files into the newly created configuration directories:

for i in {1..5}; do cp sutton-chen_alloy.lib ./c0000\$i; cp gulp-script.sh ./c0000\$i; done
5. Now you can navigate to each configuration directory and run gulp :

qsub gulp-script.sh

and check the status by typing **qstat -u username** or just qstat if you have aliased this.

6. Once the script has completed running (see if the file gulp_done has been created) do the following :
 - cp gulp_output c0000X.gout (X being the configuration number you are busy with)
 - mv c0000X.gout ../GOUT

Doing all this by hand takes a while, but you can automate it up to a certain step by using a script like [Listing 1](#). This script does everything you do within the CALCS.

If this is the first time using GULP on the CHPC: Check the email address that you input into the script, if the email contains the following:

```
root <helpdesk@chpc.ac.za>

PBS Job Id: 2643737.sched01
Job Name: GULPtest
Execution terminated
Exit_status=0
resources_used.cpus=1
resources_used.mem=0kb
resources_used.ncpus=1
resources_used.vmem=0kb
resources_used.walltime=00:00:01
```

You will need to email the LAMM Group's contact person at the CHPC to request yourself being added to the ACCELRYG group since this could be a permission error.

4 Statistical data

These statistic scripts will give you the statistics data and probabilities data that you will need to analyse the bulks that have been built with SOD and optimized with GULP. Follow the steps once the gulp submissions for a combination is complete.

4.1 Steps

These steps are all followed within the GOUT directory.

1. Run the script : `sod_gulp.ener.sh`
2. Run the script : `sod_gulp.cell.sh`
3. `cp ENERGIES ../`
4. `cp cell.dat DATA`
5. Need to edit DATA :
 - Open DATA with vi DATA
 - Add the number of columns at the top
 - esc and then :wq!

Listing 6: Example of DATA before adding number of cols

1	7.119707	7.119708	3.549339	90.000000
	90.000000	90.000000	179.916805	

Listing 7: Example of DATA after adding number of cols

1	7			
2	7.119707	7.119708	3.549339	90.000000
	90.000000	90.000000	179.916805	

These listings are wrapping the columns, but the originals aren't wrapped.

6. `cp DATA ../`

For the stats calculations:

1. Navigate back to CALCS and make sure all the necessary files are now present.
 - TEMPERATURES (A file containing the temperatures used in the study, can be from 0.1K - 1200K, see [Listing 8](#))

Listing 8: Example of TEMPERATURES

```
1 0.1
2 100
3 200
4 300
5 400
6 500
7 600
8 700
9 800
10 900
11 1000
12 1100
13 1200
```

- ENERGIES
- DATA
- OUTSOD (output from SOD)

2. Run the script `sod_stat.sh`.

The data you need for further analysis will be the `statistics.dat` and the `probabilities.dat`.

5 Final data from SOD and GULP

All the data can now be downloaded by running Rsync as shown in [section 1.2.3](#).

Once all the data is downloaded, further data manipulation can be done. It will be the easiest to do with Microsoft Excel. The data to be used for further calculations are those in the probabilities.dat and statistics.dat files within the CALCS directory. Examples of these data output can be seen in [listing 9](#) and [listing 10](#). For ease of data import use the following steps:

1. Open probabilities.dat file with notepad++
2. Make all column separations only one space. This can be done by double clicking on the larger space and opening the "Find" function (CTRL+F), then navigate to the "Replace" tab, finally add a single space within the "Replace with" space.
3. Now in the same manner replace the single spaces with a ","
4. Once this is done save the document as a .csv file. If it is not given under file types select "All types" and type in .csv after the file name before saving.
5. The .csv file can now be opened with Microsoft excel.

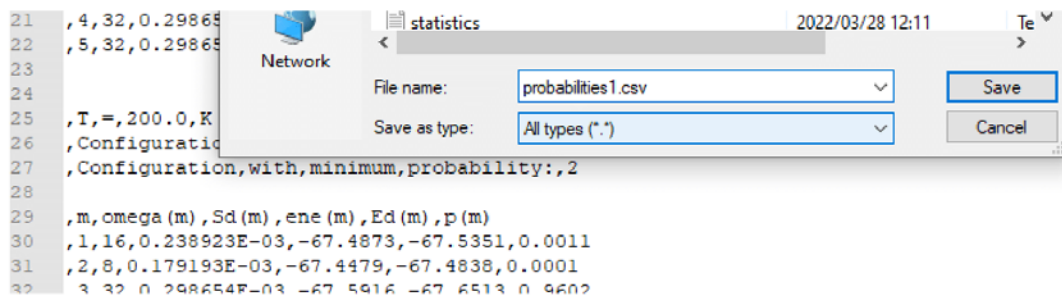


Figure 2: Save file as .csv

[Listing 9](#) shows the layout of the probability data. For each temperature defined in [Chapter 4](#) a data set as shown is produced. For each temperature the most and least probable configuration is identified. The variable descriptions are given in the [table 4](#).

Listing 9: Example of probabilities.dat data

```

1 T =      0.1 K
2 Configuration with maximum probability:      3
3 Configuration with minimum probability:      2
4
```

5	m	omega(m)	Sd(m)	ene(m)	Ed(m)	p(m)
6	1	16	0.238923E-03	-67.4873	-67.4873	0.0000
7	2	8	0.179193E-03	-67.4479	-67.4480	0.0000
8	3	32	0.298654E-03	-67.5916	-67.5916	1.0000
9	4	32	0.298654E-03	-67.4691	-67.4692	0.0000
10	5	32	0.298654E-03	-67.5359	-67.5359	0.0000
11						
12	T = 100.0 K					
13	Configuration with maximum probability:					3
14	Configuration with minimum probability:					2
15						
16	m	omega(m)	Sd(m)	ene(m)	Ed(m)	p(m)
17	1	16	0.238923E-03	-67.4873	-67.5112	0.0000
18	2	8	0.179193E-03	-67.4479	-67.4659	0.0000
19	3	32	0.298654E-03	-67.5916	-67.6215	0.9984
20	4	32	0.298654E-03	-67.4691	-67.4990	0.0000
21	5	32	0.298654E-03	-67.5359	-67.5657	0.0016
22						
23	T = 200.0 K					
24	Configuration with maximum probability:					3
25	Configuration with minimum probability:					2
26						
27	m	omega(m)	Sd(m)	ene(m)	Ed(m)	p(m)
28	1	16	0.238923E-03	-67.4873	-67.5351	0.0011
29	2	8	0.179193E-03	-67.4479	-67.4838	0.0001
30	3	32	0.298654E-03	-67.5916	-67.6513	0.9602
31	4	32	0.298654E-03	-67.4691	-67.5289	0.0008
32	5	32	0.298654E-03	-67.5359	-67.5956	0.0378
33						
34						
35						
36						

Table 4: Variable/Data description of probability data.

Heading	Symbol	Name	Description	Formula
m	m	Independent configuration number	n/a	n/a
omega(m)	Ω_m	Degeneracy of configuration m	How many times a given independent configuration appears within the full configuration space	n/a

Sd(m)	$S_{d(m)}$	Degeneracy entropy	n/a	$S_{d(m)} = k \ln(\Omega_m)$
ene(m)	E_m	Energy of configuration	Calculated from DFT or forcefields	n/a
Ed(m)	$E_{d(m)}$	"Reduced energy" of configuration	Characterises the probability of the occurrence. The lower the energy, the higher the degeneracy, the more likely the configuration appears.	$E_{d(m)} = E_m - (T)(S_{d(m)})$
p(m)	p_m	Probability	n/a	$p_m = \Omega_m^{(-E_m/kT)/Z}$

listing 10 shows the layout of the statistical data. For each temperature defined in [Chapter 4](#) a data set as shown is produced. In this data set the variables are as follows: T - Temperature, H - Enthalpy, G - Gibbs free energy, S - Entropy and the average values of data represent the lattice parameters (a,b,c) and lattice angles (α, β, γ).

Listing 10: Example of statistics.dat data

	T	H	G	S	average values of DATA		
1	0.1	-67.5916	-67.5916	0.298654E-03	7.2090	7.1878	3.5767
2		90.0000	90.0000	90.0000	185.3317		
3	100.0	-67.5915	-67.6215	0.299657E-03	7.2090	7.1878	3.5767
4		90.0000	90.0000	90.0005	185.3318		
5	200.0	-67.5893	-67.6520	0.313816E-03	7.2087	7.1883	3.5766
6		90.0000	90.0000	90.0118	185.3331		
7				.			
				.			
				.			

This listing is wrapping the columns, but the originals isn't wrapped.

Appendix E Final fractional coordinates for pure Ni and Al structures

E.1 Fractional coordinates for pure Ni and Al bulk structures

Table E-1 and Table E-2 contain the fractional coordinates of the final pure Ni and Al bulk structures, post geometrical optimisations for the 9×9×9 k-point grid.

Table E-1 Final fractional coordinates for the optimised pure Ni bulk structure

Ni bulk final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Ni	1	0.000000	0.000000	0.000000
Ni	2	0.000000	0.250000	0.250000
Ni	3	0.250000	0.000000	0.250000
Ni	4	0.250000	0.250000	0.000000
Ni	5	0.500000	0.000000	0.000000
Ni	6	0.500000	0.249999	0.250000
Ni	7	0.750000	0.000000	0.250000
Ni	8	0.750000	0.249999	0.000000
Ni	9	0.000000	0.500000	0.000000
Ni	10	0.000000	0.750000	0.250000
Ni	11	0.250000	0.500000	0.250000
Ni	12	0.250000	0.750000	0.000000
Ni	13	0.500000	0.500000	0.000000
Ni	14	0.500000	0.750001	0.250000
Ni	15	0.750000	0.500000	0.250000
Ni	16	0.750000	0.750001	0.000000
Ni	17	0.000000	0.000000	0.500000
Ni	18	0.000000	0.250000	0.750000
Ni	19	0.250000	0.000000	0.750000
Ni	20	0.250000	0.250000	0.500000
Ni	21	0.500000	0.000000	0.500000
Ni	22	0.500000	0.250000	0.750000
Ni	23	0.750000	0.000000	0.750000
Ni	24	0.750000	0.250000	0.500000
Ni	25	0.000000	0.500000	0.500000
Ni	26	0.000000	0.750000	0.750000
Ni	27	0.250000	0.500000	0.750000
Ni	28	0.250000	0.750000	0.500000
Ni	29	0.500000	0.500000	0.500000
Ni	30	0.500000	0.750000	0.750000
Ni	31	0.750000	0.500000	0.750000
Ni	32	0.750000	0.750000	0.500000

Table E-2 Final fractional coordinates for the optimised pure Al bulk structure

Al bulk final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.000000	0.000000	0.000000
Al	2	0.000000	0.250000	0.250000
Al	3	0.250000	0.000000	0.250000
Al	4	0.250000	0.250000	0.000000
Al	5	0.500000	0.000000	0.000000
Al	6	0.500000	0.250000	0.250000
Al	7	0.750000	0.000000	0.250000
Al	8	0.750000	0.250000	0.000000
Al	9	0.000000	0.500000	0.000000
Al	10	0.000000	0.750000	0.250000
Al	11	0.250000	0.500000	0.250000
Al	12	0.250000	0.750000	0.000000
Al	13	0.500000	0.500000	0.000000
Al	14	0.500000	0.750000	0.250000
Al	15	0.750000	0.500000	0.250000
Al	16	0.750000	0.750000	0.000000
Al	17	0.000000	0.000000	0.500000
Al	18	0.000000	0.250000	0.750000
Al	19	0.250000	0.000000	0.750000
Al	20	0.250000	0.250000	0.500000
Al	21	0.500000	0.000000	0.500000
Al	22	0.500000	0.250000	0.750000
Al	23	0.750000	0.000000	0.750000
Al	24	0.750000	0.250000	0.500000
Al	25	0.000000	0.500000	0.500000
Al	26	0.000000	0.750000	0.750000
Al	27	0.250000	0.500000	0.750000
Al	28	0.250000	0.750000	0.500000
Al	29	0.500000	0.500000	0.500000
Al	30	0.500000	0.750000	0.750000
Al	31	0.750000	0.500000	0.750000
Al	32	0.750000	0.750000	0.500000

E.2 Fractional coordinates for pure Ni (111) and Al (111) surface slab structures

Table E-3 and Table E-4 contain the fractional coordinates of the final pure Ni (111) and Al (111) surface slab structures, post geometrical optimisations for the 9×9×1 k-point grid.

Table E-3 Final fractional coordinates for the optimised pure Ni (111) surface slab structure

Ni (111) surface slab final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Ni	1	0.666668	0.666665	0.094655
Ni	2	0.333335	0.333331	0.285919
Ni	3	0.833335	0.083331	-0.001407
Ni	4	0.500001	0.749998	0.189859
Ni	5	0.083335	0.833331	-0.001407
Ni	6	0.750001	0.499998	0.189859
Ni	7	0.083335	0.083331	-0.001406
Ni	8	0.750001	0.749998	0.189859
Ni	9	0.333335	0.833331	-0.001407
Ni	10	0.000001	0.499998	0.189860
Ni	11	0.166668	0.916665	0.094656
Ni	12	0.833334	0.583332	0.285919
Ni	13	0.416668	0.666665	0.094655
Ni	14	0.083335	0.333331	0.285919
Ni	15	0.416668	0.916665	0.094656
Ni	16	0.083334	0.583332	0.285918
Ni	17	0.833335	0.333331	-0.001407
Ni	18	0.500001	0.999998	0.189859
Ni	19	0.666668	0.416664	0.094655
Ni	20	0.333334	0.083332	0.285919
Ni	21	0.916668	0.166665	0.094656
Ni	22	0.583334	0.833332	0.285919
Ni	23	0.916668	0.416664	0.094656
Ni	24	0.583334	0.083332	0.285918
Ni	25	0.166668	0.166664	0.094655
Ni	26	0.833334	0.833332	0.285919
Ni	27	0.333335	0.583331	-0.001407
Ni	28	0.000001	0.249998	0.189859
Ni	29	0.583335	0.333331	-0.001407
Ni	30	0.250002	0.999998	0.189859
Ni	31	0.583335	0.583331	-0.001407
Ni	32	0.250002	0.249998	0.189859
Ni	33	0.833335	0.833331	-0.001407
Ni	34	0.500002	0.499998	0.189859
Ni	35	0.666668	0.916665	0.094655
Ni	36	0.333335	0.583331	0.285919
Ni	37	0.916668	0.666665	0.094655
Ni	38	0.583334	0.333332	0.285919

Ni	39	0.916668	0.916665	0.094656
Ni	40	0.583334	0.583331	0.285919
Ni	41	0.166669	0.666665	0.094655
Ni	42	0.833334	0.333332	0.285919
Ni	43	0.333335	0.083331	-0.001407
Ni	44	0.000002	0.749998	0.189860
Ni	45	0.583335	0.833331	-0.001407
Ni	46	0.250002	0.499998	0.189859
Ni	47	0.583335	0.083331	-0.001406
Ni	48	0.250001	0.749998	0.189859
Ni	49	0.666668	0.166665	0.094655
Ni	50	0.333334	0.833332	0.285919
Ni	51	0.833335	0.583331	-0.001407
Ni	52	0.500002	0.249998	0.189859
Ni	53	0.083335	0.333331	-0.001407
Ni	54	0.750001	0.999999	0.189859
Ni	55	0.083335	0.583331	-0.001407
Ni	56	0.750001	0.249998	0.189859
Ni	57	0.333335	0.333331	-0.001407
Ni	58	0.000001	0.999999	0.189859
Ni	59	0.166668	0.416665	0.094655
Ni	60	0.833335	0.083331	0.285919
Ni	61	0.416668	0.166664	0.094655
Ni	62	0.083334	0.833332	0.285919
Ni	63	0.416668	0.416665	0.094655
Ni	64	0.083335	0.083331	0.285918

Table E-4 Final fractional coordinates for the optimised pure Al (111) surface slab structure

Al (111) surface slab final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.666668	0.666665	0.103265
Al	2	0.333335	0.333332	0.317377
Al	3	0.833335	0.083332	-0.005370
Al	4	0.500001	0.749999	0.208721
Al	5	0.083334	0.833332	-0.005370
Al	6	0.750001	0.499999	0.208721
Al	7	0.083334	0.083332	-0.005370
Al	8	0.750001	0.749999	0.208721
Al	9	0.333334	0.833332	-0.005370
Al	10	0.000001	0.499999	0.208721
Al	11	0.166668	0.916665	0.103265
Al	12	0.833334	0.583332	0.317377
Al	13	0.416667	0.666665	0.103265
Al	14	0.083335	0.333332	0.317377
Al	15	0.416667	0.916665	0.103264
Al	16	0.083334	0.583332	0.317377

AI	17	0.833334	0.333332	-0.005370
AI	18	0.500001	0.999999	0.208721
AI	19	0.666668	0.416665	0.103265
AI	20	0.333335	0.083332	0.317377
AI	21	0.916668	0.166666	0.103265
AI	22	0.583334	0.833332	0.317377
AI	23	0.916668	0.416666	0.103265
AI	24	0.583334	0.083332	0.317377
AI	25	0.166667	0.166666	0.103265
AI	26	0.833334	0.833332	0.317377
AI	27	0.333334	0.583332	-0.005370
AI	28	0.000001	0.249999	0.208721
AI	29	0.583335	0.333332	-0.005370
AI	30	0.250001	0.999999	0.208721
AI	31	0.583335	0.583332	-0.005370
AI	32	0.250001	0.249999	0.208721
AI	33	0.833335	0.833332	-0.005370
AI	34	0.500001	0.499999	0.208721
AI	35	0.666668	0.916665	0.103264
AI	36	0.333334	0.583332	0.317377
AI	37	0.916668	0.666665	0.103265
AI	38	0.583334	0.333332	0.317377
AI	39	0.916668	0.916665	0.103265
AI	40	0.583334	0.583332	0.317377
AI	41	0.166668	0.666666	0.103265
AI	42	0.833334	0.333332	0.317377
AI	43	0.333334	0.083332	-0.005370
AI	44	0.000001	0.749999	0.208721
AI	45	0.583334	0.833332	-0.005370
AI	46	0.250001	0.499999	0.208721
AI	47	0.583334	0.083332	-0.005370
AI	48	0.250001	0.749999	0.208721
AI	49	0.666668	0.166666	0.103265
AI	50	0.333335	0.833332	0.317377
AI	51	0.833335	0.583332	-0.005370
AI	52	0.500001	0.249999	0.208721
AI	53	0.083334	0.333332	-0.005370
AI	54	0.750001	0.999999	0.208721
AI	55	0.083334	0.583332	-0.005370
AI	56	0.750001	0.249999	0.208721
AI	57	0.333334	0.333332	-0.005370
AI	58	0.000001	0.999999	0.208721
AI	59	0.166667	0.416666	0.103265
AI	60	0.833334	0.083332	0.317377
AI	61	0.416667	0.166666	0.103264
AI	62	0.083335	0.833332	0.317377
AI	63	0.416667	0.416666	0.103265
AI	64	0.083334	0.083332	0.317377

Appendix F Final fractional coordinates for $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase structures

Table F-1 to Table F-20 contain the fractional coordinates of the final $\text{Ni}_{(1-x)}\text{Al}_x$ bimetallic phase bulks and corresponding (111) surface slabs post geometrical optimisations, as identified in Chapter 5.

F.1 Fractional coordinates for $\text{Ni}_3\text{Al}_{13}$ bulk and (111) surface slab structures

Table F-1 Final fractional coordinates for the optimised $\text{Ni}_3\text{Al}_{13}$ bulk structure

$\text{Ni}_3\text{Al}_{13}$ bulk structure final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	-0.007232	0.001737	0.000000
Al	2	-0.025061	0.493396	0.000000
Al	3	0.504631	-0.000502	0.000000
Al	4	0.522054	0.498379	0.000000
Al	5	-0.025595	0.258606	0.249845
Al	6	-0.007447	0.742804	0.249986
Al	7	0.525181	0.260263	0.250077
Al	8	0.255545	-0.001359	0.249906
Al	9	0.260083	0.502914	0.249876
Al	10	0.744493	-0.002109	0.249953
Al	11	0.252018	0.255336	0.000000
Al	12	0.262734	0.745065	0.000000
Al	13	0.738604	0.744263	0.000000
Al	14	-0.007250	0.001865	0.500000
Al	15	-0.025128	0.493186	0.500000
Al	16	0.504529	-0.000666	0.500000
Al	17	0.522092	0.498429	0.500000
Al	18	-0.025595	0.258606	0.750155
Al	19	-0.007447	0.742804	0.750014
Al	20	0.525181	0.260263	0.749923
Al	21	0.255545	-0.001359	0.750094
Al	22	0.260083	0.502914	0.750124
Al	23	0.744493	-0.002109	0.750047
Al	24	0.251950	0.255445	0.500000
Al	25	0.262558	0.744920	0.500000
Al	26	0.738776	0.744157	0.500000
Ni	1	0.503906	0.756775	0.250050
Ni	2	0.751804	0.507629	0.250010
Ni	3	0.744375	0.237011	0.000000
Ni	4	0.503906	0.756776	0.749950
Ni	5	0.751804	0.507629	0.749990
Ni	6	0.744412	0.236932	0.500000

Table F-2 Final fractional coordinates for the optimised Ni₃Al₁₃ (111) surface slab structure

Ni ₃ Al ₁₃ (111) surface slab structure final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.300792	0.303135	0.103238
Al	2	0.623301	0.643252	0.307828
Al	3	0.637771	0.140155	0.002152
Al	4	0.960916	0.467772	0.200756
Al	5	0.140920	0.141836	0.003349
Al	6	0.468947	0.475485	0.207099
Al	7	0.814528	0.319608	0.108891
Al	8	0.125524	0.679206	0.316784
Al	9	0.201058	0.220452	0.203613
Al	10	0.878151	0.883857	-0.000294
Al	11	0.553352	0.053377	0.105358
Al	12	0.882538	0.388032	0.309481
Al	13	0.055856	0.074334	0.115186
Al	14	0.373671	0.409704	0.314943
Al	15	0.143939	0.891768	0.005458
Al	16	0.465980	0.228743	0.207558
Al	17	0.806671	0.067152	0.109168
Al	18	0.132204	0.393573	0.311214
Al	19	0.303907	0.054712	0.105026
Al	20	0.630512	0.389883	0.311324
Al	21	0.887421	0.146252	0.005380
Al	22	0.210924	0.483106	0.207604
Al	23	0.562737	0.311893	0.106760
Al	24	0.884660	0.649152	0.308836
Al	25	0.403901	0.109806	-0.002539
Al	26	0.716209	0.468466	0.204415
Al	27	0.133811	0.642742	0.002266
Al	28	0.462330	0.970495	0.205910
Al	29	0.122340	0.133293	0.303657
Al	30	0.802592	0.799637	0.102312
Al	31	0.303602	0.809706	0.108428
Al	32	0.638242	0.140118	0.311039
Al	33	0.657045	0.664964	-0.006381
Al	34	0.965601	0.998776	0.212946
Al	35	0.043496	0.548443	0.103184
Al	36	0.356125	0.880424	0.308630
Al	37	0.389334	0.391928	-0.000742
Al	38	0.716552	0.719721	0.202624
Al	39	0.894570	0.411015	0.009530
Al	40	0.215430	0.742387	0.214073
Al	41	0.304241	0.560485	0.106786
Al	42	0.633699	0.893234	0.308721
Al	43	0.646069	0.406629	0.003778
Al	44	0.968611	0.731179	0.207244

Al	45	0.139114	0.390758	-0.004171
Al	46	0.467295	0.721605	0.204277
Al	47	0.049258	0.817912	0.108754
Al	48	0.379357	0.141055	0.311854
Al	49	0.406841	0.648904	0.002718
Al	50	0.720111	0.980594	0.205294
Al	51	0.558302	0.790670	0.099525
Al	52	0.883282	0.129323	0.319382
Ni	1	0.376338	0.892110	0.016090
Ni	2	0.707320	0.233321	0.205285
Ni	3	0.642197	0.898979	0.015553
Ni	4	0.957678	0.238132	0.208008
Ni	5	0.065753	0.301666	0.104305
Ni	6	0.395127	0.630746	0.297697
Ni	7	0.545376	0.555812	0.109796
Ni	8	0.868249	0.897274	0.296353
Ni	9	0.799065	0.560877	0.109483
Ni	10	0.118308	0.907944	0.301037
Ni	11	0.904520	0.639277	0.011368
Ni	12	0.227913	0.971290	0.202029

F.2 Fractional coordinates for Ni₄Al₁₂ bulk and (111) surface slab structures

Table F-3 Final fractional coordinates for the optimised Ni₄Al₁₂ bulk structure

Ni ₄ Al ₁₂ bulk structure final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	-0.012272	-0.004308	0.000000
Al	2	-0.033988	0.500192	-0.000001
Al	3	0.510664	-0.011704	0.000000
Al	4	0.539720	0.519837	-0.000001
Al	5	-0.024252	0.255132	0.249900
Al	6	-0.022926	0.739630	0.249788
Al	7	0.527596	0.261341	0.250002
Al	8	0.253379	-0.002527	0.249868
Al	9	0.260983	0.504124	0.250054
Al	10	0.740991	-0.016141	0.249998
Al	11	0.257276	0.257221	-0.000001
Al	12	0.256195	0.744464	0.000000
Al	13	-0.012223	-0.004657	0.500000
Al	14	-0.034000	0.500318	0.500001
Al	15	0.510683	-0.011716	0.500000
Al	16	0.539834	0.519870	0.500001
Al	17	-0.024253	0.255133	0.750100
Al	18	-0.022928	0.739631	0.750212
Al	19	0.527596	0.261342	0.749998
Al	20	0.253378	-0.002528	0.750132

Al	21	0.260981	0.504125	0.749945
Al	22	0.740990	-0.016140	0.750002
Al	23	0.257222	0.257128	0.500001
Al	24	0.256252	0.744584	0.500000
Ni	1	0.491184	0.757225	0.250022
Ni	2	0.752499	0.499336	0.250013
Ni	3	0.748093	0.237545	0.000000
Ni	4	0.754708	0.758752	0.000000
Ni	5	0.491182	0.757225	0.749978
Ni	6	0.752498	0.499335	0.749987
Ni	7	0.748173	0.237491	0.500000
Ni	8	0.754765	0.758742	0.500000

Table F-4 Final fractional coordinates for the optimised Ni₄Al₁₂ (111) surface slab structure

Ni ₄ Al ₁₂ (111) surface slab structure final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.287741	0.314704	0.102441
Al	2	0.619377	0.646224	0.307890
Al	3	0.616392	0.144970	-0.001771
Al	4	0.944154	0.471199	0.198487
Al	5	0.141327	0.147026	-0.001928
Al	6	0.474355	0.478578	0.204328
Al	7	0.789769	0.341935	0.119912
Al	8	0.122246	0.678810	0.316080
Al	9	0.194721	0.224591	0.201512
Al	10	0.861438	0.892963	-0.002446
Al	11	0.540654	0.060404	0.099877
Al	12	0.873331	0.391247	0.305731
Al	13	0.042374	0.085013	0.114497
Al	14	0.373303	0.410999	0.312851
Al	15	0.128746	0.904796	0.004044
Al	16	0.459936	0.233314	0.205923
Al	17	0.792397	0.075531	0.108803
Al	18	0.123857	0.397957	0.307668
Al	19	0.297143	0.060549	0.098888
Al	20	0.631427	0.392419	0.307505
Al	21	0.873994	0.157306	0.007833
Al	22	0.205514	0.488475	0.206288
Al	23	0.548494	0.319046	0.104702
Al	24	0.877376	0.652205	0.308940
Al	25	0.119991	0.652157	0.000432
Al	26	0.455854	0.976753	0.202583
Al	27	0.109553	0.131529	0.302895
Al	28	0.779688	0.807425	0.098408
Al	29	0.304387	0.814796	0.104304
Al	30	0.656288	0.136422	0.311097
Al	31	0.627250	0.682413	0.014139
Al	32	0.953607	0.009516	0.217390

Al	33	0.029935	0.559136	0.101940
Al	34	0.355248	0.883805	0.305421
Al	35	0.375820	0.395482	-0.002792
Al	36	0.707550	0.721193	0.198761
Al	37	0.877958	0.416961	0.011272
Al	38	0.208997	0.748326	0.211560
Al	39	0.294902	0.569953	0.105193
Al	40	0.626444	0.897882	0.305759
Al	41	0.627883	0.412261	0.005894
Al	42	0.958460	0.733511	0.205238
Al	43	0.126100	0.397586	-0.007160
Al	44	0.467246	0.723030	0.199960
Al	45	0.038020	0.826612	0.108278
Al	46	0.373071	0.146987	0.309849
Al	47	0.386453	0.658335	-0.002197
Al	48	0.711633	0.983773	0.203694
Ni	1	0.365323	0.898366	0.011641
Ni	2	0.695956	0.233530	0.202959
Ni	3	0.621258	0.913383	0.010356
Ni	4	0.957620	0.237994	0.207196
Ni	5	0.050241	0.313043	0.104259
Ni	6	0.388436	0.634717	0.295618
Ni	7	0.369120	0.162037	0.011007
Ni	8	0.702918	0.490596	0.210832
Ni	9	0.532720	0.565019	0.104954
Ni	10	0.868119	0.891159	0.295324
Ni	11	0.789421	0.568836	0.106162
Ni	12	0.118605	0.901274	0.300974
Ni	13	0.890015	0.645843	0.009511
Ni	14	0.221515	0.977374	0.199779
Ni	15	0.536833	0.822557	0.110427
Ni	16	0.866424	0.164854	0.303999

F.3 Fractional coordinates for Ni₅Al₁₁ bulk and (111) surface slab structures

Table F-5 Final fractional coordinates for the optimised Ni₅Al₁₁ bulk structure

Ni ₅ Al ₁₁ bulk structure final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	-0.007268	-0.006783	0.000000
Al	2	-0.042219	0.500713	0.000000
Al	3	0.511780	-0.007578	0.000000
Al	4	-0.022789	0.261046	0.249893
Al	5	-0.017553	0.736563	0.249880
Al	6	0.535403	0.272203	0.249847
Al	7	0.258258	0.000715	0.249880
Al	8	0.270929	0.504812	0.249868
Al	9	0.742805	-0.017051	0.250021
Al	10	0.262729	0.260254	0.000000

Al	11	0.266464	0.738131	0.000000
Al	12	-0.007262	-0.006864	0.500000
Al	13	-0.042051	0.500769	0.500000
Al	14	0.511715	-0.007603	0.500000
Al	15	-0.022789	0.261046	0.750107
Al	16	-0.017553	0.736563	0.750120
Al	17	0.535403	0.272203	0.750153
Al	18	0.258258	0.000715	0.750120
Al	19	0.270929	0.504812	0.750132
Al	20	0.742805	-0.017051	0.749979
Al	21	0.262559	0.260296	0.500000
Al	22	0.266402	0.738112	0.500000
Ni	1	0.499052	0.499749	0.000000
Ni	2	0.492368	0.762813	0.250038
Ni	3	0.747564	0.509305	0.250075
Ni	4	0.754655	0.230838	0.000000
Ni	5	0.747929	0.754364	0.000000
Ni	6	0.498973	0.499629	0.500000
Ni	7	0.492368	0.762813	0.749962
Ni	8	0.747564	0.509305	0.749925
Ni	9	0.754633	0.230849	0.500000
Ni	10	0.747938	0.754315	0.500000

Table F-6 Final fractional coordinates for the optimised Ni₅Al₁₁ (111) surface slab structure

Ni ₅ Al ₁₁ (111) surface slab structure final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.294243	0.325582	0.103180
Al	2	0.628486	0.649371	0.309734
Al	3	0.618948	0.149255	-0.006141
Al	4	0.944684	0.473210	0.196804
Al	5	0.144473	0.158005	-0.003715
Al	6	0.474346	0.485247	0.204600
Al	7	0.193458	0.231873	0.203037
Al	8	0.864909	0.904500	0.000110
Al	9	0.549206	0.069188	0.100100
Al	10	0.879053	0.392607	0.304141
Al	11	0.040483	0.097626	0.117007
Al	12	0.367799	0.429004	0.315481
Al	13	0.134243	0.915294	0.005542
Al	14	0.463188	0.239944	0.207978
Al	15	0.801075	0.084062	0.110145
Al	16	0.125488	0.404972	0.309392
Al	17	0.298614	0.072914	0.099942
Al	18	0.635329	0.396208	0.306742
Al	19	0.876700	0.167520	0.005879
Al	20	0.206939	0.492366	0.206570
Al	21	0.560766	0.327593	0.105522
Al	22	0.886837	0.661189	0.313455

Al	23	0.126094	0.663946	0.000654
Al	24	0.462231	0.985002	0.203588
Al	25	0.105002	0.128284	0.299676
Al	26	0.782567	0.811830	0.098634
Al	27	0.308028	0.824073	0.105476
Al	28	0.648399	0.145779	0.315404
Al	29	0.030335	0.569063	0.103333
Al	30	0.349486	0.886065	0.307421
Al	31	0.384964	0.408307	-0.001760
Al	32	0.715557	0.728747	0.201396
Al	33	0.876925	0.431323	0.016651
Al	34	0.209192	0.758665	0.216373
Al	35	0.296702	0.581100	0.106552
Al	36	0.629923	0.901893	0.308850
Al	37	0.636499	0.424936	0.007688
Al	38	0.962089	0.744674	0.208606
Al	39	0.128356	0.410283	-0.006711
Al	40	0.472676	0.729959	0.201154
Al	41	0.042817	0.833639	0.110026
Al	42	0.371999	0.150325	0.311396
Al	43	0.400663	0.672832	-0.000957
Al	44	0.723032	0.995487	0.207030
Ni	1	0.796898	0.324081	0.105286
Ni	2	0.125983	0.645378	0.296916
Ni	3	0.371229	0.915091	0.013348
Ni	4	0.695593	0.243194	0.204269
Ni	5	0.622497	0.914302	0.011713
Ni	6	0.952310	0.243276	0.206895
Ni	7	0.061137	0.318780	0.103844
Ni	8	0.405158	0.635590	0.294555
Ni	9	0.372788	0.173737	0.011100
Ni	10	0.705884	0.491337	0.207056
Ni	11	0.633344	0.662270	0.017133
Ni	12	0.962247	0.989542	0.201552
Ni	13	0.531611	0.575836	0.107638
Ni	14	0.866354	0.904127	0.298706
Ni	15	0.786344	0.576345	0.109764
Ni	16	0.106218	0.902172	0.302377
Ni	17	0.895114	0.655844	0.010102
Ni	18	0.230847	0.982510	0.199325
Ni	19	0.541900	0.829561	0.110632
Ni	20	0.864213	0.160187	0.295192

F.4 Fractional coordinates for Ni₇Al₉ bulk and (111) surface slab structures for configurations 65 and 61

Table F-7 Final fractional coordinates for the optimised Ni₇Al₉, configuration 65, bulk structure

Ni ₇ Al ₉ , configuration 65, bulk structure final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	-0.001033	0.000000	0.000000
Al	2	-0.029277	0.500000	0.000000
Al	3	0.508241	0.000000	0.000000
Al	4	-0.013197	0.262184	0.249948
Al	5	-0.013197	0.737816	0.249948
Al	6	0.259180	0.000000	0.250005
Al	7	0.737415	0.000000	0.249872
Al	8	0.275615	0.282311	0.000000
Al	9	0.275615	0.717689	0.000000
Al	10	-0.001321	0.000000	0.500000
Al	11	-0.029230	0.500000	0.500000
Al	12	0.508203	0.000000	0.500000
Al	13	-0.013197	0.262184	0.750052
Al	14	-0.013197	0.737816	0.750052
Al	15	0.259179	0.000000	0.749995
Al	16	0.737415	0.000000	0.750128
Al	17	0.275648	0.282219	0.500000
Al	18	0.275648	0.717781	0.500000
Ni	1	0.515296	0.500000	0.000000
Ni	2	0.498034	0.243153	0.250016
Ni	3	0.498034	0.756847	0.250016
Ni	4	0.231837	0.500000	0.250030
Ni	5	0.744803	0.500000	0.250028
Ni	6	0.756396	0.239586	0.000000
Ni	7	0.756396	0.760414	0.000000
Ni	8	0.515248	0.500000	0.500000
Ni	9	0.498033	0.243150	0.749984
Ni	10	0.498033	0.756850	0.749984
Ni	11	0.231838	0.500000	0.749970
Ni	12	0.744801	0.500000	0.749973
Ni	13	0.756369	0.239588	0.500000
Ni	14	0.756369	0.760412	0.500000

Table F-8 Final fractional coordinates for the optimised Ni₇Al₉, configuration 65, (111) surface slab structure

Ni ₇ Al ₉ , configuration 65, (111) surface slab structure final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.277156	0.334715	0.101415
Al	2	0.620086	0.653167	0.307066
Al	3	0.598559	0.164189	-0.011739
Al	4	0.935451	0.479777	0.196636
Al	5	0.106240	0.171154	-0.004087

Al	6	0.453322	0.493825	0.203250
Al	7	0.187424	0.237546	0.199884
Al	8	0.841448	0.915109	-0.006920
Al	9	0.529929	0.078538	0.095112
Al	10	0.868794	0.397139	0.302940
Al	11	0.108205	0.923520	-0.001947
Al	12	0.455346	0.242253	0.202961
Al	13	0.269436	0.081200	0.097841
Al	14	0.612835	0.405590	0.306656
Al	15	0.841640	0.190536	0.013979
Al	16	0.183910	0.509108	0.212024
Al	17	0.560504	0.326852	0.100879
Al	18	0.911339	0.649466	0.303210
Al	19	0.102042	0.672187	-0.002402
Al	20	0.451273	0.993091	0.203363
Al	21	0.104350	0.142116	0.299862
Al	22	0.764346	0.822609	0.095367
Al	23	0.277953	0.833536	0.102266
Al	24	0.636588	0.150527	0.310404
Al	25	0.014691	0.576955	0.100645
Al	26	0.355166	0.898396	0.310218
Al	27	0.361806	0.418841	-0.008539
Al	28	0.701562	0.736879	0.199374
Al	29	0.280122	0.584179	0.102265
Al	30	0.632647	0.900964	0.308375
Al	31	0.089325	0.421380	-0.009418
Al	32	0.441513	0.743213	0.200751
Al	33	0.011910	0.850099	0.110375
Al	34	0.355038	0.175508	0.313773
Al	35	0.391427	0.667775	-0.004249
Al	36	0.730997	0.992069	0.198927
Ni	1	0.786320	0.335167	0.109485
Ni	2	0.131597	0.667482	0.294984
Ni	3	0.031585	0.077639	0.101370
Ni	4	0.380581	0.395225	0.293212
Ni	5	0.348338	0.920913	0.009982
Ni	6	0.689707	0.248791	0.200722
Ni	7	0.771825	0.073445	0.099807
Ni	8	0.108246	0.388484	0.290185
Ni	9	0.599751	0.922149	0.006563
Ni	10	0.948339	0.241311	0.199895
Ni	11	0.041349	0.327408	0.102499
Ni	12	0.379739	0.654151	0.292363
Ni	13	0.342907	0.187531	0.009433
Ni	14	0.688507	0.502884	0.205424
Ni	15	0.616552	0.671784	0.017321
Ni	16	0.957264	1.000962	0.199522
Ni	17	0.858493	0.418353	0.013554
Ni	18	0.200650	0.739658	0.193984
Ni	19	0.516296	0.586474	0.106492

Ni	20	0.869245	0.906462	0.292305
Ni	21	0.601227	0.419515	0.008724
Ni	22	0.940271	0.733029	0.193372
Ni	23	0.774223	0.580206	0.107206
Ni	24	0.121210	0.905314	0.288106
Ni	25	0.865374	0.664415	0.007967
Ni	26	0.214678	0.991158	0.197150
Ni	27	0.517758	0.841870	0.110511
Ni	28	0.861329	0.161657	0.291986

Table F-9 Final fractional coordinates for the optimised Ni₇Al₉, configuration 61, bulk structure

Ni ₇ Al ₉ , configuration 61, bulk structure final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	-0.024814	0.000000	-0.000002
Al	2	-0.030106	0.500000	-0.000001
Al	3	0.545352	0.000000	-0.000001
Al	4	-0.033646	0.256488	0.249950
Al	5	-0.033646	0.743512	0.249950
Al	6	0.261465	0.000000	0.249811
Al	7	0.282940	0.500000	0.250000
Al	8	0.272083	0.255339	-0.000001
Al	9	0.272083	0.744661	-0.000001
Al	10	-0.024839	0.000000	0.500002
Al	11	-0.030146	0.500000	0.500002
Al	12	0.545438	0.000000	0.500001
Al	13	-0.033648	0.256487	0.750050
Al	14	-0.033648	0.743513	0.750050
Al	15	0.261466	0.000000	0.750189
Al	16	0.282940	0.500000	0.750000
Al	17	0.271799	0.255195	0.500001
Al	18	0.271799	0.744805	0.500001
Ni	1	0.500387	0.500000	-0.000001
Ni	2	0.497096	0.239159	0.250077
Ni	3	0.497096	0.760841	0.250077
Ni	4	0.760726	0.000000	0.249991
Ni	5	0.738405	0.500000	0.250042
Ni	6	0.747412	0.255350	-0.000001
Ni	7	0.747412	0.744650	-0.000001
Ni	8	0.500251	0.500000	0.500001
Ni	9	0.497096	0.239159	0.749923
Ni	10	0.497096	0.760841	0.749923
Ni	11	0.760723	0.000000	0.750009
Ni	12	0.738413	0.500000	0.749958
Ni	13	0.747508	0.255378	0.500001
Ni	14	0.747508	0.744622	0.500001

Table F-10 Final fractional coordinates for the optimised Ni₇Al₉, configuration 61, (111) surface slab structure

Ni ₇ Al ₉ , configuration 61, (111) surface slab structure final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.313450	0.341169	0.099219
Al	2	0.619332	0.642858	0.302944
Al	3	0.662625	0.180816	-0.007769
Al	4	0.968303	0.490049	0.197813
Al	5	0.184227	0.201434	0.010450
Al	6	0.490624	0.518156	0.208324
Al	7	0.210401	0.241415	0.199061
Al	8	0.904345	0.929550	-0.008524
Al	9	0.569283	0.085723	0.097604
Al	10	0.871043	0.391633	0.298797
Al	11	0.171858	0.944163	0.002421
Al	12	0.480808	0.253322	0.205574
Al	13	0.834374	0.105844	0.109216
Al	14	0.138591	0.411849	0.312992
Al	15	0.923602	0.199601	0.007803
Al	16	0.229954	0.508160	0.208379
Al	17	0.581539	0.352359	0.104852
Al	18	0.888935	0.662662	0.313181
Al	19	0.155883	0.684805	-0.007254
Al	20	0.469096	0.993779	0.200710
Al	21	0.117088	0.142070	0.300903
Al	22	0.815805	0.835171	0.097304
Al	23	0.336331	0.860027	0.112886
Al	24	0.649801	0.172528	0.319517
Al	25	0.056729	0.585024	0.098211
Al	26	0.364735	0.891912	0.302320
Al	27	0.411319	0.432927	-0.012620
Al	28	0.723305	0.739021	0.198311
Al	29	0.323031	0.600492	0.103253
Al	30	0.633982	0.907725	0.311205
Al	31	0.681683	0.455564	0.007542
Al	32	0.987703	0.759912	0.209906
Al	33	0.076328	0.851618	0.106813
Al	34	0.383017	0.158700	0.311568
Al	35	0.429488	0.699573	0.001864
Al	36	0.736686	0.008595	0.207225
Ni	1	0.820629	0.345378	0.104315
Ni	2	0.130798	0.652531	0.299607
Ni	3	0.081634	0.086645	0.103538
Ni	4	0.388778	0.395079	0.296992
Ni	5	0.408246	0.943921	0.015738
Ni	6	0.715546	0.254906	0.199997
Ni	7	0.327024	0.103273	0.109423
Ni	8	0.631160	0.406511	0.296677
Ni	9	0.664014	0.939117	0.007193
Ni	10	0.972207	0.248041	0.199515

Ni	11	0.070283	0.341633	0.106454
Ni	12	0.374421	0.653513	0.296447
Ni	13	0.424776	0.192817	0.008535
Ni	14	0.731455	0.499455	0.200631
Ni	15	0.664447	0.695526	0.014183
Ni	16	0.979413	-0.002289	0.198428
Ni	17	0.925799	0.434983	0.012751
Ni	18	0.235202	0.745433	0.196972
Ni	19	0.559394	0.599710	0.106296
Ni	20	0.870489	0.911360	0.299546
Ni	21	0.171298	0.446523	0.008493
Ni	22	0.482376	0.757046	0.205691
Ni	23	0.817042	0.592054	0.105263
Ni	24	0.125978	0.900602	0.291245
Ni	25	0.225742	0.001025	0.204645
Ni	26	0.914417	0.687884	0.007177
Ni	27	0.577242	0.846229	0.107656
Ni	28	0.882930	0.150718	0.289970

F.5 Fractional coordinates for Ni₈Al₈ bulk and (111) surface slab structures

Table F-11 Final fractional coordinates for the optimised Ni₈Al₈ bulk structure

Ni ₈ Al ₈ bulk structure final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	-0.014536	-0.029895	-0.000001
Al	2	0.000472	0.541742	-0.000002
Al	3	0.513733	-0.033732	-0.000002
Al	4	-0.000627	0.255983	0.249912
Al	5	0.500046	0.274602	0.249934
Al	6	0.255209	-0.036983	0.249984
Al	7	0.254027	0.266072	-0.000001
Al	8	0.744745	0.266101	-0.000001
Al	9	-0.014456	-0.030107	0.500001
Al	10	0.000403	0.541763	0.500002
Al	11	0.513736	-0.033702	0.500002
Al	12	-0.000627	0.255984	0.750088
Al	13	0.500046	0.274601	0.750066
Al	14	0.255211	-0.036984	0.750016
Al	15	0.253963	0.266256	0.500001
Al	16	0.744778	0.266072	0.500001
Ni	1	0.500073	0.499193	0.000000
Ni	2	-0.005301	0.757482	0.249986
Ni	3	0.505112	0.740182	0.250015
Ni	4	0.241516	0.497614	0.250001
Ni	5	0.746115	0.017877	0.250016
Ni	6	0.758698	0.492654	0.250035
Ni	7	0.255922	0.749145	0.000000
Ni	8	0.744836	0.741962	0.000001
Ni	9	0.500090	0.499149	0.500000

Ni	10	-0.005300	0.757481	0.750014
Ni	11	0.505106	0.740192	0.749985
Ni	12	0.241514	0.497611	0.749999
Ni	13	0.746116	0.017880	0.749984
Ni	14	0.758701	0.492649	0.749965
Ni	15	0.255896	0.749176	0.500000
Ni	16	0.744783	0.741980	0.500000

Table F-12 Final fractional coordinates for the optimised Ni₈Al₈ (111) surface slab structure

Ni₈Al₈ (111) surface slab structure final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.244743	0.335838	0.097303
Al	2	0.626237	0.634332	0.295258
Al	3	0.521705	0.198418	0.010216
Al	4	0.895435	0.515881	0.207783
Al	5	0.065164	0.191230	-0.005663
Al	6	0.443675	0.500139	0.198839
Al	7	0.169133	0.251942	0.204179
Al	8	0.791350	0.940328	0.001463
Al	9	0.967050	0.101504	0.106498
Al	10	0.348274	0.414402	0.313083
Al	11	0.071016	0.931532	-0.010032
Al	12	0.447055	0.242880	0.196599
Al	13	0.783262	0.197393	0.005705
Al	14	0.164128	0.507383	0.206946
Al	15	0.969090	0.349523	0.103686
Al	16	0.348009	0.661038	0.312562
Al	17	0.063673	0.671024	-0.009135
Al	18	0.432587	0.987345	0.195625
Al	19	0.081477	0.171097	0.317975
Al	20	0.708740	0.859322	0.112100
Al	21	0.256227	0.839963	0.100628
Al	22	0.636397	0.157531	0.300683
Al	23	0.980979	0.600059	0.104100
Al	24	0.358669	0.903630	0.306712
Al	25	0.770518	0.452485	0.004153
Al	26	0.155506	0.759071	0.209149
Al	27	0.261431	0.584916	0.097010
Al	28	0.639664	0.891920	0.299759
Al	29	0.358418	0.157612	0.308006
Al	30	0.978086	0.848779	0.105716
Al	31	0.157323	0.005292	0.206147
Al	32	0.778030	0.694883	-0.001732
Ni	1	0.735823	0.343869	0.102692
Ni	2	0.108567	0.656155	0.298970
Ni	3	0.473071	0.098353	0.107330
Ni	4	0.856438	0.400112	0.292919
Ni	5	0.298440	0.944510	0.011346

Ni	6	0.680409	0.248810	0.198022
Ni	7	0.732447	0.087633	0.103404
Ni	8	0.112581	0.396607	0.296647
Ni	9	0.213030	0.102509	0.111207
Ni	10	0.591253	0.413744	0.292828
Ni	11	0.553714	0.939746	0.013159
Ni	12	0.933500	0.251149	0.196793
Ni	13	0.489242	0.343730	0.106613
Ni	14	0.864701	0.650948	0.297492
Ni	15	0.296781	0.183309	0.011866
Ni	16	0.674239	0.499852	0.196085
Ni	17	0.540995	0.696444	0.011807
Ni	18	0.920834	-0.001647	0.197456
Ni	19	0.290075	0.440109	0.008861
Ni	20	0.659973	0.752574	0.202574
Ni	21	0.493514	0.594694	0.104778
Ni	22	0.866930	0.907028	0.292195
Ni	23	0.542006	0.436616	0.012235
Ni	24	0.916468	0.748021	0.198331
Ni	25	0.024230	0.448748	0.013999
Ni	26	0.403373	0.758637	0.202830
Ni	27	0.745678	0.597630	0.102679
Ni	28	0.114771	0.911543	0.298792
Ni	29	0.297271	0.691033	0.007443
Ni	30	0.668531	0.003221	0.205042
Ni	31	0.485590	0.842641	0.104676
Ni	32	0.864835	0.157372	0.287714

F.6 Fractional coordinates for Ni₉Al₇ bulk and (111) surface slab structures

Table F-13 Final fractional coordinates for the optimised Ni₉Al₇ bulk structure

Ni ₉ Al ₇ bulk structure final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	-0.003961	-0.002256	0.000001
Al	2	-0.009703	0.504164	0.000002
Al	3	-0.011767	0.257630	0.249992
Al	4	-0.002324	0.740308	0.249943
Al	5	0.279824	-0.010707	0.249968
Al	6	0.714939	-0.001976	0.249897
Al	7	0.283943	0.263035	0.000000
Al	8	-0.004111	-0.002396	0.499999
Al	9	-0.009766	0.504102	0.499998
Al	10	-0.011764	0.257627	0.750008
Al	11	-0.002324	0.740309	0.750057
Al	12	0.279818	-0.010700	0.750032
Al	13	0.714946	-0.001968	0.750103
Al	14	0.283891	0.262933	0.500000
Ni	1	0.496745	-0.001548	-0.000002
Ni	2	0.504367	0.506224	-0.000001

Ni	3	0.501322	0.254329	0.250014
Ni	4	0.500701	0.740482	0.250015
Ni	5	0.241893	0.495574	0.250020
Ni	6	0.751443	0.501783	0.249998
Ni	7	0.242097	0.751286	0.000000
Ni	8	0.755050	0.247931	-0.000001
Ni	9	0.755562	0.753927	0.000000
Ni	10	0.496777	-0.001557	0.500002
Ni	11	0.504364	0.506214	0.500001
Ni	12	0.501323	0.254334	0.749986
Ni	13	0.500702	0.740460	0.749985
Ni	14	0.241896	0.495576	0.749980
Ni	15	0.751440	0.501783	0.750002
Ni	16	0.242057	0.751284	0.500000
Ni	17	0.755052	0.247897	0.500001
Ni	18	0.755569	0.753916	0.500000

Table F-14 Final fractional coordinates for the optimised Ni₉Al₇ (111) surface slab structure

Ni ₉ Al ₇ (111) surface slab structure final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.317161	0.343431	0.099017
Al	2	0.628845	0.651090	0.306090
Al	3	0.661557	0.186114	-0.003589
Al	4	0.970639	0.496115	0.200068
Al	5	0.222463	0.245396	0.200250
Al	6	0.909441	0.933148	-0.006530
Al	7	0.572893	0.091162	0.098078
Al	8	0.883344	0.402221	0.304163
Al	9	0.187515	0.939574	0.002230
Al	10	0.494602	0.255733	0.203100
Al	11	0.306875	0.079818	0.097443
Al	12	0.623205	0.387397	0.293130
Al	13	0.914899	0.207113	0.010173
Al	14	0.229530	0.518089	0.207028
Al	15	0.165877	0.685431	-0.007332
Al	16	0.477494	0.999719	0.205395
Al	17	0.124127	0.148423	0.301676
Al	18	0.815636	0.840308	0.098037
Al	19	0.065333	0.588023	0.097697
Al	20	0.371232	0.897788	0.306072
Al	21	0.422787	0.436628	-0.007746
Al	22	0.729099	0.750060	0.202239
Al	23	0.339487	0.597145	0.103074
Al	24	0.658225	0.901906	0.314971
Al	25	0.145050	0.423614	-0.012400
Al	26	0.465298	0.739530	0.194428
Al	27	0.069773	0.860849	0.108619
Al	28	0.384717	0.175306	0.318219

Ni	1	0.163710	0.184940	0.007381
Ni	2	0.481770	0.494462	0.195123
Ni	3	0.817939	0.345820	0.108205
Ni	4	0.123419	0.663601	0.292789
Ni	5	0.060793	0.099720	0.105487
Ni	6	0.375122	0.410431	0.294972
Ni	7	0.429144	0.930383	0.011044
Ni	8	0.734533	0.247165	0.194669
Ni	9	0.819713	0.087117	0.097393
Ni	10	0.130411	0.398930	0.291079
Ni	11	0.666618	0.938275	0.007074
Ni	12	0.978067	0.254000	0.203514
Ni	13	0.564811	0.336957	0.099078
Ni	14	0.877015	0.651754	0.293173
Ni	15	0.073237	0.342354	0.105733
Ni	16	0.384077	0.654122	0.290533
Ni	17	0.410669	0.194779	0.008306
Ni	18	0.724628	0.506220	0.204644
Ni	19	0.318454	0.840383	0.101278
Ni	20	0.635992	0.140388	0.291866
Ni	21	0.664768	0.687824	0.015779
Ni	22	0.971334	0.008012	0.198157
Ni	23	0.902621	0.449373	0.015411
Ni	24	0.220678	0.755765	0.197421
Ni	25	0.581006	0.588734	0.104432
Ni	26	0.887582	0.902485	0.285099
Ni	27	0.664251	0.431960	0.011455
Ni	28	0.976076	0.741716	0.190545
Ni	29	0.821359	0.598552	0.109843
Ni	30	0.127409	0.908557	0.291425
Ni	31	0.414297	0.679311	0.008121
Ni	32	0.721247	0.996021	0.191890
Ni	33	0.920384	0.685297	0.006287
Ni	34	0.233213	0.999472	0.199944
Ni	35	0.569087	0.850292	0.111274
Ni	36	0.878667	0.158371	0.291539

F.7 Fractional coordinates for Ni₁₁Al₅ bulk and (111) surface slab structures

Table F-15 Final fractional coordinates for the optimised Ni₁₁Al₅ bulk structure

Ni ₁₁ Al ₅ bulk structure final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	-0.019219	-0.019667	0.000000
Al	2	-0.008903	0.525056	0.000000
Al	3	-0.018525	0.254315	0.249988
Al	4	0.272152	-0.020934	0.249985
Al	5	0.276392	0.261333	-0.000001
Al	6	-0.019195	-0.019581	0.500000
Al	7	-0.008964	0.525096	0.500000

Al	8	-0.018525	0.254314	0.750012
Al	9	0.272149	-0.020931	0.750016
Al	10	0.276359	0.261252	0.500001
Ni	1	0.502794	-0.000426	0.000000
Ni	2	0.503833	0.504389	0.000000
Ni	3	-0.001119	0.754158	0.249999
Ni	4	0.502254	0.250048	0.249993
Ni	5	0.503947	0.744000	0.250000
Ni	6	0.243897	0.495899	0.250008
Ni	7	0.745943	0.000072	0.249996
Ni	8	0.748328	0.501127	0.249986
Ni	9	0.254260	0.749587	0.000000
Ni	10	0.753033	0.253024	0.000000
Ni	11	0.740977	0.748009	0.000000
Ni	12	0.502794	-0.000430	0.500000
Ni	13	0.503834	0.504384	0.500000
Ni	14	-0.001119	0.754159	0.750001
Ni	15	0.502253	0.250047	0.750007
Ni	16	0.503950	0.743997	0.750000
Ni	17	0.243898	0.495899	0.749992
Ni	18	0.745943	0.000072	0.750004
Ni	19	0.748328	0.501128	0.750014
Ni	20	0.254242	0.749568	0.500000
Ni	21	0.753041	0.253015	0.500000
Ni	22	0.740969	0.748023	0.500000

Table F-16 Final fractional coordinates for the optimised Ni₁₁Al₅ (111) surface slab structure

Ni ₁₁ Al ₅ (111) surface slab structure final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.304539	0.314981	0.093790
Al	2	0.634440	0.635108	0.293746
Al	3	0.609603	0.177550	0.005557
Al	4	0.938760	0.497571	0.201729
Al	5	0.204936	0.235442	0.196958
Al	6	0.873372	0.914863	-0.005638
Al	7	0.151520	0.920239	0.000519
Al	8	0.483119	0.241754	0.200133
Al	9	0.879749	0.186387	0.006345
Al	10	0.211339	0.506712	0.204608
Al	11	0.142353	0.648987	-0.013934
Al	12	0.468868	0.977363	0.191243
Al	13	0.102251	0.160113	0.302444
Al	14	0.775224	0.836834	0.104391
Al	15	0.039049	0.574827	0.097667
Al	16	0.366129	0.895082	0.298100
Al	17	0.317354	0.581205	0.100311
Al	18	0.648096	0.901907	0.299580
Al	19	0.044502	0.843410	0.107729

Al	20	0.375652	0.170955	0.312909
Ni	1	0.130450	0.170379	0.009265
Ni	2	0.460514	0.493164	0.196227
Ni	3	0.797835	0.329692	0.103616
Ni	4	0.122908	0.657979	0.294432
Ni	5	0.541872	0.081713	0.103715
Ni	6	0.872121	0.401927	0.293116
Ni	7	0.043984	0.082691	0.102426
Ni	8	0.375604	0.406148	0.293107
Ni	9	0.389941	0.914949	0.008149
Ni	10	0.719220	0.238156	0.195044
Ni	11	0.797288	0.075212	0.098618
Ni	12	0.126411	0.398151	0.290069
Ni	13	0.292671	0.077377	0.102535
Ni	14	0.624369	0.396570	0.288783
Ni	15	0.632068	0.918258	0.007210
Ni	16	0.961946	0.241294	0.198761
Ni	17	0.551069	0.328802	0.103410
Ni	18	0.880552	0.653272	0.294234
Ni	19	0.045621	0.332407	0.106046
Ni	20	0.375783	0.650837	0.290975
Ni	21	0.377439	0.162358	0.003841
Ni	22	0.705696	0.489959	0.196548
Ni	23	0.292667	0.832095	0.101967
Ni	24	0.624827	0.152238	0.295316
Ni	25	0.634257	0.667218	0.008787
Ni	26	0.960869	0.996514	0.197858
Ni	27	0.376864	0.420665	0.007047
Ni	28	0.704223	0.743854	0.200542
Ni	29	0.880580	0.426022	0.011858
Ni	30	0.210730	0.745769	0.196982
Ni	31	0.552790	0.578703	0.102348
Ni	32	0.884723	0.901860	0.289684
Ni	33	0.628578	0.419391	0.010037
Ni	34	0.960017	0.736192	0.192834
Ni	35	0.129800	0.415326	0.005869
Ni	36	0.458921	0.740483	0.197693
Ni	37	0.795231	0.581692	0.105073
Ni	38	0.122247	0.907540	0.292087
Ni	39	0.381685	0.668213	0.005856
Ni	40	0.713007	0.992106	0.198470
Ni	41	0.883590	0.672493	0.007868
Ni	42	0.213507	0.993267	0.199703
Ni	43	0.543878	0.824255	0.101216
Ni	44	0.867835	0.153455	0.291192

F.8 Fractional coordinates for Ni₁₂Al₄ bulk and (111) surface slab structures

Table F-17 Final fractional coordinates for the optimised Ni₁₂Al₄ bulk structure

Ni ₁₂ Al ₄ bulk structure final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.000176	-0.021962	-0.000001
Al	2	-0.015786	0.517953	0.000000
Al	3	-0.007254	0.244133	0.249940
Al	4	0.275946	0.508741	0.249912
Al	5	0.000162	-0.021782	0.500001
Al	6	-0.015839	0.517773	0.500000
Al	7	-0.007253	0.244132	0.750059
Al	8	0.275951	0.508741	0.750088
Ni	1	0.497703	0.003500	-0.000001
Ni	2	0.506581	0.497058	-0.000001
Ni	3	0.001057	0.743379	0.250037
Ni	4	0.500317	0.246093	0.250004
Ni	5	0.503539	0.756470	0.250010
Ni	6	0.248287	0.002084	0.250000
Ni	7	0.750129	0.000333	0.249994
Ni	8	0.747191	0.496611	0.249988
Ni	9	0.237450	0.257561	-0.000001
Ni	10	0.258326	0.748642	0.000000
Ni	11	0.755980	0.245627	0.000000
Ni	12	0.740407	0.753796	0.000000
Ni	13	0.497698	0.003490	0.500001
Ni	14	0.506568	0.497058	0.500001
Ni	15	0.001056	0.743380	0.749963
Ni	16	0.500313	0.246096	0.749996
Ni	17	0.503536	0.756467	0.749990
Ni	18	0.248284	0.002086	0.750000
Ni	19	0.750128	0.000333	0.750006
Ni	20	0.747192	0.496610	0.750012
Ni	21	0.237436	0.257574	0.500001
Ni	22	0.258272	0.748615	0.500001
Ni	23	0.755998	0.245617	0.500000
Ni	24	0.740450	0.753795	0.500000

Table F-18 Final fractional coordinates for the optimised Ni₁₂Al₄ (111) surface slab structure

Ni ₁₂ Al ₄ (111) surface slab structure final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.314530	0.321142	0.094735
Al	2	0.640939	0.641732	0.289182
Al	3	0.618801	0.170206	0.000463
Al	4	0.945783	0.491230	0.195538
Al	5	0.213460	0.237209	0.192374
Al	6	0.886574	0.916247	-0.005213
Al	7	0.801078	0.090098	0.105864

Al	8	0.128229	0.414202	0.301827
Al	9	0.150908	0.659192	-0.004354
Al	10	0.477708	0.982395	0.190445
Al	11	0.111422	0.151121	0.293966
Al	12	0.782115	0.830414	0.099129
Al	13	0.049563	0.576088	0.096202
Al	14	0.376506	0.898496	0.293450
Al	15	0.636458	0.427630	0.005620
Al	16	0.964903	0.752551	0.201504
Ni	1	0.130013	0.168225	0.006242
Ni	2	0.457696	0.491780	0.194611
Ni	3	0.802511	0.331645	0.100066
Ni	4	0.133198	0.654296	0.290058
Ni	5	0.554705	0.077366	0.098427
Ni	6	0.883112	0.397446	0.288338
Ni	7	0.051357	0.078123	0.099541
Ni	8	0.378936	0.400658	0.286707
Ni	9	0.381872	0.917736	0.005536
Ni	10	0.708749	0.244724	0.196049
Ni	11	0.131421	0.917652	0.006274
Ni	12	0.460175	0.240236	0.192866
Ni	13	0.299450	0.077862	0.100004
Ni	14	0.626321	0.400877	0.288430
Ni	15	0.635488	0.917106	0.003499
Ni	16	0.964742	0.238289	0.192874
Ni	17	0.875446	0.166148	0.006885
Ni	18	0.201589	0.489152	0.191933
Ni	19	0.553512	0.332417	0.101417
Ni	20	0.882264	0.655270	0.290102
Ni	21	0.055137	0.329886	0.101011
Ni	22	0.383690	0.650530	0.287517
Ni	23	0.377772	0.164761	0.003674
Ni	24	0.705107	0.490053	0.193154
Ni	25	0.292861	0.829988	0.100018
Ni	26	0.620524	0.152896	0.288749
Ni	27	0.637626	0.671370	0.005681
Ni	28	0.969115	0.992192	0.194981
Ni	29	0.389698	0.415811	0.004016
Ni	30	0.717843	0.738218	0.192708
Ni	31	0.888552	0.417874	0.006080
Ni	32	0.215610	0.739550	0.192879
Ni	33	0.545728	0.580882	0.101310
Ni	34	0.875184	0.905860	0.292357
Ni	35	0.295768	0.579501	0.099298
Ni	36	0.625231	0.901571	0.287601
Ni	37	0.137557	0.415475	0.004351
Ni	38	0.462649	0.741337	0.194620
Ni	39	0.799047	0.577922	0.098877
Ni	40	0.127741	0.900055	0.287175
Ni	41	0.037348	0.828578	0.099406

Ni	42	0.366049	0.152276	0.286030
Ni	43	0.387610	0.672528	0.008275
Ni	44	0.717247	0.993839	0.195480
Ni	45	0.890798	0.669804	0.004991
Ni	46	0.220145	0.990961	0.194832
Ni	47	0.541461	0.826958	0.098616
Ni	48	0.868433	0.153004	0.287360

F.9 Fractional coordinates for Ni₁₃Al₃ bulk and (111) surface slab structures

Table F-19 Final fractional coordinates for the optimised Ni₁₃Al₃ bulk structure

Ni ₁₃ Al ₃ bulk structure final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	-0.000995	-0.017520	0.000002
Al	2	-0.008472	0.258267	0.250049
Al	3	0.261257	0.508864	0.250015
Al	4	-0.000958	-0.017451	0.499998
Al	5	-0.008470	0.258265	0.749951
Al	6	0.261255	0.508865	0.749985
Ni	1	-0.000074	0.503528	-0.000001
Ni	2	0.500086	0.001244	0.000000
Ni	3	0.502784	0.498612	-0.000001
Ni	4	-0.003155	0.745918	0.249991
Ni	5	0.501050	0.248701	0.249990
Ni	6	0.502437	0.753395	0.249995
Ni	7	0.247528	0.001457	0.249985
Ni	8	0.751220	0.000621	0.249995
Ni	9	0.745356	0.501744	0.249989
Ni	10	0.246955	0.247491	0.000000
Ni	11	0.255779	0.751912	0.000000
Ni	12	0.751957	0.247281	-0.000001
Ni	13	0.746277	0.748439	0.000000
Ni	14	-0.000092	0.503558	0.500001
Ni	15	0.500084	0.001239	0.500000
Ni	16	0.502795	0.498610	0.500001
Ni	17	-0.003157	0.745915	0.750009
Ni	18	0.501054	0.248699	0.750010
Ni	19	0.502438	0.753393	0.750005
Ni	20	0.247533	0.001457	0.750015
Ni	21	0.751220	0.000622	0.750005
Ni	22	0.745351	0.501748	0.750011
Ni	23	0.246969	0.247479	0.500000
Ni	24	0.255781	0.751924	0.500000
Ni	25	0.751925	0.247272	0.500001
Ni	26	0.746282	0.748450	0.500001

Table F-20 Final fractional coordinates for the optimised Ni₁₃Al₃ (111) surface slab structure

Ni ₁₃ Al ₃ (111) surface slab structure final cell contents				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.312888	0.308550	0.094289
Al	2	0.636756	0.640229	0.290675
Al	3	0.205718	0.235777	0.194705
Al	4	0.880439	0.904147	-0.005057
Al	5	0.801283	0.069440	0.101675
Al	6	0.125994	0.404263	0.300188
Al	7	0.150992	0.641254	-0.007014
Al	8	0.475612	0.974766	0.190827
Al	9	0.043263	0.567942	0.097356
Al	10	0.366351	0.906538	0.297059
Al	11	0.640598	0.398978	0.000841
Al	12	0.963360	0.738192	0.197698
Ni	1	0.635416	0.148769	0.005955
Ni	2	0.961590	0.483787	0.193979
Ni	3	0.137428	0.149752	0.006165
Ni	4	0.463411	0.482854	0.192740
Ni	5	0.802420	0.317073	0.098963
Ni	6	0.131223	0.649801	0.288865
Ni	7	0.554272	0.062926	0.097929
Ni	8	0.879886	0.394410	0.285897
Ni	9	0.053306	0.065604	0.099805
Ni	10	0.379003	0.397887	0.285482
Ni	11	0.386100	0.898423	0.005040
Ni	12	0.712772	0.234059	0.193906
Ni	13	0.135263	0.898559	0.005494
Ni	14	0.462451	0.230923	0.191239
Ni	15	0.302665	0.065139	0.100137
Ni	16	0.627377	0.396529	0.286935
Ni	17	0.634552	0.899327	0.004670
Ni	18	0.962120	0.231416	0.192162
Ni	19	0.890070	0.148154	0.006225
Ni	20	0.214102	0.481601	0.190603
Ni	21	0.553389	0.318770	0.099965
Ni	22	0.880365	0.650455	0.289363
Ni	23	0.054629	0.316381	0.100112
Ni	24	0.381165	0.649292	0.286856
Ni	25	0.388038	0.146281	0.002469
Ni	26	0.713310	0.481306	0.192410
Ni	27	0.122481	0.152211	0.287503
Ni	28	0.799180	0.817376	0.099652
Ni	29	0.299812	0.816212	0.099827
Ni	30	0.625240	0.147696	0.286902
Ni	31	0.639726	0.649905	0.004743
Ni	32	0.967154	0.983226	0.193358
Ni	33	0.391154	0.395731	0.002332
Ni	34	0.716745	0.728073	0.192150

Ni	35	0.890334	0.401891	0.005846
Ni	36	0.216877	0.731263	0.192357
Ni	37	0.550230	0.565901	0.099749
Ni	38	0.876461	0.900335	0.290039
Ni	39	0.298133	0.565511	0.097367
Ni	40	0.625655	0.895577	0.287457
Ni	41	0.139530	0.398310	0.003825
Ni	42	0.465407	0.732312	0.194323
Ni	43	0.798108	0.565656	0.098595
Ni	44	0.125440	0.896906	0.286128
Ni	45	0.051527	0.814643	0.098210
Ni	46	0.376849	0.149428	0.285459
Ni	47	0.390907	0.651615	0.006575
Ni	48	0.716359	0.983628	0.194394
Ni	49	0.891399	0.651862	0.003314
Ni	50	0.219915	0.981523	0.193845
Ni	51	0.550440	0.813146	0.098285
Ni	52	0.875782	0.149083	0.286709

Appendix G Final fractional coordinates for $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase structures after each manual leaching step

This section contains the final fractional coordinates of the $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase surface slabs identified for Al leaching. The fractional coordinates are given for the surface slab with the lowest energy to remove an Al atom.

G.1 Fractional coordinates for Ni_7Al_9 (111) surface slab structures after Al atom removal

Table G-1 Final fractional coordinates for the optimised Ni_7Al_9 (111) surface slab structure after the first Al atom removal

Ni_7Al_9 (111) surface slab structure final cell contents after the first Al atom removal				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.313770	0.341662	0.099515
Al	2	0.618953	0.641108	0.301434
Al	3	0.663261	0.180766	-0.008057
Al	4	0.967594	0.490801	0.198782
Al	5	0.185424	0.201755	0.011831
Al	6	0.489366	0.517791	0.206898
Al	7	0.212668	0.242942	0.202186
Al	8	0.904217	0.929787	-0.008624
Al	9	0.569534	0.085395	0.098088
Al	10	0.869460	0.389814	0.297527
Al	11	0.171944	0.944770	0.002155
Al	12	0.480431	0.252515	0.207510
Al	13	0.835193	0.104942	0.108688
Al	14	0.150151	0.399465	0.313943
Al	15	0.924982	0.199672	0.007602
Al	16	0.228675	0.508889	0.207725
Al	17	0.581056	0.351621	0.103953
Al	18	0.889773	0.658623	0.312226
Al	19	0.155865	0.685376	-0.007745
Al	20	0.471036	0.993295	0.202817
Al	21	0.114743	0.142725	0.300900
Al	22	0.815259	0.835048	0.097712
Al	23	0.334420	0.861898	0.113090
Al	24	0.639976	0.173145	0.317908
Al	25	0.056194	0.584490	0.098293
Al	26	0.367547	0.892641	0.302286
Al	27	0.412026	0.433624	-0.013154
Al	28	0.723619	0.739335	0.199339
Al	29	0.322038	0.601192	0.102459
Al	30	0.627908	0.910787	0.312772
Al	31	0.682685	0.456170	0.006917
Al	32	0.988070	0.760769	0.210250
Al	33	0.075489	0.851061	0.106238
Al	34	0.429818	0.701084	0.001585
Al	35	0.736702	0.009138	0.207920

Ni	1	0.820778	0.345074	0.103622
Ni	2	0.131391	0.650247	0.299818
Ni	3	0.082683	0.085722	0.103934
Ni	4	0.386480	0.404715	0.294242
Ni	5	0.407991	0.945445	0.016884
Ni	6	0.716524	0.254762	0.198247
Ni	7	0.327392	0.104352	0.111438
Ni	8	0.629504	0.404991	0.295459
Ni	9	0.664142	0.939611	0.007410
Ni	10	0.971956	0.248361	0.198771
Ni	11	0.071850	0.340888	0.107906
Ni	12	0.373651	0.655437	0.295076
Ni	13	0.425487	0.193964	0.009321
Ni	14	0.730160	0.498949	0.199547
Ni	15	0.665018	0.696073	0.014587
Ni	16	0.981258	-0.002611	0.198155
Ni	17	0.927346	0.434950	0.013655
Ni	18	0.234592	0.747578	0.196114
Ni	19	0.558654	0.599187	0.105071
Ni	20	0.870329	0.909244	0.299789
Ni	21	0.172306	0.446934	0.008557
Ni	22	0.482467	0.754823	0.203980
Ni	23	0.816596	0.592065	0.105986
Ni	24	0.126687	0.899484	0.291727
Ni	25	0.229103	0.003497	0.206578
Ni	26	0.914340	0.688436	0.007440
Ni	27	0.577046	0.845893	0.108323
Ni	28	0.879447	0.148963	0.289206

Table G-2 Final fractional coordinates for the optimised Ni₇Al₉ (111) surface slab structure after the second Al atom removal

Ni₇Al₉ (111) surface slab structure final cell contents after the second Al atom removal				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.314163	0.341227	0.099259
Al	2	0.618405	0.641248	0.301218
Al	3	0.663283	0.181146	-0.008120
Al	4	0.966773	0.493741	0.200016
Al	5	0.185195	0.202445	0.013117
Al	6	0.488566	0.517653	0.206983
Al	7	0.215937	0.244893	0.205422
Al	8	0.904082	0.929853	-0.008801
Al	9	0.568760	0.085218	0.098159
Al	10	0.869503	0.391144	0.298319
Al	11	0.171943	0.945628	0.002166
Al	12	0.480520	0.252624	0.206526
Al	13	0.834573	0.104291	0.108205
Al	14	0.924984	0.199615	0.007449
Al	15	0.226384	0.508297	0.208856

Al	16	0.581486	0.351911	0.103917
Al	17	0.895484	0.652121	0.312312
Al	18	0.155751	0.685707	-0.007430
Al	19	0.472652	0.993263	0.203098
Al	20	0.109359	0.134440	0.298252
Al	21	0.814952	0.834501	0.097918
Al	22	0.334307	0.861558	0.112464
Al	23	0.637411	0.173022	0.317313
Al	24	0.055603	0.584500	0.098136
Al	25	0.367175	0.894196	0.302609
Al	26	0.412368	0.433468	-0.012501
Al	27	0.722706	0.739660	0.199360
Al	28	0.321419	0.600655	0.102626
Al	29	0.630834	0.906442	0.312113
Al	30	0.683856	0.456656	0.007237
Al	31	0.987194	0.761200	0.209715
Al	32	0.075089	0.851539	0.105955
Al	33	0.429981	0.701208	0.001580
Al	34	0.737116	0.009366	0.208156
Ni	1	0.822241	0.343473	0.103726
Ni	2	0.129743	0.656036	0.297639
Ni	3	0.081586	0.087200	0.104335
Ni	4	0.390008	0.405637	0.291582
Ni	5	0.407985	0.945972	0.016985
Ni	6	0.718010	0.254291	0.197834
Ni	7	0.326592	0.104501	0.112374
Ni	8	0.630346	0.404885	0.295227
Ni	9	0.664287	0.939898	0.007740
Ni	10	0.975246	0.252097	0.200768
Ni	11	0.073315	0.341327	0.109647
Ni	12	0.372545	0.656578	0.294676
Ni	13	0.425823	0.193250	0.009020
Ni	14	0.729258	0.498601	0.199126
Ni	15	0.664386	0.696989	0.014028
Ni	16	0.980627	-0.000530	0.197843
Ni	17	0.929103	0.433948	0.014555
Ni	18	0.234287	0.748253	0.195403
Ni	19	0.558209	0.599625	0.105314
Ni	20	0.870536	0.907786	0.299921
Ni	21	0.172525	0.447068	0.008596
Ni	22	0.481431	0.755651	0.203923
Ni	23	0.815674	0.591764	0.105952
Ni	24	0.126961	0.896223	0.291004
Ni	25	0.230709	0.002715	0.205465
Ni	26	0.913990	0.688799	0.007389
Ni	27	0.576622	0.845517	0.108264
Ni	28	0.875018	0.149679	0.289929

Table G-3 Final fractional coordinates for the optimised Ni₇Al₉ (111) surface slab structure after the third Al atom removal

Ni₇Al₉ (111) surface slab structure final cell contents after the third Al atom removal				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.323986	0.359993	0.094521
Al	2	0.579550	0.600608	0.308627
Al	3	0.679936	0.201835	-0.012340
Al	4	0.971305	0.491893	0.206999
Al	5	0.202786	0.219940	0.021710
Al	6	0.477450	0.528063	0.203238
Al	7	0.215333	0.266205	0.224748
Al	8	0.920572	0.949580	-0.012274
Al	9	0.576182	0.100039	0.089076
Al	10	0.828308	0.348291	0.293538
Al	11	0.190240	0.964385	0.003427
Al	12	0.485172	0.257746	0.196234
Al	13	0.849175	0.117402	0.103731
Al	14	0.939875	0.221942	0.007497
Al	15	0.592800	0.372340	0.100224
Al	16	0.864845	0.603754	0.320159
Al	17	0.171486	0.705336	-0.010721
Al	18	0.468224	1.006859	0.221116
Al	19	0.067401	0.089999	0.293649
Al	20	0.825060	0.844449	0.090940
Al	21	0.351451	0.880062	0.117783
Al	22	0.588185	0.124934	0.308465
Al	23	0.065058	0.588290	0.093092
Al	24	0.323291	0.852385	0.296981
Al	25	0.431622	0.456047	-0.014872
Al	26	0.732366	0.746475	0.210560
Al	27	0.330204	0.616561	0.099542
Al	28	0.601683	0.853576	0.322809
Al	29	0.702902	0.486148	0.011470
Al	30	1.015969	0.744632	0.201884
Al	31	0.088811	0.861850	0.102155
Al	32	0.446634	0.724055	0.004673
Al	33	0.743210	0.008017	0.198344
Ni	1	0.836914	0.358594	0.106158
Ni	2	0.102767	0.565069	0.279662
Ni	3	0.100418	0.098263	0.103985
Ni	4	0.349493	0.364138	0.282685
Ni	5	0.423593	0.971638	0.026990
Ni	6	0.724067	0.257403	0.190975
Ni	7	0.344887	0.131271	0.128500
Ni	8	0.584410	0.367139	0.287835
Ni	9	0.680016	0.961107	-0.000346
Ni	10	0.981545	0.248802	0.201587
Ni	11	0.090749	0.349426	0.119694

Ni	12	0.328001	0.613702	0.290223
Ni	13	0.439165	0.214871	0.000984
Ni	14	0.727338	0.508242	0.204693
Ni	15	0.674254	0.729334	0.025402
Ni	16	0.987535	-0.002647	0.193735
Ni	17	0.950824	0.451308	0.022242
Ni	18	0.245563	0.761431	0.192089
Ni	19	0.567587	0.622817	0.110090
Ni	20	0.837761	0.847959	0.286287
Ni	21	0.190383	0.464086	0.001836
Ni	22	0.492350	0.763816	0.212221
Ni	23	0.827089	0.608480	0.116382
Ni	24	0.086890	0.844418	0.289931
Ni	25	0.229547	0.021301	0.208003
Ni	26	0.930809	0.705864	0.001701
Ni	27	0.592589	0.874159	0.124546
Ni	28	0.828585	0.107096	0.287069

Table G-4 Final fractional coordinates for the optimised Ni₇Al₉ (111) surface slab structure after the fourth Al atom removal

Ni₇Al₉ (111) surface slab structure final cell contents after the fourth Al atom removal				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.257603	0.403917	0.120928
Al	2	0.554531	0.580459	0.305042
Al	3	0.679123	0.213832	-0.006711
Al	4	0.959167	0.484067	0.203221
Al	5	0.196785	0.276734	0.019219
Al	6	0.453186	0.516099	0.194574
Al	7	0.181107	0.249346	0.237537
Al	8	0.937782	0.994127	0.000173
Al	9	0.591834	0.135079	0.105824
Al	10	0.795636	0.324476	0.303414
Al	11	0.261120	0.946448	-0.020488
Al	12	0.444196	0.254729	0.209353
Al	13	0.901230	0.156753	0.122173
Al	14	0.927198	0.269130	0.012100
Al	15	0.621208	0.382452	0.097411
Al	16	0.849954	0.560975	0.316971
Al	17	0.180154	0.736912	-0.028123
Al	18	0.416397	0.994890	0.219987
Al	19	0.044331	0.050623	0.280997
Al	20	0.845255	0.855986	0.114487
Al	21	0.355491	0.888239	0.109634
Al	22	0.558119	0.108211	0.318737
Al	23	0.297112	0.820986	0.290065
Al	24	0.450284	0.489337	-0.017500
Al	25	0.722709	0.695795	0.171392
Al	26	0.325464	0.621530	0.088996

Al	27	0.626390	0.818244	0.295012
Al	28	0.699388	0.523103	0.004798
Al	29	1.109184	0.657470	0.193086
Al	30	0.093162	0.873522	0.099503
Al	31	0.549529	0.807733	0.008765
Al	32	0.697690	-0.016877	0.211792
Ni	1	0.824605	0.449720	0.107964
Ni	2	0.095296	0.521537	0.284024
Ni	3	0.126337	0.080703	0.062609
Ni	4	0.328622	0.321216	0.303338
Ni	5	0.402928	1.046442	0.030699
Ni	6	0.687509	0.232240	0.187154
Ni	7	0.340103	0.151027	0.132995
Ni	8	0.553170	0.349586	0.286576
Ni	9	0.694487	0.967476	0.021889
Ni	10	0.938461	0.258726	0.213962
Ni	11	0.075324	0.301149	0.124661
Ni	12	0.308348	0.574301	0.283306
Ni	13	0.435610	0.281213	0.029270
Ni	14	0.701203	0.477902	0.207066
Ni	15	0.767564	0.696574	0.059427
Ni	16	0.951865	-0.054149	0.193040
Ni	17	0.963498	0.483485	0.014699
Ni	18	0.255918	0.772374	0.182678
Ni	19	0.555202	0.637669	0.104813
Ni	20	0.875290	0.742433	0.246754
Ni	21	0.203358	0.519620	0.020808
Ni	22	0.494687	0.742387	0.215505
Ni	23	1.006004	0.577913	0.110405
Ni	24	0.070580	0.801317	0.286823
Ni	25	0.164075	0.046349	0.179911
Ni	26	0.967584	0.752978	0.022386
Ni	27	0.578427	0.911625	0.119583
Ni	28	0.792768	0.096350	0.284338

G.2 Fractional coordinates for Ni₈Al₈ (111) surface slab structures after Al atom removal

Table G-5 Final fractional coordinates for the optimised Ni₈Al₈ (111) surface slab structure after the first Al atom removal

Ni ₈ Al ₈ (111) surface slab structure final cell contents after the first Al atom removal				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.245756	0.335908	0.097850
Al	2	0.617543	0.633179	0.292858
Al	3	0.521956	0.198175	0.011459
Al	4	0.896085	0.515169	0.206601
Al	5	0.065440	0.191531	-0.006884
Al	6	0.442927	0.503262	0.202137
Al	7	0.169141	0.252221	0.204636

Al	8	0.792409	0.939952	0.000902
Al	9	0.967980	0.100894	0.105713
Al	10	0.350591	0.434585	0.313250
Al	11	0.071672	0.931197	-0.010590
Al	12	0.445842	0.244191	0.198180
Al	13	0.783581	0.197585	0.004561
Al	14	0.165604	0.507435	0.206635
Al	15	0.970166	0.349004	0.102740
Al	16	0.064514	0.670583	-0.009371
Al	17	0.431992	0.987683	0.196922
Al	18	0.082146	0.171317	0.317520
Al	19	0.709659	0.859514	0.111496
Al	20	0.257147	0.839503	0.101370
Al	21	0.635831	0.156145	0.301534
Al	22	0.981507	0.599524	0.103433
Al	23	0.354146	0.894246	0.306642
Al	24	0.770643	0.452918	0.003480
Al	25	0.159669	0.757161	0.213419
Al	26	0.262705	0.584014	0.098240
Al	27	0.634897	0.893030	0.300032
Al	28	0.358309	0.160026	0.308694
Al	29	0.980721	0.847026	0.105713
Al	30	0.157006	0.004961	0.206419
Al	31	0.777876	0.695140	-0.002037
Ni	1	0.737101	0.343198	0.101776
Ni	2	0.097674	0.654942	0.297896
Ni	3	0.473098	0.098508	0.108561
Ni	4	0.856776	0.402394	0.292781
Ni	5	0.297798	0.945103	0.012215
Ni	6	0.682298	0.245107	0.196222
Ni	7	0.733605	0.086462	0.102208
Ni	8	0.113908	0.398087	0.296510
Ni	9	0.213033	0.102791	0.111831
Ni	10	0.606683	0.398284	0.290219
Ni	11	0.554018	0.940189	0.013661
Ni	12	0.934032	0.251328	0.195920
Ni	13	0.490217	0.343571	0.107951
Ni	14	0.858738	0.650774	0.296686
Ni	15	0.296687	0.183262	0.012780
Ni	16	0.674380	0.498750	0.195738
Ni	17	0.540651	0.696694	0.012618
Ni	18	0.921657	-0.003177	0.196481
Ni	19	0.290919	0.440317	0.009512
Ni	20	0.661758	0.752959	0.201967
Ni	21	0.493539	0.594266	0.105826
Ni	22	0.865640	0.906365	0.291232
Ni	23	0.541979	0.436951	0.013198
Ni	24	0.916666	0.747607	0.197496
Ni	25	0.025141	0.448720	0.013405
Ni	26	0.404284	0.759972	0.203278

Ni	27	0.745875	0.597394	0.102294
Ni	28	0.104693	0.920355	0.298184
Ni	29	0.296923	0.691056	0.008581
Ni	30	0.668592	0.003366	0.204694
Ni	31	0.485966	0.843241	0.105472
Ni	32	0.864564	0.157437	0.286788

Table G-6 Final fractional coordinates for the optimised Ni₈Al₈ (111) surface slab structure after the second Al atom removal

Ni₈Al₈ (111) surface slab structure final cell contents after the second Al atom removal				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.246661	0.334890	0.098800
Al	2	0.607740	0.638250	0.288428
Al	3	0.523228	0.196581	0.011961
Al	4	0.897834	0.515771	0.206784
Al	5	0.065968	0.191732	-0.007359
Al	6	0.444592	0.503110	0.201109
Al	7	0.171303	0.250643	0.205471
Al	8	0.793929	0.939228	0.000724
Al	9	0.970185	0.099199	0.106259
Al	10	0.347340	0.437918	0.312138
Al	11	0.073095	0.930351	-0.010589
Al	12	0.446974	0.243973	0.198647
Al	13	0.785636	0.196020	0.003720
Al	14	0.167120	0.506875	0.205990
Al	15	0.970433	0.348989	0.102737
Al	16	0.066122	0.670056	-0.009245
Al	17	0.431364	0.985502	0.199892
Al	18	0.082059	0.171061	0.316658
Al	19	0.710536	0.858600	0.111377
Al	20	0.257505	0.838724	0.101974
Al	21	0.634159	0.160427	0.300708
Al	22	0.982795	0.599064	0.103276
Al	23	0.770347	0.453277	0.003398
Al	24	0.163356	0.755695	0.215396
Al	25	0.263586	0.583377	0.098280
Al	26	0.629375	0.900679	0.299858
Al	27	0.356745	0.162070	0.309363
Al	28	0.981489	0.846323	0.106076
Al	29	0.163096	0.000480	0.211086
Al	30	0.779549	0.694579	-0.002428
Ni	1	0.738964	0.340554	0.100429
Ni	2	0.089838	0.655694	0.297145
Ni	3	0.472973	0.097247	0.109752
Ni	4	0.853395	0.405326	0.292447
Ni	5	0.297608	0.945522	0.013281
Ni	6	0.684320	0.245093	0.195875
Ni	7	0.734608	0.085673	0.101964

Ni	8	0.108621	0.402164	0.296321
Ni	9	0.212278	0.102181	0.113375
Ni	10	0.605235	0.402593	0.289717
Ni	11	0.554944	0.939866	0.013960
Ni	12	0.937092	0.249882	0.195599
Ni	13	0.491429	0.342569	0.107957
Ni	14	0.848175	0.654327	0.297997
Ni	15	0.297428	0.182080	0.013990
Ni	16	0.678009	0.496006	0.193983
Ni	17	0.541417	0.698428	0.012489
Ni	18	0.924260	-0.004429	0.196584
Ni	19	0.291422	0.438573	0.010143
Ni	20	0.661285	0.754231	0.202812
Ni	21	0.496143	0.591615	0.103783
Ni	22	0.861247	0.909036	0.290890
Ni	23	0.543069	0.434374	0.012321
Ni	24	0.917276	0.747242	0.197886
Ni	25	0.026334	0.447929	0.013421
Ni	26	0.406946	0.755757	0.199909
Ni	27	0.746289	0.598476	0.102186
Ni	28	0.096448	0.920226	0.299525
Ni	29	0.298584	0.690004	0.008814
Ni	30	0.670941	0.003765	0.203434
Ni	31	0.485617	0.844876	0.105812
Ni	32	0.863891	0.158785	0.286603

Table G-7 Final fractional coordinates for the optimised Ni₈Al₈ (111) surface slab structure after the third Al atom removal

Ni₈Al₈ (111) surface slab structure final cell contents after the third Al atom removal				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.246063	0.335100	0.098751
Al	2	0.605723	0.637769	0.288947
Al	3	0.524382	0.195403	0.012326
Al	4	0.898019	0.516202	0.206121
Al	5	0.066749	0.191348	-0.007199
Al	6	0.445390	0.503662	0.199652
Al	7	0.172051	0.249602	0.206811
Al	8	0.795587	0.938037	0.001222
Al	9	0.970786	0.098284	0.106166
Al	10	0.343006	0.449622	0.311468
Al	11	0.073986	0.929642	-0.010221
Al	12	0.441780	0.246951	0.201270
Al	13	0.786514	0.195286	0.003763
Al	14	0.166712	0.507597	0.205549
Al	15	0.971008	0.348505	0.102687
Al	16	0.067426	0.668842	-0.009393
Al	17	0.430718	0.984241	0.199055

Al	18	0.086352	0.173237	0.313373
Al	19	0.711390	0.859021	0.112240
Al	20	0.258283	0.838101	0.102307
Al	21	0.634437	0.159735	0.301028
Al	22	0.982996	0.599264	0.103105
Al	23	0.770906	0.452778	0.003393
Al	24	0.163675	0.755517	0.217375
Al	25	0.264871	0.582314	0.097828
Al	26	0.637445	0.895225	0.298087
Al	27	0.983800	0.844753	0.106651
Al	28	0.162945	0.000969	0.210951
Al	29	0.780310	0.694296	-0.002579
Ni	1	0.738785	0.339917	0.100401
Ni	2	0.084939	0.656280	0.297561
Ni	3	0.472924	0.098259	0.110665
Ni	4	0.852598	0.404855	0.291955
Ni	5	0.298537	0.944980	0.013511
Ni	6	0.683468	0.244339	0.195755
Ni	7	0.735628	0.084347	0.102205
Ni	8	0.101488	0.408242	0.293401
Ni	9	0.212248	0.102446	0.113362
Ni	10	0.603295	0.401384	0.289504
Ni	11	0.556476	0.939591	0.014520
Ni	12	0.934264	0.250273	0.194732
Ni	13	0.491574	0.340785	0.108331
Ni	14	0.846301	0.650539	0.298674
Ni	15	0.298471	0.181207	0.014437
Ni	16	0.678554	0.495504	0.194231
Ni	17	0.542205	0.698103	0.011589
Ni	18	0.924060	-0.004887	0.196809
Ni	19	0.292358	0.437134	0.009907
Ni	20	0.660992	0.752944	0.202791
Ni	21	0.497302	0.591814	0.103270
Ni	22	0.861509	0.911810	0.291681
Ni	23	0.543723	0.433333	0.012281
Ni	24	0.915983	0.748658	0.198181
Ni	25	0.026646	0.447757	0.013228
Ni	26	0.406903	0.756189	0.199945
Ni	27	0.747106	0.597602	0.101775
Ni	28	0.097104	0.923471	0.300202
Ni	29	0.299517	0.689347	0.008813
Ni	30	0.663877	0.006838	0.205475
Ni	31	0.487272	0.843451	0.105201
Ni	32	0.864039	0.159223	0.286401

Table G-8 Final fractional coordinates for the optimised Ni₈Al₈ (111) surface slab structure after the fourth Al atom removal

Ni₈Al₈ (111) surface slab structure final cell contents after the fourth Al atom removal				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.243779	0.330662	0.103627
Al	2	0.602452	0.639547	0.288653
Al	3	0.524744	0.194907	0.012772
Al	4	0.907818	0.505548	0.206061
Al	5	0.067014	0.190505	-0.007624
Al	6	0.445910	0.504790	0.199442
Al	7	0.796822	0.937150	0.001289
Al	8	0.971493	0.098860	0.106996
Al	9	0.340014	0.447010	0.310083
Al	10	0.075179	0.928538	-0.010470
Al	11	0.432401	0.249554	0.204166
Al	12	0.787522	0.194335	0.004085
Al	13	0.166010	0.507463	0.205159
Al	14	0.973009	0.345720	0.102996
Al	15	0.068857	0.667173	-0.009312
Al	16	0.424849	0.990084	0.198740
Al	17	0.093045	0.181729	0.302429
Al	18	0.712746	0.858487	0.112424
Al	19	0.259722	0.837200	0.101384
Al	20	0.635670	0.160722	0.300746
Al	21	0.984452	0.597127	0.103531
Al	22	0.770043	0.452355	0.004170
Al	23	0.162841	0.755821	0.217591
Al	24	0.266589	0.581447	0.098036
Al	25	0.639688	0.893623	0.297302
Al	26	0.984966	0.843938	0.106982
Al	27	0.161137	0.003368	0.207660
Al	28	0.781214	0.693462	-0.002237
Ni	1	0.738634	0.339215	0.100973
Ni	2	0.082054	0.656939	0.297190
Ni	3	0.474179	0.098598	0.111829
Ni	4	0.849936	0.406382	0.292247
Ni	5	0.299137	0.944966	0.013159
Ni	6	0.681524	0.244734	0.195854
Ni	7	0.736594	0.083858	0.102416
Ni	8	0.102511	0.409885	0.291194
Ni	9	0.213841	0.100907	0.114901
Ni	10	0.600945	0.402941	0.289418
Ni	11	0.557113	0.940061	0.015150
Ni	12	0.937755	0.251140	0.195509
Ni	13	0.490301	0.339296	0.109556
Ni	14	0.845349	0.647526	0.297760
Ni	15	0.297073	0.182166	0.016557
Ni	16	0.680070	0.495601	0.194335

Ni	17	0.543011	0.698784	0.011716
Ni	18	0.921716	-0.004099	0.196962
Ni	19	0.289596	0.434087	0.012626
Ni	20	0.661619	0.751591	0.202140
Ni	21	0.498609	0.591962	0.103285
Ni	22	0.861571	0.914907	0.291680
Ni	23	0.543261	0.430992	0.013356
Ni	24	0.912915	0.750804	0.198427
Ni	25	0.026576	0.446510	0.013144
Ni	26	0.406573	0.757889	0.200085
Ni	27	0.747803	0.597052	0.101754
Ni	28	0.099365	0.927283	0.298360
Ni	29	0.300397	0.688228	0.008624
Ni	30	0.658478	0.009900	0.205982
Ni	31	0.487691	0.844102	0.105585
Ni	32	0.865226	0.162107	0.286264

G.3 Fractional coordinates for Ni₉Al₇ (111) surface slab structures after Al atom removal

Table G-9 Final fractional coordinates for the optimised Ni₉Al₇ (111) surface slab structure after the first Al atom removal

Ni ₉ Al ₇ (111) surface slab structure final cell contents after the first Al atom removal				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.316857	0.343527	0.098697
Al	2	0.661527	0.186311	-0.003790
Al	3	0.970060	0.495585	0.199584
Al	4	0.222367	0.245555	0.200584
Al	5	0.909535	0.933277	-0.006828
Al	6	0.572571	0.091014	0.097713
Al	7	0.877389	0.412700	0.302313
Al	8	0.188593	0.939464	0.002809
Al	9	0.494551	0.255384	0.202926
Al	10	0.306964	0.079646	0.098001
Al	11	0.621902	0.393042	0.290674
Al	12	0.914841	0.207538	0.010255
Al	13	0.228347	0.518291	0.207126
Al	14	0.165985	0.685520	-0.007710
Al	15	0.477763	0.999210	0.206266
Al	16	0.123904	0.148830	0.301754
Al	17	0.814928	0.839826	0.097983
Al	18	0.064829	0.587818	0.097269
Al	19	0.378889	0.889847	0.306893
Al	20	0.422803	0.436949	-0.007989
Al	21	0.728977	0.747438	0.204659
Al	22	0.339082	0.597088	0.102745
Al	23	0.657799	0.892961	0.314625
Al	24	0.145100	0.423753	-0.013067
Al	25	0.467765	0.736969	0.197077

Al	26	0.069189	0.861155	0.107871
Al	27	0.384317	0.175419	0.318107
Ni	1	0.163817	0.185320	0.007908
Ni	2	0.480786	0.494747	0.195280
Ni	3	0.818274	0.345892	0.108428
Ni	4	0.124695	0.664649	0.293200
Ni	5	0.060951	0.099209	0.105485
Ni	6	0.376399	0.410414	0.295057
Ni	7	0.429887	0.930241	0.011939
Ni	8	0.734517	0.245778	0.194062
Ni	9	0.819715	0.086948	0.096976
Ni	10	0.130396	0.399550	0.291335
Ni	11	0.667073	0.938095	0.006820
Ni	12	0.978545	0.252842	0.203539
Ni	13	0.564507	0.337415	0.098987
Ni	14	0.889202	0.652378	0.290946
Ni	15	0.073069	0.342284	0.106116
Ni	16	0.373016	0.656458	0.288178
Ni	17	0.410539	0.195359	0.008068
Ni	18	0.724459	0.504786	0.205966
Ni	19	0.320181	0.839637	0.102334
Ni	20	0.635959	0.138772	0.291591
Ni	21	0.664984	0.688278	0.016354
Ni	22	0.971253	0.007395	0.198588
Ni	23	0.903102	0.449724	0.015961
Ni	24	0.218620	0.756964	0.196102
Ni	25	0.580553	0.589121	0.105128
Ni	26	0.885750	0.903266	0.285199
Ni	27	0.664240	0.432402	0.011916
Ni	28	0.976128	0.742517	0.189651
Ni	29	0.820158	0.598965	0.110517
Ni	30	0.129419	0.908039	0.291507
Ni	31	0.414477	0.679653	0.008462
Ni	32	0.720961	0.995649	0.191164
Ni	33	0.920149	0.685567	0.005935
Ni	34	0.233115	0.999946	0.199944
Ni	35	0.569897	0.849647	0.112784
Ni	36	0.876733	0.161562	0.291503

Table G-10 Final fractional coordinates for the optimised Ni₉Al₇ (111) surface slab structure after the second Al atom removal

Ni ₉ Al ₇ (111) surface slab structure final cell contents after the second Al atom removal				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.316110	0.343346	0.098232
Al	2	0.661980	0.187789	-0.004509
Al	3	0.969997	0.494119	0.199220
Al	4	0.222611	0.245090	0.201031
Al	5	0.911017	0.934292	-0.007329

Al	6	0.571843	0.091088	0.096365
Al	7	0.875864	0.411368	0.301782
Al	8	0.191118	0.939166	0.003457
Al	9	0.493566	0.257355	0.201782
Al	10	0.308254	0.078809	0.099981
Al	11	0.622480	0.384641	0.289698
Al	12	0.915223	0.209947	0.010062
Al	13	0.227545	0.518757	0.206767
Al	14	0.166028	0.686399	-0.008346
Al	15	0.482183	1.001337	0.212352
Al	16	0.118454	0.150529	0.301575
Al	17	0.814436	0.839270	0.096853
Al	18	0.063214	0.586914	0.096203
Al	19	0.369051	0.895651	0.305529
Al	20	0.422598	0.437765	-0.008352
Al	21	0.730914	0.753658	0.212710
Al	22	0.338206	0.597027	0.102522
Al	23	0.144907	0.423711	-0.013810
Al	24	0.470505	0.738757	0.198554
Al	25	0.070126	0.859462	0.107386
Al	26	0.381113	0.174304	0.318047
Ni	1	0.165635	0.185145	0.009095
Ni	2	0.480254	0.496239	0.195156
Ni	3	0.817233	0.348057	0.108365
Ni	4	0.128897	0.664162	0.293443
Ni	5	0.061024	0.098226	0.104731
Ni	6	0.375592	0.410382	0.295014
Ni	7	0.432385	0.930887	0.014372
Ni	8	0.734257	0.246285	0.192335
Ni	9	0.819983	0.087396	0.095330
Ni	10	0.133572	0.394822	0.291779
Ni	11	0.668344	0.939228	0.005410
Ni	12	0.977789	0.252232	0.202683
Ni	13	0.563552	0.338184	0.098348
Ni	14	0.906678	0.638558	0.290515
Ni	15	0.073456	0.341060	0.106528
Ni	16	0.375893	0.656792	0.288682
Ni	17	0.410962	0.195986	0.007366
Ni	18	0.722434	0.508754	0.207396
Ni	19	0.322450	0.838543	0.103244
Ni	20	0.633194	0.129687	0.287790
Ni	21	0.665379	0.690671	0.018413
Ni	22	0.970807	0.007133	0.197098
Ni	23	0.902937	0.452273	0.017582
Ni	24	0.220240	0.756821	0.196079
Ni	25	0.579354	0.590398	0.105571
Ni	26	0.879707	0.899557	0.281666
Ni	27	0.663815	0.434254	0.012196
Ni	28	0.976798	0.740526	0.188715
Ni	29	0.816915	0.602624	0.113282

Ni	30	0.122708	0.910283	0.290497
Ni	31	0.414842	0.680218	0.008871
Ni	32	0.721970	0.995743	0.188085
Ni	33	0.920005	0.686687	0.004782
Ni	34	0.231418	1.001394	0.199273
Ni	35	0.571113	0.851389	0.117360
Ni	36	0.873628	0.159476	0.290034

Table G-11 Final fractional coordinates for the optimised Ni₉Al₇ (111) surface slab structure after the third Al atom removal

Ni₉Al₇ (111) surface slab structure final cell contents after the third Al atom removal				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.318326	0.342113	0.084440
Al	2	0.679498	0.202291	-0.009690
Al	3	0.967342	0.500838	0.213345
Al	4	0.224186	0.245071	0.220278
Al	5	0.926565	0.949151	-0.010756
Al	6	0.573394	0.088055	0.081966
Al	7	0.857635	0.394652	0.306866
Al	8	0.207213	0.959042	0.008861
Al	9	0.496090	0.240687	0.186952
Al	10	0.315565	0.083216	0.117888
Al	11	0.600655	0.372725	0.286846
Al	12	0.933604	0.224570	0.013876
Al	13	0.225207	0.514492	0.192921
Al	14	0.182120	0.702416	-0.013793
Al	15	0.479083	0.998120	0.235499
Al	16	0.105752	0.136163	0.307054
Al	17	0.807915	0.835310	0.085747
Al	18	0.058537	0.586662	0.087338
Al	19	0.345087	0.856753	0.309140
Al	20	0.440414	0.453632	-0.014493
Al	21	0.730609	0.757511	0.219282
Al	22	0.341807	0.601033	0.097713
Al	23	0.153861	0.435242	-0.025745
Al	24	0.469575	0.729074	0.202715
Al	25	0.068595	0.863032	0.103148
Ni	1	0.185943	0.207095	0.023495
Ni	2	0.479282	0.485580	0.189642
Ni	3	0.823445	0.352083	0.111604
Ni	4	0.100525	0.643867	0.281835
Ni	5	0.066796	0.102622	0.108913
Ni	6	0.356462	0.365356	0.276975
Ni	7	0.448692	0.951409	0.026343
Ni	8	0.733456	0.242765	0.190267
Ni	9	0.822628	0.090928	0.092033
Ni	10	0.102738	0.393451	0.305456
Ni	11	0.684132	0.950345	-0.009277

Ni	12	0.976360	0.250340	0.207081
Ni	13	0.569037	0.338999	0.092681
Ni	14	0.868901	0.635211	0.305862
Ni	15	0.086043	0.347420	0.123870
Ni	16	0.356543	0.620574	0.283911
Ni	17	0.425889	0.214424	-0.008549
Ni	18	0.719004	0.503411	0.211049
Ni	19	0.324323	0.844307	0.107585
Ni	20	0.627804	0.116624	0.277074
Ni	21	0.681364	0.706419	0.025630
Ni	22	0.966964	0.003990	0.194949
Ni	23	0.924070	0.466768	0.026800
Ni	24	0.213368	0.756881	0.194211
Ni	25	0.583301	0.594861	0.108032
Ni	26	0.862569	0.885173	0.275132
Ni	27	0.681022	0.448174	0.014470
Ni	28	0.970803	0.741637	0.177951
Ni	29	0.819622	0.604484	0.125093
Ni	30	0.097863	0.898480	0.290833
Ni	31	0.429070	0.696047	0.011102
Ni	32	0.717232	0.992300	0.177221
Ni	33	0.938107	0.698453	-0.007645
Ni	34	0.232182	0.998572	0.208662
Ni	35	0.568878	0.857258	0.130635
Ni	36	0.860397	0.148159	0.288476

Table G-12 Final fractional coordinates for the optimised Ni₉Al₇ (111) surface slab structure after the fourth Al atom removal

Ni₉Al₇ (111) surface slab structure final cell contents after the fourth Al atom removal				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.321080	0.341383	0.083632
Al	2	0.680118	0.203650	-0.010221
Al	3	0.963059	0.503232	0.213725
Al	4	0.242302	0.223615	0.227501
Al	5	0.927156	0.950062	-0.011679
Al	6	0.575030	0.087729	0.081385
Al	7	0.857540	0.392972	0.306798
Al	8	0.207223	0.960927	0.008564
Al	9	0.496636	0.231235	0.187533
Al	10	0.321043	0.080436	0.121497
Al	11	0.599953	0.372435	0.286506
Al	12	0.934634	0.226828	0.013900
Al	13	0.223128	0.505910	0.191667
Al	14	0.182880	0.703147	-0.014125
Al	15	0.102169	0.131670	0.308115
Al	16	0.808948	0.835719	0.084586
Al	17	0.057530	0.586078	0.087827

Al	18	0.342886	0.861485	0.306111
Al	19	0.441444	0.454581	-0.014569
Al	20	0.710533	0.781969	0.223450
Al	21	0.341440	0.601245	0.097411
Al	22	0.154083	0.435315	-0.025332
Al	23	0.465977	0.734494	0.201062
Al	24	0.067743	0.864617	0.102612
Ni	1	0.188421	0.207942	0.025865
Ni	2	0.476518	0.484724	0.189556
Ni	3	0.825717	0.354057	0.112993
Ni	4	0.100069	0.639489	0.280663
Ni	5	0.067728	0.105161	0.108675
Ni	6	0.357370	0.365986	0.276609
Ni	7	0.447920	0.953913	0.026339
Ni	8	0.732095	0.244928	0.190023
Ni	9	0.824821	0.095047	0.090494
Ni	10	0.102480	0.391472	0.304975
Ni	11	0.684361	0.951537	-0.010318
Ni	12	0.979184	0.249530	0.207824
Ni	13	0.569655	0.338572	0.093030
Ni	14	0.864702	0.635753	0.304351
Ni	15	0.094652	0.345468	0.127702
Ni	16	0.353679	0.623044	0.283457
Ni	17	0.427236	0.214931	-0.009459
Ni	18	0.714323	0.508913	0.212687
Ni	19	0.323815	0.845774	0.107270
Ni	20	0.631580	0.116053	0.276345
Ni	21	0.682036	0.706609	0.025403
Ni	22	0.966351	0.004691	0.194210
Ni	23	0.925774	0.467418	0.029193
Ni	24	0.212565	0.749728	0.192171
Ni	25	0.583268	0.593529	0.108043
Ni	26	0.862938	0.884426	0.274374
Ni	27	0.682384	0.448277	0.014893
Ni	28	0.967095	0.742875	0.177582
Ni	29	0.814519	0.609850	0.126774
Ni	30	0.099516	0.890775	0.289237
Ni	31	0.429298	0.697104	0.011019
Ni	32	0.723882	0.994407	0.175132
Ni	33	0.939365	0.698602	-0.007951
Ni	34	0.222350	0.994461	0.207582
Ni	35	0.572983	0.854438	0.128347
Ni	36	0.859182	0.147981	0.288257

G.4 Fractional coordinates for Ni₁₁Al₅ (111) surface slab structures after Al atom removal

Table G-13 Final fractional coordinates for the optimised Ni₁₁Al₅ (111) surface slab structure after the first Al atom removal

Ni ₁₁ Al ₅ (111) surface slab structure final cell contents after the first Al atom removal				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.304354	0.315124	0.093688
Al	2	0.609525	0.177280	0.005350
Al	3	0.939029	0.497320	0.201138
Al	4	0.205852	0.235033	0.197044
Al	5	0.873137	0.914726	-0.005566
Al	6	0.151382	0.920229	0.000334
Al	7	0.483072	0.241149	0.199854
Al	8	0.879405	0.186716	0.007387
Al	9	0.211065	0.506716	0.204375
Al	10	0.142405	0.648623	-0.014419
Al	11	0.470072	0.976328	0.191584
Al	12	0.100788	0.162088	0.301897
Al	13	0.773897	0.836364	0.105096
Al	14	0.038850	0.575026	0.097170
Al	15	0.377511	0.883195	0.296519
Al	16	0.316769	0.581411	0.099584
Al	17	0.650583	0.895651	0.298843
Al	18	0.043164	0.844878	0.107130
Al	19	0.377788	0.167724	0.313250
Ni	1	0.130441	0.170207	0.009660
Ni	2	0.460599	0.492945	0.195440
Ni	3	0.796636	0.332246	0.104992
Ni	4	0.124447	0.658989	0.294083
Ni	5	0.541528	0.081505	0.103680
Ni	6	0.864292	0.412053	0.292873
Ni	7	0.043452	0.083961	0.103119
Ni	8	0.376149	0.403648	0.292805
Ni	9	0.389916	0.914753	0.008249
Ni	10	0.718589	0.239829	0.195341
Ni	11	0.796481	0.076056	0.098940
Ni	12	0.127745	0.396459	0.290220
Ni	13	0.292840	0.077290	0.102770
Ni	14	0.622813	0.399863	0.288119
Ni	15	0.632047	0.917935	0.007368
Ni	16	0.960578	0.243664	0.199787
Ni	17	0.550821	0.328378	0.103148
Ni	18	0.889962	0.651092	0.292209
Ni	19	0.045903	0.332362	0.106355
Ni	20	0.371321	0.647739	0.288466
Ni	21	0.377507	0.161862	0.003950
Ni	22	0.701720	0.495945	0.199799
Ni	23	0.292764	0.832368	0.101841
Ni	24	0.625511	0.151936	0.294948

Ni	25	0.634282	0.666902	0.009354
Ni	26	0.960947	0.997284	0.198071
Ni	27	0.376844	0.420335	0.006722
Ni	28	0.702328	0.741831	0.203262
Ni	29	0.880353	0.426141	0.012457
Ni	30	0.209108	0.746580	0.195651
Ni	31	0.552742	0.578342	0.102916
Ni	32	0.884933	0.903127	0.289580
Ni	33	0.628735	0.419290	0.010371
Ni	34	0.959660	0.736810	0.191891
Ni	35	0.129676	0.414967	0.005732
Ni	36	0.458556	0.739377	0.198149
Ni	37	0.794596	0.582262	0.105863
Ni	38	0.124818	0.907744	0.291802
Ni	39	0.382062	0.668047	0.005558
Ni	40	0.713301	0.992596	0.198359
Ni	41	0.883231	0.672446	0.007771
Ni	42	0.213746	0.993890	0.199787
Ni	43	0.543043	0.824388	0.101523
Ni	44	0.866932	0.155801	0.291619

Table G-14 Final fractional coordinates for the optimised Ni₁₁Al₅ (111) surface slab structure after the second Al atom removal

Ni₁₁Al₅ (111) surface slab structure final cell contents after the second Al atom removal				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.304502	0.314671	0.093510
Al	2	0.609084	0.177164	0.005749
Al	3	0.938680	0.497459	0.201061
Al	4	0.205974	0.234134	0.196885
Al	5	0.872865	0.914954	-0.005665
Al	6	0.151224	0.920309	0.000288
Al	7	0.483121	0.241101	0.199628
Al	8	0.879178	0.186807	0.007763
Al	9	0.210609	0.505987	0.204089
Al	10	0.142365	0.648667	-0.014682
Al	11	0.466771	0.975136	0.195034
Al	12	0.105961	0.157550	0.300728
Al	13	0.773846	0.836156	0.104736
Al	14	0.038861	0.574953	0.096907
Al	15	0.316814	0.581142	0.099329
Al	16	0.652298	0.894231	0.297085
Al	17	0.042810	0.845039	0.106721
Al	18	0.376526	0.171302	0.312173
Ni	1	0.130334	0.170164	0.010121
Ni	2	0.460416	0.493450	0.195488
Ni	3	0.796236	0.332782	0.105398
Ni	4	0.125800	0.659243	0.293629
Ni	5	0.540701	0.080504	0.104633

Ni	6	0.865341	0.410933	0.292753
Ni	7	0.043490	0.084132	0.103537
Ni	8	0.376309	0.406687	0.292293
Ni	9	0.389861	0.914605	0.008752
Ni	10	0.718727	0.239445	0.195601
Ni	11	0.796271	0.076240	0.098747
Ni	12	0.127293	0.396989	0.290161
Ni	13	0.292984	0.076808	0.103410
Ni	14	0.623414	0.399277	0.288040
Ni	15	0.631662	0.918179	0.007501
Ni	16	0.960380	0.244048	0.199804
Ni	17	0.550666	0.328376	0.103246
Ni	18	0.890731	0.651140	0.292034
Ni	19	0.045974	0.332553	0.106375
Ni	20	0.371361	0.652304	0.287562
Ni	21	0.377327	0.161465	0.004018
Ni	22	0.700840	0.496917	0.200107
Ni	23	0.292845	0.832328	0.102131
Ni	24	0.625794	0.150896	0.294897
Ni	25	0.633737	0.667554	0.009881
Ni	26	0.961097	0.996946	0.197935
Ni	27	0.376669	0.420278	0.006638
Ni	28	0.700400	0.742432	0.203404
Ni	29	0.880058	0.426276	0.012620
Ni	30	0.208931	0.746053	0.195237
Ni	31	0.552097	0.579464	0.103271
Ni	32	0.886178	0.903402	0.289275
Ni	33	0.628285	0.419910	0.010686
Ni	34	0.959416	0.736270	0.191384
Ni	35	0.129564	0.414904	0.005622
Ni	36	0.456338	0.740271	0.198591
Ni	37	0.794586	0.582659	0.105984
Ni	38	0.127231	0.905000	0.290130
Ni	39	0.381606	0.668384	0.005509
Ni	40	0.714436	0.992109	0.197667
Ni	41	0.883014	0.672557	0.007632
Ni	42	0.213978	0.992132	0.200900
Ni	43	0.542338	0.825691	0.102525
Ni	44	0.868886	0.155114	0.291870

Table G-15 Final fractional coordinates for the optimised Ni₁₁Al₅ (111) surface slab structure after the third Al atom removal

Ni₁₁Al₅ (111) surface slab structure final cell contents after the third Al atom removal				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.304011	0.315286	0.093406
Al	2	0.608799	0.177074	0.006252
Al	3	0.938365	0.498076	0.200819

Al	4	0.207003	0.235364	0.198137
Al	5	0.872445	0.915112	-0.005907
Al	6	0.151010	0.920318	0.000088
Al	7	0.481384	0.240398	0.200949
Al	8	0.878949	0.186674	0.007803
Al	9	0.210911	0.506203	0.203281
Al	10	0.142109	0.648686	-0.014858
Al	11	0.466969	0.973785	0.195599
Al	12	0.107502	0.159245	0.298793
Al	13	0.773519	0.836646	0.105059
Al	14	0.038431	0.575124	0.096680
Al	15	0.316699	0.581061	0.099161
Al	16	0.657334	0.894382	0.296891
Al	17	0.042794	0.844852	0.106288
Ni	1	0.130427	0.170031	0.010516
Ni	2	0.460279	0.493014	0.195548
Ni	3	0.795547	0.333181	0.105081
Ni	4	0.125997	0.658704	0.293326
Ni	5	0.539794	0.080720	0.105210
Ni	6	0.867533	0.409757	0.292808
Ni	7	0.043489	0.083978	0.103490
Ni	8	0.375648	0.400453	0.291253
Ni	9	0.389323	0.914844	0.009285
Ni	10	0.718086	0.239674	0.195261
Ni	11	0.795598	0.076101	0.098873
Ni	12	0.126087	0.400494	0.287658
Ni	13	0.292736	0.077516	0.104065
Ni	14	0.622684	0.398363	0.288459
Ni	15	0.631261	0.918388	0.008009
Ni	16	0.958516	0.244612	0.198946
Ni	17	0.549859	0.328142	0.103560
Ni	18	0.891047	0.651126	0.292131
Ni	19	0.046096	0.332482	0.106751
Ni	20	0.371434	0.648252	0.287775
Ni	21	0.377105	0.161493	0.004250
Ni	22	0.701127	0.496364	0.200447
Ni	23	0.292541	0.832514	0.102342
Ni	24	0.631017	0.150826	0.293815
Ni	25	0.633281	0.667425	0.010046
Ni	26	0.960889	0.996947	0.197353
Ni	27	0.376523	0.420221	0.006424
Ni	28	0.700276	0.741693	0.203610
Ni	29	0.880059	0.426226	0.012684
Ni	30	0.208436	0.747032	0.195372
Ni	31	0.551523	0.579775	0.103752
Ni	32	0.888833	0.903749	0.289192
Ni	33	0.627725	0.420210	0.010941
Ni	34	0.958787	0.737254	0.191206
Ni	35	0.129341	0.414851	0.005510
Ni	36	0.455864	0.740084	0.199035

Ni	37	0.794124	0.582965	0.105909
Ni	38	0.129273	0.904796	0.290080
Ni	39	0.381275	0.668536	0.005418
Ni	40	0.710837	0.993203	0.198852
Ni	41	0.882581	0.672779	0.007539
Ni	42	0.214745	0.994178	0.201793
Ni	43	0.542190	0.825606	0.102863
Ni	44	0.870539	0.155484	0.291288

Table G-16 Final fractional coordinates for the optimised Ni₁₁Al₅ (111) surface slab structure after the fourth Al atom removal

Ni₁₁Al₅ (111) surface slab structure final cell contents after the fourth Al atom removal				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
Al	1	0.299024	0.312935	0.097328
Al	2	0.606943	0.177098	0.007349
Al	3	0.949645	0.487558	0.200931
Al	4	0.870784	0.915662	-0.006133
Al	5	0.150175	0.919898	-0.000899
Al	6	0.479962	0.240095	0.202694
Al	7	0.875954	0.188134	0.006846
Al	8	0.211203	0.501511	0.203157
Al	9	0.141092	0.648222	-0.014672
Al	10	0.451430	0.984628	0.198234
Al	11	0.132012	0.162912	0.284426
Al	12	0.771878	0.837002	0.105208
Al	13	0.038366	0.572919	0.096992
Al	14	0.316753	0.579424	0.099630
Al	15	0.658633	0.896841	0.296921
Al	16	0.042090	0.842962	0.105392
Ni	1	0.128589	0.170085	0.010323
Ni	2	0.461474	0.492464	0.196292
Ni	3	0.794051	0.333407	0.105254
Ni	4	0.127390	0.660749	0.292280
Ni	5	0.533278	0.082222	0.108109
Ni	6	0.879057	0.402466	0.291296
Ni	7	0.040380	0.083172	0.101383
Ni	8	0.378891	0.399856	0.291338
Ni	9	0.388841	0.914347	0.010335
Ni	10	0.717831	0.239800	0.195655
Ni	11	0.792564	0.075358	0.098793
Ni	12	0.128361	0.408835	0.289179
Ni	13	0.287832	0.078429	0.103975
Ni	14	0.627399	0.398340	0.288821
Ni	15	0.629247	0.920197	0.009731
Ni	16	0.959965	0.241109	0.196094
Ni	17	0.548599	0.327261	0.104510
Ni	18	0.891377	0.651649	0.291021
Ni	19	0.047795	0.328407	0.107439

Ni	20	0.373109	0.648057	0.287990
Ni	21	0.374927	0.162394	0.005904
Ni	22	0.702878	0.497469	0.201472
Ni	23	0.291488	0.831360	0.101515
Ni	24	0.638817	0.151270	0.293852
Ni	25	0.632056	0.668500	0.012251
Ni	26	0.958571	0.995858	0.195994
Ni	27	0.373875	0.418923	0.008369
Ni	28	0.697223	0.744110	0.204324
Ni	29	0.878261	0.427365	0.014100
Ni	30	0.207754	0.744230	0.194490
Ni	31	0.550877	0.580420	0.105051
Ni	32	0.892208	0.904445	0.288531
Ni	33	0.625186	0.420760	0.011959
Ni	34	0.956808	0.736370	0.190607
Ni	35	0.128254	0.414204	0.006133
Ni	36	0.452993	0.742453	0.199939
Ni	37	0.794384	0.583256	0.107970
Ni	38	0.133556	0.907400	0.287476
Ni	39	0.380243	0.667602	0.005655
Ni	40	0.708068	0.993284	0.199122
Ni	41	0.881381	0.673202	0.008208
Ni	42	0.208478	0.995358	0.196297
Ni	43	0.539326	0.827911	0.105419
Ni	44	0.881976	0.154815	0.290165

Appendix H Final fractional coordinates for leached $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase structures after the adsorption of OH^-

This section contains the final fractional coordinates of the leached $\text{Ni}_{1-x}\text{Al}_x$ bimetallic phase surface slabs after the adsorption of OH^- . The fractional coordinates are given for the surface slab for each of the 5 chosen adsorption positions.

H.1 Fractional coordinates for the leached Ni_7Al_9 (111) surface slab structures after the adsorption of OH^-

Table H-1 Final fractional coordinates for the optimised leached Ni_7Al_9 (111) surface slab structure after the first adsorption position

The leached Ni_7Al_9 (111) surface slab structure final cell contents after the first adsorption position				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.398238	0.237479	0.418412
O	1	0.396470	0.170464	0.386436
Al	1	0.236390	0.402864	0.112734
Al	2	0.536234	0.530664	0.333131
Al	3	0.676008	0.291994	-0.011375
Al	4	0.961172	0.508324	0.165011
Al	5	0.213487	0.274800	0.009157
Al	6	0.445643	0.530491	0.214160
Al	7	0.180764	0.241349	0.229271
Al	8	0.913167	1.027112	0.000158
Al	9	0.554160	0.160117	0.105001
Al	10	0.783007	0.277139	0.295775
Al	11	0.363202	0.888802	-0.025971
Al	12	0.409449	0.285317	0.212733
Al	13	0.899730	0.167582	0.131331
Al	14	0.942305	0.281275	0.017226
Al	15	0.592734	0.396906	0.108259
Al	16	0.823917	0.540388	0.277329
Al	17	0.161101	0.789323	-0.007280
Al	18	0.408989	0.954247	0.223625
Al	19	0.026983	0.040132	0.269093
Al	20	0.816243	0.907384	0.098781
Al	21	0.346674	0.914190	0.097782
Al	22	0.546213	0.103651	0.332194
Al	23	0.280241	0.781240	0.294989
Al	24	0.442628	0.564641	-0.005108
Al	25	0.658623	0.701583	0.179863
Al	26	0.315154	0.618226	0.102505
Al	27	0.707661	0.826611	0.304980
Al	28	0.724019	0.545711	0.009583
Al	29	1.144642	0.673367	0.206629
Al	30	0.098750	0.887257	0.112696
Al	31	0.646473	0.836735	0.005442
Al	32	0.659861	-0.006745	0.203878

Ni	1	0.809125	0.427882	0.108756
Ni	2	0.078228	0.495561	0.263407
Ni	3	0.135609	0.039519	0.033617
Ni	4	0.296686	0.297681	0.310530
Ni	5	0.424021	1.058124	0.027161
Ni	6	0.678920	0.218321	0.190755
Ni	7	0.343622	0.142949	0.142380
Ni	8	0.543164	0.319993	0.290530
Ni	9	0.668733	1.060655	0.010320
Ni	10	0.942854	0.292344	0.220521
Ni	11	0.081289	0.269292	0.114551
Ni	12	0.287221	0.539170	0.294565
Ni	13	0.441557	0.326311	0.025646
Ni	14	0.688435	0.461000	0.210027
Ni	15	0.791479	0.683568	0.087464
Ni	16	0.920902	-0.051100	0.188777
Ni	17	0.999607	0.484981	0.044660
Ni	18	0.332236	0.775472	0.182274
Ni	19	0.540488	0.653392	0.091894
Ni	20	0.878571	0.737257	0.218792
Ni	21	0.200802	0.547935	0.018574
Ni	22	0.540608	0.719886	0.274823
Ni	23	1.045374	0.673572	0.109538
Ni	24	0.029225	0.808926	0.293623
Ni	25	0.154672	0.046569	0.177637
Ni	26	0.922692	0.778438	0.008345
Ni	27	0.576136	0.913379	0.116993
Ni	28	0.779687	0.034943	0.289493

Table H-2 Final fractional coordinates for the optimised leached Ni₇Al₉ (111) surface slab structure after the second adsorption position

The leached Ni₇Al₉ (111) surface slab structure final cell contents after the second adsorption position				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.284095	0.109259	0.333291
O	1	0.241434	0.087664	0.295540
Al	1	0.260933	0.397394	0.118953
Al	2	0.569712	0.569827	0.309030
Al	3	0.674840	0.217454	-0.007298
Al	4	0.958859	0.484569	0.198055
Al	5	0.190993	0.283162	0.013727
Al	6	0.455546	0.516584	0.194969
Al	7	0.176420	0.254089	0.236325
Al	8	0.935683	1.001108	-0.000987
Al	9	0.581178	0.141018	0.106308
Al	10	0.807909	0.318618	0.302644
Al	11	0.272089	0.943632	-0.024311
Al	12	0.439676	0.256022	0.212914
Al	13	0.892419	0.160558	0.117486

Al	14	0.917657	0.279609	0.008695
Al	15	0.615926	0.385997	0.096645
Al	16	0.858012	0.559828	0.312626
Al	17	0.178111	0.742410	-0.028233
Al	18	0.394221	0.983189	0.223609
Al	19	0.067022	0.043651	0.273847
Al	20	0.843201	0.856377	0.116443
Al	21	0.351521	0.891778	0.106316
Al	22	0.575903	0.108316	0.322085
Al	23	0.305657	0.789183	0.299156
Al	24	0.446363	0.496161	-0.016567
Al	25	0.715823	0.697967	0.171979
Al	26	0.321270	0.623892	0.091458
Al	27	0.633631	0.819026	0.293679
Al	28	0.690006	0.535068	0.005069
Al	29	1.124464	0.651861	0.193133
Al	30	0.090600	0.874764	0.098185
Al	31	0.554778	0.821676	0.008064
Al	32	0.694526	-0.012394	0.212312
Ni	1	0.819962	0.451886	0.106477
Ni	2	0.101775	0.510066	0.279553
Ni	3	0.116914	0.081429	0.052918
Ni	4	0.337865	0.320432	0.309034
Ni	5	0.395846	1.057056	0.033304
Ni	6	0.684517	0.232860	0.186481
Ni	7	0.337215	0.147085	0.140772
Ni	8	0.564298	0.343026	0.287187
Ni	9	0.696235	0.971663	0.023265
Ni	10	0.935998	0.259204	0.209546
Ni	11	0.073105	0.302367	0.118549
Ni	12	0.314595	0.559373	0.282858
Ni	13	0.431566	0.286534	0.027379
Ni	14	0.702816	0.476744	0.207374
Ni	15	0.766756	0.699425	0.061198
Ni	16	0.951572	-0.050979	0.191113
Ni	17	0.958937	0.489246	0.014605
Ni	18	0.252802	0.790287	0.186206
Ni	19	0.549936	0.641152	0.106588
Ni	20	0.881951	0.740899	0.239394
Ni	21	0.199877	0.525871	0.020895
Ni	22	0.497794	0.732905	0.222489
Ni	23	1.012424	0.583131	0.108939
Ni	24	0.072161	0.806129	0.284790
Ni	25	0.145507	0.056588	0.166564
Ni	26	0.964668	0.760663	0.022536
Ni	27	0.574499	0.914901	0.119865
Ni	28	0.810338	0.091039	0.282873

Table H-3 Final fractional coordinates for the optimised leached Ni₇Al₉ (111) surface slab structure after the third adsorption position

The leached Ni₇Al₉ (111) surface slab structure final cell contents after the third adsorption position				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	1.039941	0.251498	0.361105
O	1	0.978258	0.202047	0.352176
Al	1	0.244020	0.406012	0.121429
Al	2	0.557959	0.564450	0.316200
Al	3	0.673561	0.216969	-0.008122
Al	4	0.961006	0.479722	0.200155
Al	5	0.196394	0.279292	0.015686
Al	6	0.465788	0.512888	0.197497
Al	7	0.186515	0.242243	0.231413
Al	8	0.938716	1.002839	0.001249
Al	9	0.590345	0.140286	0.103659
Al	10	0.804216	0.313830	0.306857
Al	11	0.268556	0.953661	-0.025814
Al	12	0.440577	0.257613	0.209819
Al	13	0.894748	0.150474	0.119911
Al	14	0.915890	0.282506	0.014301
Al	15	0.618979	0.386834	0.095504
Al	16	0.829992	0.577461	0.304549
Al	17	0.180412	0.745715	-0.028048
Al	18	0.414454	0.972864	0.212124
Al	19	0.045353	0.057286	0.287020
Al	20	0.846434	0.861511	0.116455
Al	21	0.353357	0.901114	0.097839
Al	22	0.555920	0.112950	0.321726
Al	23	0.287667	0.814360	0.285740
Al	24	0.446816	0.495164	-0.022160
Al	25	0.717130	0.701424	0.172380
Al	26	0.331900	0.608275	0.088152
Al	27	0.626177	0.839778	0.299034
Al	28	0.687999	0.538834	0.007185
Al	29	1.135319	0.658507	0.196249
Al	30	0.099786	0.867773	0.099815
Al	31	0.562941	0.822789	-0.000111
Al	32	0.686362	-0.011045	0.208508
Ni	1	0.816023	0.456261	0.108960
Ni	2	0.089652	0.522126	0.281751
Ni	3	0.116707	0.080179	0.056778
Ni	4	0.322372	0.320257	0.303041
Ni	5	0.407654	1.057245	0.026344
Ni	6	0.680980	0.241113	0.187024
Ni	7	0.340773	0.151583	0.132289
Ni	8	0.558890	0.339633	0.289402
Ni	9	0.707544	0.967913	0.020924
Ni	10	0.936586	0.252876	0.209620

Ni	11	0.069598	0.301185	0.119131
Ni	12	0.311941	0.565864	0.284589
Ni	13	0.427828	0.302555	0.033183
Ni	14	0.713202	0.475125	0.214290
Ni	15	0.766357	0.701734	0.060389
Ni	16	0.961756	-0.055218	0.194501
Ni	17	0.966493	0.486827	0.021467
Ni	18	0.293171	0.767443	0.172969
Ni	19	0.547408	0.646281	0.112408
Ni	20	0.884934	0.747624	0.234061
Ni	21	0.195649	0.529232	0.020710
Ni	22	0.511899	0.724388	0.233199
Ni	23	1.001980	0.596991	0.115283
Ni	24	0.062311	0.806313	0.290604
Ni	25	0.159276	0.044238	0.175410
Ni	26	0.967897	0.761094	0.023294
Ni	27	0.578838	0.916910	0.114793
Ni	28	0.791904	0.087926	0.279078

Table H-4 Final fractional coordinates for the optimised leached Ni₇Al₉ (111) surface slab structure after the fourth adsorption position

The leached Ni₇Al₉ (111) surface slab structure final cell contents after the fourth adsorption position				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.914267	0.752862	0.391466
O	1	1.017419	0.699162	0.379247
Al	1	0.216873	0.429301	0.111369
Al	2	0.532093	0.550285	0.318961
Al	3	0.652396	0.204675	-0.010004
Al	4	0.918277	0.488256	0.228308
Al	5	0.203725	0.272389	0.016045
Al	6	0.447500	0.507445	0.195253
Al	7	0.180424	0.216364	0.237648
Al	8	0.928307	1.013949	0.006207
Al	9	0.588389	0.137029	0.102546
Al	10	0.770435	0.293731	0.295791
Al	11	0.278694	0.983817	-0.029683
Al	12	0.417207	0.256099	0.205509
Al	13	0.890576	0.167663	0.123854
Al	14	0.916288	0.300159	0.019421
Al	15	0.616665	0.384448	0.096830
Al	16	1.065520	0.580381	0.314229
Al	17	0.188358	0.774931	-0.021788
Al	18	0.416187	0.953241	0.204791
Al	19	0.022110	0.061444	0.286669
Al	20	0.844805	0.859988	0.120636
Al	21	0.349177	0.904461	0.088758
Al	22	0.513286	0.099972	0.316957
Al	23	0.266501	0.827206	0.279137

Al	24	0.452693	0.494307	-0.028178
Al	25	0.705891	0.704160	0.174199
Al	26	0.335860	0.612921	0.081884
Al	27	0.651257	0.802329	0.295230
Al	28	0.679224	0.545816	0.010609
Al	29	1.115968	0.704673	0.198250
Al	30	0.093239	0.878842	0.103921
Al	31	0.570409	0.826214	-0.001394
Al	32	0.666469	-0.008061	0.208883
Ni	1	0.812073	0.458991	0.111885
Ni	2	0.164124	0.457382	0.216525
Ni	3	0.108015	0.085364	0.055803
Ni	4	0.295218	0.328679	0.304683
Ni	5	0.437746	1.072231	0.020227
Ni	6	0.668851	0.229966	0.189608
Ni	7	0.328785	0.151390	0.126395
Ni	8	0.531603	0.326345	0.289450
Ni	9	0.723655	0.953639	0.022586
Ni	10	0.935418	0.254282	0.216515
Ni	11	0.065170	0.305728	0.126973
Ni	12	0.297476	0.574312	0.281857
Ni	13	0.422649	0.326810	0.041092
Ni	14	0.692868	0.465874	0.208756
Ni	15	0.773971	0.698116	0.061555
Ni	16	0.929900	-0.030106	0.197397
Ni	17	0.994978	0.491402	0.037363
Ni	18	0.305723	0.764613	0.168311
Ni	19	0.546473	0.649851	0.111654
Ni	20	0.875027	0.754429	0.237699
Ni	21	0.204258	0.540970	0.010409
Ni	22	0.507096	0.710000	0.240713
Ni	23	0.969866	0.598760	0.138567
Ni	24	0.036950	0.829651	0.301459
Ni	25	0.154377	0.038384	0.174130
Ni	26	0.983024	0.759952	0.031042
Ni	27	0.575009	0.915238	0.111851
Ni	28	0.771719	0.052778	0.293426

Table H-5 Final fractional coordinates for the optimised leached Ni₇Al₉ (111) surface slab structure after the fifth adsorption position

The leached Ni₇Al₉ (111) surface slab structure final cell contents after the fifth adsorption position				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.722168	0.120905	0.405437
O	1	0.718996	0.051329	0.375091
Al	1	0.260703	0.405289	0.122084
Al	2	0.562655	0.574899	0.308242
Al	3	0.678389	0.218301	-0.004047

Al	4	0.963928	0.488800	0.199719
Al	5	0.197881	0.281883	0.017545
Al	6	0.446289	0.522784	0.196982
Al	7	0.182905	0.252803	0.236364
Al	8	0.939607	1.001639	0.000592
Al	9	0.596330	0.134701	0.108376
Al	10	0.798667	0.316324	0.300787
Al	11	0.270284	0.945597	-0.022506
Al	12	0.446453	0.254359	0.210757
Al	13	0.900148	0.165728	0.120651
Al	14	0.925344	0.277112	0.010371
Al	15	0.617245	0.385119	0.101631
Al	16	0.852541	0.557643	0.312388
Al	17	0.180449	0.741580	-0.027127
Al	18	0.403458	0.988971	0.219863
Al	19	0.059659	0.050021	0.275789
Al	20	0.845312	0.856111	0.118688
Al	21	0.353448	0.890999	0.107072
Al	22	0.560223	0.112537	0.325335
Al	23	0.304066	0.812063	0.297401
Al	24	0.448980	0.493528	-0.014165
Al	25	0.718725	0.696075	0.172932
Al	26	0.321613	0.626815	0.092178
Al	27	0.626395	0.815434	0.292760
Al	28	0.695534	0.529243	0.006939
Al	29	1.117821	0.658905	0.195298
Al	30	0.089585	0.879045	0.100686
Al	31	0.557296	0.816144	0.008427
Al	32	0.696995	-0.014196	0.216224
Ni	1	0.822512	0.452488	0.108828
Ni	2	0.098526	0.518153	0.282919
Ni	3	0.123320	0.082565	0.057609
Ni	4	0.332529	0.319575	0.305059
Ni	5	0.402694	1.051591	0.031870
Ni	6	0.698555	0.222135	0.190991
Ni	7	0.342580	0.153176	0.135227
Ni	8	0.553729	0.351802	0.285064
Ni	9	0.699336	0.969405	0.024605
Ni	10	0.940988	0.267237	0.212537
Ni	11	0.075733	0.306184	0.120544
Ni	12	0.309230	0.572961	0.287426
Ni	13	0.436386	0.285286	0.033055
Ni	14	0.698340	0.475854	0.207268
Ni	15	0.769179	0.699268	0.062323
Ni	16	0.946792	-0.041841	0.193304
Ni	17	0.963351	0.488326	0.016479
Ni	18	0.251092	0.788956	0.186104
Ni	19	0.552721	0.641052	0.104869
Ni	20	0.878532	0.743184	0.244133
Ni	21	0.202591	0.525522	0.022040

Ni	22	0.495440	0.736862	0.218320
Ni	23	1.013193	0.585531	0.110081
Ni	24	0.071807	0.808178	0.286685
Ni	25	0.156250	0.058196	0.172784
Ni	26	0.967122	0.761899	0.024232
Ni	27	0.576556	0.914364	0.122091
Ni	28	0.815902	0.074284	0.292918

H.2 Fractional coordinates for the leached Ni_8Al_8 (111) surface slab structures after the adsorption of OH^-

Table H-6 Final fractional coordinates for the optimised leached Ni_8Al_8 (111) surface slab structure after the first adsorption position

The leached Ni_8Al_8 (111) surface slab structure final cell contents after the first adsorption position				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.665459	0.530390	0.390348
O	1	0.583265	0.565769	0.359050
Al	1	0.245153	0.325336	0.108979
Al	2	0.624455	0.639462	0.291841
Al	3	0.521973	0.196817	0.018636
Al	4	0.918274	0.500061	0.204536
Al	5	0.065974	0.190294	-0.008358
Al	6	0.453713	0.501639	0.207397
Al	7	0.794110	0.938100	0.001688
Al	8	0.974497	0.096320	0.106134
Al	9	0.357019	0.423113	0.315128
Al	10	0.075470	0.927406	-0.009843
Al	11	0.433418	0.241328	0.211727
Al	12	0.785478	0.194398	0.005872
Al	13	0.173782	0.507217	0.206454
Al	14	0.973585	0.343325	0.102114
Al	15	0.068344	0.666571	-0.009536
Al	16	0.428295	0.985697	0.204308
Al	17	0.120544	0.171996	0.298758
Al	18	0.716893	0.856019	0.113670
Al	19	0.265193	0.833848	0.102060
Al	20	0.658668	0.148394	0.302923
Al	21	0.990150	0.593402	0.102383
Al	22	0.763805	0.453571	0.007108
Al	23	0.167407	0.755090	0.212439
Al	24	0.273293	0.578585	0.101388
Al	25	0.660207	0.884431	0.299606
Al	26	0.987412	0.843389	0.104854
Al	27	0.162942	0.000566	0.206504
Al	28	0.778609	0.693430	-0.001162
Ni	1	0.738090	0.336233	0.104814
Ni	2	0.114344	0.651837	0.298027
Ni	3	0.476575	0.095044	0.116666

Ni	4	0.878157	0.393823	0.290684
Ni	5	0.298481	0.945757	0.014499
Ni	6	0.683794	0.244730	0.201573
Ni	7	0.736191	0.084511	0.104977
Ni	8	0.128788	0.398686	0.291071
Ni	9	0.215712	0.098957	0.116117
Ni	10	0.620269	0.391731	0.297713
Ni	11	0.555885	0.941000	0.018313
Ni	12	0.941324	0.247558	0.194312
Ni	13	0.486693	0.337003	0.117975
Ni	14	0.876235	0.640697	0.294594
Ni	15	0.294814	0.182620	0.019988
Ni	16	0.686397	0.494161	0.198721
Ni	17	0.540332	0.700683	0.015982
Ni	18	0.924333	-0.005673	0.196188
Ni	19	0.283193	0.434103	0.018081
Ni	20	0.668959	0.749313	0.204222
Ni	21	0.503273	0.589340	0.108408
Ni	22	0.882208	0.902534	0.291543
Ni	23	0.539682	0.428042	0.019531
Ni	24	0.922518	0.747381	0.196201
Ni	25	0.022649	0.445952	0.012731
Ni	26	0.412605	0.754219	0.203771
Ni	27	0.750902	0.596017	0.103737
Ni	28	0.12258	0.90897	0.29735
Ni	29	0.29939	0.68628	0.01091
Ni	30	0.66539	0.0055	0.20805
Ni	31	0.48951	0.8441	0.10966
Ni	32	0.88985	0.15047	0.28704

Table H-7 Final fractional coordinates for the optimised leached Ni_8Al_8 (111) surface slab structure after the second adsorption position

The leached Ni_8Al_8 (111) surface slab structure final cell contents after the second adsorption position				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.977906	0.854221	0.403223
O	1	0.956215	0.804994	0.370052
Al	1	0.238735	0.332320	0.106639
Al	2	0.597604	0.642009	0.289148
Al	3	0.523779	0.195271	0.014482
Al	4	0.906316	0.505678	0.206577
Al	5	0.065843	0.191259	-0.006576
Al	6	0.441860	0.507468	0.200480
Al	7	0.796807	0.936949	0.003531
Al	8	0.969254	0.098571	0.107672
Al	9	0.337196	0.449417	0.311660
Al	10	0.074927	0.927858	-0.009132
Al	11	0.424807	0.253887	0.206931
Al	12	0.786942	0.194021	0.004178

Al	13	0.160462	0.515224	0.208486
Al	14	0.968495	0.346931	0.103625
Al	15	0.068230	0.666755	-0.007889
Al	16	0.421734	0.992214	0.199570
Al	17	0.092245	0.185981	0.300283
Al	18	0.710287	0.860915	0.114564
Al	19	0.258604	0.836462	0.101439
Al	20	0.626458	0.168653	0.302323
Al	21	0.981726	0.599379	0.105303
Al	22	0.765472	0.454281	0.005874
Al	23	0.158718	0.759056	0.222461
Al	24	0.263800	0.583038	0.099264
Al	25	0.626976	0.899112	0.296446
Al	26	0.983023	0.845103	0.110733
Al	27	0.158985	0.003667	0.206370
Al	28	0.779776	0.694525	-0.000861
Ni	1	0.735454	0.337799	0.101851
Ni	2	0.080638	0.660400	0.306717
Ni	3	0.471689	0.101688	0.113982
Ni	4	0.847001	0.409137	0.292969
Ni	5	0.297729	0.946374	0.014165
Ni	6	0.676541	0.247852	0.197447
Ni	7	0.734712	0.085266	0.103715
Ni	8	0.099128	0.413747	0.292232
Ni	9	0.210821	0.102477	0.115582
Ni	10	0.595553	0.409119	0.290762
Ni	11	0.555967	0.941633	0.017195
Ni	12	0.933953	0.251777	0.196027
Ni	13	0.486703	0.340031	0.111552
Ni	14	0.836943	0.649957	0.297488
Ni	15	0.295372	0.183697	0.018757
Ni	16	0.677657	0.496618	0.194589
Ni	17	0.541001	0.701640	0.013032
Ni	18	0.916671	-0.000679	0.200582
Ni	19	0.286620	0.433194	0.015161
Ni	20	0.659400	0.752597	0.202781
Ni	21	0.496825	0.591852	0.103842
Ni	22	0.847113	0.923975	0.298661
Ni	23	0.541258	0.428636	0.014661
Ni	24	0.910211	0.754054	0.201929
Ni	25	0.023571	0.447776	0.014589
Ni	26	0.403263	0.758730	0.200813
Ni	27	0.745663	0.598936	0.102682
Ni	28	0.092869	0.945447	0.298335
Ni	29	0.300915	0.686584	0.008882
Ni	30	0.656711	0.014909	0.207583
Ni	31	0.485187	0.845681	0.107027
Ni	32	0.855568	0.172676	0.288014

Table H-8 Final fractional coordinates for the optimised leached Ni₈Al₈ (111) surface slab structure after the third adsorption position

The leached Ni₈Al₈ (111) surface slab structure final cell contents after the third adsorption position				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.353450	0.155885	0.298382
O	1	0.324443	0.083359	0.284899
Al	1	0.244674	0.327723	0.103891
Al	2	0.602335	0.634169	0.285980
Al	3	0.525017	0.191574	0.012470
Al	4	0.907491	0.505524	0.203986
Al	5	0.066972	0.190193	-0.010228
Al	6	0.447481	0.504751	0.197246
Al	7	0.798591	0.934882	-0.000311
Al	8	0.971208	0.096418	0.101739
Al	9	0.339700	0.451842	0.308070
Al	10	0.077618	0.925503	-0.013751
Al	11	0.440017	0.253051	0.201464
Al	12	0.787611	0.192655	0.000042
Al	13	0.166767	0.504769	0.204311
Al	14	0.972443	0.345112	0.100412
Al	15	0.070493	0.664215	-0.011546
Al	16	0.418463	0.994635	0.205457
Al	17	0.106849	0.172226	0.293856
Al	18	0.713891	0.856243	0.111976
Al	19	0.263503	0.831672	0.096002
Al	20	0.640032	0.161065	0.298676
Al	21	0.986623	0.594715	0.101954
Al	22	0.767041	0.453898	0.002507
Al	23	0.161872	0.750224	0.216088
Al	24	0.268313	0.578488	0.095572
Al	25	0.666377	0.879967	0.295328
Al	26	0.986746	0.840581	0.104257
Al	27	0.156063	-0.006639	0.199204
Al	28	0.782550	0.692497	-0.003695
Ni	1	0.740229	0.336050	0.097676
Ni	2	0.075169	0.659631	0.296686
Ni	3	0.472242	0.095710	0.114206
Ni	4	0.857908	0.396074	0.288871
Ni	5	0.299640	0.945155	0.010319
Ni	6	0.685793	0.243705	0.193009
Ni	7	0.734872	0.081520	0.100116
Ni	8	0.097330	0.417693	0.291372
Ni	9	0.213298	0.099071	0.113467
Ni	10	0.603873	0.400894	0.286636
Ni	11	0.558098	0.939377	0.016015
Ni	12	0.943921	0.245188	0.191714
Ni	13	0.492447	0.338001	0.107102
Ni	14	0.844254	0.633514	0.299341

Ni	15	0.297275	0.180097	0.016481
Ni	16	0.683888	0.491487	0.191334
Ni	17	0.542967	0.702764	0.012600
Ni	18	0.919478	-0.006261	0.192384
Ni	19	0.289037	0.429856	0.011565
Ni	20	0.656720	0.754398	0.202451
Ni	21	0.500779	0.588572	0.101012
Ni	22	0.868996	0.920943	0.290156
Ni	23	0.543871	0.426945	0.010844
Ni	24	0.911797	0.749530	0.197687
Ni	25	0.026441	0.445204	0.011168
Ni	26	0.404129	0.757012	0.198103
Ni	27	0.747101	0.598970	0.100876
Ni	28	0.107941	0.922645	0.294020
Ni	29	0.303234	0.683349	0.004900
Ni	30	0.659203	0.009351	0.205253
Ni	31	0.483347	0.849232	0.107816
Ni	32	0.872928	0.157973	0.282933

Table H-9 Final fractional coordinates for the optimised leached Ni_8Al_8 (111) surface slab structure after the fourth adsorption position

The leached Ni_8Al_8 (111) surface slab structure final cell contents after the fourth adsorption position				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.410772	0.745170	0.382957
O	1	0.410301	0.771266	0.339490
Al	1	0.242113	0.330844	0.103466
Al	2	0.579387	0.652160	0.293629
Al	3	0.523986	0.195687	0.013738
Al	4	0.906513	0.504040	0.204402
Al	5	0.065982	0.191122	-0.008655
Al	6	0.440032	0.508446	0.199868
Al	7	0.796139	0.937243	0.001234
Al	8	0.968905	0.100682	0.103729
Al	9	0.337454	0.448025	0.310081
Al	10	0.074849	0.928371	-0.012515
Al	11	0.428179	0.250781	0.207040
Al	12	0.785754	0.195586	0.002659
Al	13	0.163203	0.511424	0.203781
Al	14	0.971381	0.346476	0.101518
Al	15	0.067580	0.667539	-0.009945
Al	16	0.423417	0.990235	0.200065
Al	17	0.097346	0.184975	0.297944
Al	18	0.710661	0.858179	0.113936
Al	19	0.256778	0.838538	0.098364
Al	20	0.647505	0.154077	0.300268
Al	21	0.982512	0.597954	0.102858
Al	22	0.766018	0.454437	0.004868
Al	23	0.153909	0.762221	0.220956

Al	24	0.265094	0.582526	0.096641
Al	25	0.672879	0.881802	0.294769
Al	26	0.982833	0.844010	0.105971
Al	27	0.155719	0.007281	0.203706
Al	28	0.779912	0.694000	-0.001720
Ni	1	0.734655	0.342329	0.101646
Ni	2	0.074251	0.652920	0.297722
Ni	3	0.472113	0.099549	0.112777
Ni	4	0.843504	0.406247	0.290784
Ni	5	0.298947	0.945600	0.011142
Ni	6	0.679424	0.245512	0.195304
Ni	7	0.733220	0.085190	0.101306
Ni	8	0.107065	0.405663	0.288491
Ni	9	0.212272	0.102032	0.111919
Ni	10	0.601540	0.395888	0.288560
Ni	11	0.556477	0.941277	0.015574
Ni	12	0.930569	0.254296	0.193224
Ni	13	0.485318	0.340410	0.111281
Ni	14	0.844535	0.632188	0.298211
Ni	15	0.296720	0.182679	0.015713
Ni	16	0.670784	0.502936	0.197297
Ni	17	0.541446	0.701101	0.011830
Ni	18	0.919357	-0.000430	0.193157
Ni	19	0.287463	0.433708	0.012043
Ni	20	0.655499	0.751473	0.205225
Ni	21	0.496633	0.592388	0.102803
Ni	22	0.884852	0.917192	0.290651
Ni	23	0.541263	0.429165	0.013845
Ni	24	0.909782	0.752959	0.198933
Ni	25	0.025212	0.447015	0.012241
Ni	26	0.398048	0.761028	0.195426
Ni	27	0.744827	0.598479	0.103337
Ni	28	0.138499	0.924287	0.301220
Ni	29	0.300500	0.687263	0.006799
Ni	30	0.657000	0.013575	0.205546
Ni	31	0.485015	0.846679	0.105607
Ni	32	0.879962	0.152995	0.284908

Table H-10 Final fractional coordinates for the optimised leached Ni_8Al_8 (111) surface slab structure after the fifth adsorption position

The leached Ni_8Al_8 (111) surface slab structure final cell contents after the fifth adsorption position				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.086450	0.928754	0.411868
O	1	0.169492	0.878389	0.380973
Al	1	0.242384	0.329713	0.106159
Al	2	0.599881	0.640462	0.288946
Al	3	0.524618	0.193977	0.014928

Al	4	0.908833	0.505454	0.206517
Al	5	0.066540	0.190569	-0.007125
Al	6	0.446128	0.505253	0.200373
Al	7	0.797973	0.936183	0.002881
Al	8	0.972505	0.096689	0.107921
Al	9	0.339087	0.449767	0.311567
Al	10	0.076044	0.927315	-0.009721
Al	11	0.429670	0.250554	0.206836
Al	12	0.788129	0.192911	0.004567
Al	13	0.165354	0.510689	0.206019
Al	14	0.970882	0.345517	0.103407
Al	15	0.069768	0.666137	-0.008406
Al	16	0.421381	0.990816	0.201376
Al	17	0.098200	0.191448	0.296579
Al	18	0.713085	0.858311	0.113902
Al	19	0.260513	0.835862	0.101939
Al	20	0.634060	0.163499	0.302171
Al	21	0.985062	0.596798	0.104120
Al	22	0.766539	0.453171	0.005870
Al	23	0.164469	0.755888	0.219477
Al	24	0.267807	0.580672	0.098588
Al	25	0.633662	0.895725	0.298834
Al	26	0.985900	0.842789	0.109054
Al	27	0.161698	-0.000151	0.209529
Al	28	0.781473	0.693331	-0.001438
Ni	1	0.738302	0.335947	0.101855
Ni	2	0.079553	0.660456	0.298898
Ni	3	0.473854	0.098383	0.114688
Ni	4	0.849182	0.409186	0.292661
Ni	5	0.298613	0.945359	0.014209
Ni	6	0.681604	0.244020	0.197696
Ni	7	0.737504	0.082529	0.104124
Ni	8	0.102590	0.416543	0.292795
Ni	9	0.212385	0.100629	0.116064
Ni	10	0.600339	0.404582	0.290445
Ni	11	0.557412	0.940742	0.016888
Ni	12	0.938164	0.249470	0.195914
Ni	13	0.489804	0.337790	0.112119
Ni	14	0.842274	0.650361	0.298220
Ni	15	0.296535	0.181754	0.018819
Ni	16	0.681212	0.494811	0.194575
Ni	17	0.542535	0.701327	0.012949
Ni	18	0.923469	-0.004863	0.200167
Ni	19	0.287935	0.432087	0.014578
Ni	20	0.660598	0.752251	0.203147
Ni	21	0.500307	0.590010	0.103264
Ni	22	0.853624	0.916161	0.293554
Ni	23	0.542254	0.427277	0.014592
Ni	24	0.912382	0.751086	0.199719
Ni	25	0.025099	0.446026	0.013937

Ni	26	0.408321	0.755534	0.199450
Ni	27	0.747595	0.598222	0.102592
Ni	28	0.088263	0.926778	0.303783
Ni	29	0.302195	0.686718	0.008939
Ni	30	0.658122	0.010478	0.207834
Ni	31	0.486694	0.846004	0.106915
Ni	32	0.864078	0.166743	0.287358

H.3 Fractional coordinates for the leached Ni₉Al₇ (111) surface slab structures after the adsorption of OH⁻

Table H-11 Final fractional coordinates for the optimised leached Ni₉Al₇ (111) surface slab structure after the first adsorption position

The leached Ni ₉ Al ₇ (111) surface slab structure final cell contents after the first adsorption position				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.891284	0.806039	0.390700
O	1	0.918545	0.757976	0.349929
Al	1	0.321984	0.343216	0.084177
Al	2	0.680973	0.205241	-0.009546
Al	3	0.965428	0.504772	0.216347
Al	4	0.246872	0.220409	0.230398
Al	5	0.927899	0.951645	-0.010943
Al	6	0.575270	0.089900	0.082132
Al	7	0.856821	0.389545	0.308469
Al	8	0.207310	0.963988	0.009160
Al	9	0.496093	0.235984	0.187799
Al	10	0.321920	0.081982	0.122915
Al	11	0.597902	0.376305	0.287441
Al	12	0.934884	0.229038	0.015513
Al	13	0.224713	0.506055	0.193042
Al	14	0.184431	0.705608	-0.013316
Al	15	0.100159	0.130482	0.309774
Al	16	0.809950	0.838123	0.086087
Al	17	0.059496	0.587815	0.089425
Al	18	0.342797	0.863564	0.306931
Al	19	0.443156	0.456580	-0.013946
Al	20	0.711666	0.783318	0.220702
Al	21	0.343275	0.602297	0.098112
Al	22	0.155180	0.437386	-0.024279
Al	23	0.463794	0.739349	0.201329
Al	24	0.068313	0.867664	0.103082
Ni	1	0.188791	0.210613	0.027586
Ni	2	0.478920	0.487590	0.190184
Ni	3	0.827716	0.357259	0.115051
Ni	4	0.102035	0.635179	0.282028
Ni	5	0.067716	0.108460	0.110233
Ni	6	0.356572	0.367687	0.278523
Ni	7	0.447671	0.956928	0.026715

Ni	8	0.732508	0.249686	0.190946
Ni	9	0.825128	0.097237	0.091279
Ni	10	0.102844	0.384637	0.307016
Ni	11	0.685554	0.952918	-0.009188
Ni	12	0.981499	0.250235	0.209717
Ni	13	0.571114	0.340738	0.093872
Ni	14	0.844709	0.635024	0.306677
Ni	15	0.097277	0.347189	0.130336
Ni	16	0.354716	0.625041	0.283915
Ni	17	0.427689	0.217524	-0.009014
Ni	18	0.713670	0.520803	0.217185
Ni	19	0.323597	0.847836	0.107504
Ni	20	0.623334	0.124190	0.277443
Ni	21	0.683642	0.708000	0.026314
Ni	22	0.965071	0.006479	0.194955
Ni	23	0.927828	0.468723	0.030624
Ni	24	0.212812	0.749601	0.191987
Ni	25	0.585475	0.595375	0.109589
Ni	26	0.855597	0.890145	0.277805
Ni	27	0.684106	0.449987	0.016401
Ni	28	0.967886	0.745953	0.179304
Ni	29	0.817951	0.610574	0.127715
Ni	30	0.101086	0.891412	0.288199
Ni	31	0.431174	0.698630	0.011909
Ni	32	0.724822	0.998548	0.176758
Ni	33	0.941430	0.700240	-0.006307
Ni	34	0.222198	0.995433	0.208336
Ni	35	0.573213	0.856140	0.127518
Ni	36	0.855698	0.149340	0.288570

Table H-12 Final fractional coordinates for the optimised leached Ni₉Al₇ (111) surface slab structure after the second adsorption position

The leached Ni₉Al₇ (111) surface slab structure final cell contents after the second adsorption position				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.321821	0.731840	0.396332
O	1	0.396188	0.721400	0.364563
Al	1	0.320447	0.342308	0.084124
Al	2	0.680078	0.205036	-0.010007
Al	3	0.959561	0.503674	0.214320
Al	4	0.240655	0.221379	0.229885
Al	5	0.927209	0.950809	-0.011004
Al	6	0.573679	0.089150	0.081328
Al	7	0.851393	0.394956	0.307287
Al	8	0.206237	0.962282	0.009329
Al	9	0.493110	0.232610	0.187523
Al	10	0.321538	0.079837	0.123588
Al	11	0.597942	0.367581	0.286329
Al	12	0.934932	0.227571	0.015780

Al	13	0.220565	0.505159	0.193303
Al	14	0.182986	0.704270	-0.013015
Al	15	0.092975	0.134968	0.310328
Al	16	0.808864	0.837124	0.085050
Al	17	0.056853	0.586730	0.088846
Al	18	0.328878	0.866860	0.307178
Al	19	0.441482	0.456270	-0.013960
Al	20	0.706962	0.782467	0.223140
Al	21	0.339702	0.602412	0.098538
Al	22	0.154220	0.435372	-0.024595
Al	23	0.462453	0.737358	0.201514
Al	24	0.068709	0.863650	0.103919
Ni	1	0.189003	0.208237	0.027511
Ni	2	0.472423	0.485456	0.190022
Ni	3	0.825776	0.356141	0.114283
Ni	4	0.096438	0.641759	0.281634
Ni	5	0.068662	0.104779	0.110412
Ni	6	0.354374	0.362663	0.277652
Ni	7	0.446814	0.955823	0.026555
Ni	8	0.728556	0.247388	0.189557
Ni	9	0.823855	0.095891	0.090448
Ni	10	0.097366	0.393021	0.305800
Ni	11	0.684291	0.952682	-0.009991
Ni	12	0.977478	0.250100	0.209039
Ni	13	0.568934	0.340068	0.093130
Ni	14	0.860236	0.636788	0.304579
Ni	15	0.095354	0.345995	0.129242
Ni	16	0.364283	0.611116	0.286788
Ni	17	0.426950	0.216758	-0.009336
Ni	18	0.708486	0.513358	0.214285
Ni	19	0.322107	0.846549	0.107997
Ni	20	0.622969	0.115075	0.276630
Ni	21	0.681676	0.707525	0.025835
Ni	22	0.960248	0.007466	0.192908
Ni	23	0.926051	0.468305	0.030134
Ni	24	0.212900	0.747660	0.195684
Ni	25	0.581797	0.594338	0.109052
Ni	26	0.854962	0.885910	0.274755
Ni	27	0.682569	0.449841	0.015727
Ni	28	0.965810	0.744040	0.178631
Ni	29	0.812868	0.611538	0.127317
Ni	30	0.082636	0.900798	0.287593
Ni	31	0.429124	0.698436	0.011957
Ni	32	0.719879	0.996076	0.175050
Ni	33	0.939598	0.699023	-0.007232
Ni	34	0.222054	0.992303	0.210405
Ni	35	0.572272	0.854451	0.127604
Ni	36	0.851296	0.149183	0.287839

Table H-13 Final fractional coordinates for the optimised leached Ni₉Al₇ (111) surface slab structure after the third adsorption position

The leached Ni₉Al₇ (111) surface slab structure final cell contents after the third adsorption position				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.654303	0.606849	0.366611
O	1	0.764160	0.550961	0.364256
Al	1	0.319754	0.342990	0.082847
Al	2	0.680308	0.205064	-0.011758
Al	3	0.955746	0.510812	0.217244
Al	4	0.243011	0.219183	0.229086
Al	5	0.927080	0.951275	-0.012935
Al	6	0.574513	0.089590	0.080442
Al	7	0.844624	0.396347	0.309464
Al	8	0.207060	0.963649	0.008322
Al	9	0.492979	0.231752	0.186872
Al	10	0.320785	0.082110	0.121858
Al	11	0.592799	0.365630	0.283619
Al	12	0.935722	0.227233	0.012433
Al	13	0.218219	0.504991	0.189995
Al	14	0.182526	0.704867	-0.015088
Al	15	0.092885	0.132795	0.308018
Al	16	0.807786	0.836689	0.083413
Al	17	0.055750	0.588258	0.086829
Al	18	0.342343	0.864816	0.304625
Al	19	0.441251	0.456574	-0.015542
Al	20	0.707681	0.786548	0.225122
Al	21	0.339219	0.603486	0.096147
Al	22	0.153607	0.436755	-0.025877
Al	23	0.467116	0.732293	0.200585
Al	24	0.067162	0.867660	0.101862
Ni	1	0.188000	0.210852	0.026641
Ni	2	0.471377	0.485666	0.188194
Ni	3	0.826052	0.353178	0.111140
Ni	4	0.097201	0.638607	0.278930
Ni	5	0.065842	0.110197	0.109372
Ni	6	0.350121	0.369377	0.276092
Ni	7	0.448066	0.955501	0.026480
Ni	8	0.729541	0.243285	0.187570
Ni	9	0.825022	0.096044	0.089149
Ni	10	0.098112	0.387971	0.304018
Ni	11	0.683987	0.953143	-0.011290
Ni	12	0.972625	0.257360	0.209287
Ni	13	0.568008	0.340310	0.091337
Ni	14	0.860344	0.648409	0.310856
Ni	15	0.093662	0.349780	0.129640
Ni	16	0.351611	0.624588	0.283050
Ni	17	0.427069	0.217060	-0.010197
Ni	18	0.714484	0.496998	0.208275

Ni	19	0.323718	0.847335	0.106809
Ni	20	0.624474	0.109292	0.275332
Ni	21	0.682217	0.707692	0.025509
Ni	22	0.964868	0.007067	0.193397
Ni	23	0.925879	0.468522	0.029730
Ni	24	0.212245	0.748837	0.190894
Ni	25	0.582234	0.594238	0.106642
Ni	26	0.863247	0.885329	0.273433
Ni	27	0.682777	0.448952	0.013631
Ni	28	0.964604	0.745971	0.176258
Ni	29	0.813163	0.610574	0.128146
Ni	30	0.099494	0.889331	0.287951
Ni	31	0.428577	0.699330	0.010190
Ni	32	0.723047	0.995376	0.173752
Ni	33	0.938952	0.699650	-0.009178
Ni	34	0.218621	0.995302	0.206953
Ni	35	0.572788	0.855170	0.128690
Ni	36	0.850212	0.149815	0.287216

Table H-14 Final fractional coordinates for the optimised leached Ni₉Al₇ (111) surface slab structure after the fourth adsorption position

The leached Ni₉Al₇ (111) surface slab structure final cell contents after the fourth adsorption position				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.489730	1.013275	0.304331
O	1	0.519050	0.903498	0.304684
Al	1	0.321862	0.341926	0.082096
Al	2	0.680132	0.204484	-0.012847
Al	3	0.957914	0.503404	0.209400
Al	4	0.237430	0.227420	0.223271
Al	5	0.927072	0.951826	-0.013613
Al	6	0.575153	0.087542	0.079350
Al	7	0.857762	0.399810	0.304490
Al	8	0.206946	0.963508	0.005236
Al	9	0.497806	0.226725	0.185956
Al	10	0.321537	0.080021	0.119098
Al	11	0.601213	0.377088	0.284425
Al	12	0.934031	0.229215	0.011953
Al	13	0.220958	0.504514	0.189817
Al	14	0.183090	0.705105	-0.016147
Al	15	0.102845	0.136952	0.305966
Al	16	0.807431	0.836657	0.082345
Al	17	0.055028	0.587728	0.086869
Al	18	0.355290	0.867206	0.300507
Al	19	0.441350	0.455404	-0.016697
Al	20	0.672963	0.817903	0.238307
Al	21	0.339628	0.602429	0.095143
Al	22	0.153569	0.437153	-0.026635
Al	23	0.458316	0.730962	0.193939

Al	24	0.064526	0.865755	0.100892
Ni	1	0.188566	0.209274	0.023857
Ni	2	0.475370	0.480385	0.186297
Ni	3	0.824289	0.357253	0.111314
Ni	4	0.108748	0.642205	0.279218
Ni	5	0.066253	0.106592	0.106187
Ni	6	0.360761	0.365259	0.274133
Ni	7	0.449264	0.953718	0.025163
Ni	8	0.731508	0.246380	0.187975
Ni	9	0.823659	0.095803	0.088748
Ni	10	0.105378	0.394705	0.301314
Ni	11	0.684268	0.952991	-0.012622
Ni	12	0.976743	0.250709	0.205256
Ni	13	0.571116	0.337438	0.090431
Ni	14	0.874090	0.638887	0.297901
Ni	15	0.094835	0.345587	0.125143
Ni	16	0.361794	0.627974	0.279447
Ni	17	0.427240	0.216072	-0.011302
Ni	18	0.705100	0.521319	0.213194
Ni	19	0.319796	0.848002	0.103339
Ni	20	0.642869	0.118974	0.273645
Ni	21	0.680716	0.709000	0.023478
Ni	22	0.964593	0.005651	0.192505
Ni	23	0.924401	0.470389	0.027772
Ni	24	0.207024	0.749842	0.189667
Ni	25	0.582669	0.592348	0.104675
Ni	26	0.873970	0.885785	0.272487
Ni	27	0.682773	0.448500	0.012076
Ni	28	0.960852	0.741761	0.177221
Ni	29	0.808777	0.614417	0.124874
Ni	30	0.111488	0.893720	0.288156
Ni	31	0.429320	0.697697	0.008142
Ni	32	0.723694	0.991056	0.173878
Ni	33	0.940629	0.700128	-0.009673
Ni	34	0.218310	0.995910	0.203582
Ni	35	0.573407	0.854043	0.130536
Ni	36	0.863357	0.152770	0.286635

Table H-15 Final fractional coordinates for the optimised leached Ni₉Al₇ (111) surface slab structure after the fifth adsorption position

The leached Ni ₉ Al ₇ (111) surface slab structure final cell contents after the fifth adsorption position				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.044714	0.547374	0.406277
O	1	0.038108	0.556544	0.361016
Al	1	0.324392	0.341222	0.083743
Al	2	0.682418	0.204061	-0.009034
Al	3	0.965540	0.501094	0.215689

Al	4	0.252111	0.212247	0.233701
Al	5	0.929267	0.950270	-0.010825
Al	6	0.576900	0.087992	0.082497
Al	7	0.848220	0.379519	0.305166
Al	8	0.209230	0.962109	0.009699
Al	9	0.498112	0.232461	0.188373
Al	10	0.323105	0.080536	0.124409
Al	11	0.595523	0.364586	0.287512
Al	12	0.936483	0.227720	0.016244
Al	13	0.224878	0.501579	0.191751
Al	14	0.185409	0.703943	-0.013308
Al	15	0.098030	0.122333	0.310150
Al	16	0.811083	0.835877	0.085475
Al	17	0.060230	0.586028	0.088783
Al	18	0.344962	0.860728	0.307878
Al	19	0.444316	0.455190	-0.013741
Al	20	0.712792	0.780545	0.226522
Al	21	0.344325	0.600626	0.098268
Al	22	0.156078	0.435218	-0.024358
Al	23	0.463973	0.736746	0.201958
Al	24	0.069779	0.865243	0.103338
Ni	1	0.190646	0.208718	0.027980
Ni	2	0.478244	0.484948	0.190902
Ni	3	0.830061	0.355716	0.115945
Ni	4	0.101941	0.633642	0.282389
Ni	5	0.069538	0.106350	0.110872
Ni	6	0.355640	0.364631	0.277634
Ni	7	0.449370	0.955138	0.028697
Ni	8	0.735244	0.246409	0.191426
Ni	9	0.826886	0.095594	0.091808
Ni	10	0.094212	0.372872	0.310164
Ni	11	0.686037	0.952513	-0.009323
Ni	12	0.987652	0.246697	0.210812
Ni	13	0.572926	0.338963	0.094485
Ni	14	0.856205	0.618299	0.308206
Ni	15	0.101171	0.344800	0.130497
Ni	16	0.355608	0.622206	0.284540
Ni	17	0.429687	0.215165	-0.009195
Ni	18	0.711708	0.519955	0.216690
Ni	19	0.324631	0.845944	0.108308
Ni	20	0.623324	0.108341	0.277228
Ni	21	0.684367	0.707100	0.027281
Ni	22	0.968962	0.002701	0.195349
Ni	23	0.928535	0.467704	0.031179
Ni	24	0.213153	0.744941	0.192812
Ni	25	0.585779	0.593989	0.110160
Ni	26	0.862843	0.883323	0.274842
Ni	27	0.685151	0.448630	0.017142
Ni	28	0.968715	0.742202	0.178761
Ni	29	0.817467	0.610481	0.128469

Ni	30	0.102746	0.883174	0.289919
Ni	31	0.431963	0.697317	0.012292
Ni	32	0.725781	0.994041	0.176153
Ni	33	0.942240	0.698693	-0.006936
Ni	34	0.225086	0.989063	0.209057
Ni	35	0.575696	0.853729	0.130268
Ni	36	0.854314	0.138409	0.289093

H.4 Fractional coordinates for the leached $\text{Ni}_{11}\text{Al}_5$ (111) surface slab structures after the adsorption of OH^-

Table H-16 Final fractional coordinates for the optimised leached $\text{Ni}_{11}\text{Al}_5$ (111) surface slab structure after the first adsorption position

The leached $\text{Ni}_{11}\text{Al}_5$ (111) surface slab structure final cell contents after the first adsorption position				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.249052	0.413951	0.393568
O	1	0.287118	0.338667	0.359507
Al	1	0.292927	0.313703	0.101259
Al	2	0.600573	0.178128	0.009213
Al	3	0.948144	0.487323	0.202609
Al	4	0.864352	0.916214	-0.005075
Al	5	0.144061	0.920334	-0.000328
Al	6	0.476161	0.241824	0.205448
Al	7	0.869442	0.188841	0.007388
Al	8	0.206656	0.503132	0.208029
Al	9	0.134964	0.648561	-0.012839
Al	10	0.446627	0.986530	0.199432
Al	11	0.125211	0.167741	0.283315
Al	12	0.766487	0.837991	0.107015
Al	13	0.033862	0.573675	0.099285
Al	14	0.311567	0.580014	0.102464
Al	15	0.655082	0.899075	0.297770
Al	16	0.036617	0.844101	0.106504
Ni	1	0.122191	0.170691	0.010589
Ni	2	0.456362	0.492667	0.199733
Ni	3	0.787972	0.334108	0.105904
Ni	4	0.121999	0.672865	0.293817
Ni	5	0.528082	0.083591	0.109839
Ni	6	0.875051	0.406904	0.292110
Ni	7	0.034837	0.083826	0.101674
Ni	8	0.379533	0.404511	0.296527
Ni	9	0.383077	0.914516	0.011098
Ni	10	0.713325	0.241144	0.197121
Ni	11	0.787142	0.076390	0.100011
Ni	12	0.123890	0.410962	0.297654
Ni	13	0.282536	0.078960	0.104203
Ni	14	0.626831	0.401276	0.290311
Ni	15	0.623126	0.921023	0.011552

Ni	16	0.953656	0.243311	0.196046
Ni	17	0.542728	0.328455	0.106752
Ni	18	0.888993	0.656142	0.291921
Ni	19	0.041800	0.328996	0.107823
Ni	20	0.369976	0.656271	0.289420
Ni	21	0.368443	0.163875	0.008417
Ni	22	0.698701	0.498503	0.202327
Ni	23	0.285954	0.832315	0.102307
Ni	24	0.640260	0.152146	0.295661
Ni	25	0.626158	0.668974	0.013651
Ni	26	0.954418	0.997890	0.197032
Ni	27	0.366808	0.419387	0.011536
Ni	28	0.692811	0.745103	0.205688
Ni	29	0.871680	0.428183	0.015043
Ni	30	0.203305	0.746187	0.195627
Ni	31	0.545652	0.580710	0.106581
Ni	32	0.887857	0.909116	0.289857
Ni	33	0.618345	0.421130	0.013422
Ni	34	0.952972	0.737880	0.191974
Ni	35	0.122443	0.414557	0.008497
Ni	36	0.448368	0.743888	0.200475
Ni	37	0.789642	0.583459	0.109428
Ni	38	0.129907	0.913259	0.288431
Ni	39	0.373869	0.667503	0.007473
Ni	40	0.703474	0.995222	0.200540
Ni	41	0.875863	0.673646	0.010330
Ni	42	0.204083	0.997581	0.196500
Ni	43	0.533979	0.828655	0.106586
Ni	44	0.880102	0.158109	0.291231

Table H-17 Final fractional coordinates for the optimised leached $\text{Ni}_{11}\text{Al}_5$ (111) surface slab structure after the second adsorption position

The leached $\text{Ni}_{11}\text{Al}_5$ (111) surface slab structure final cell contents after the second adsorption position				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.399054	0.087730	0.302957
O	1	0.331557	0.102292	0.266515
Al	1	0.298194	0.309363	0.098114
Al	2	0.605814	0.175692	0.005743
Al	3	0.952392	0.483546	0.200285
Al	4	0.870132	0.914513	-0.007295
Al	5	0.149408	0.919084	-0.003600
Al	6	0.482013	0.240768	0.202220
Al	7	0.873762	0.188103	0.003185
Al	8	0.212538	0.499820	0.203820
Al	9	0.140231	0.646738	-0.015353
Al	10	0.446504	0.983739	0.196457
Al	11	0.124896	0.164570	0.279246
Al	12	0.771523	0.835593	0.104519

Al	13	0.038996	0.570652	0.096900
Al	14	0.317493	0.575871	0.098765
Al	15	0.669982	0.892303	0.296750
Al	16	0.042000	0.841586	0.103703
Ni	1	0.127097	0.169966	0.007204
Ni	2	0.463145	0.491374	0.195113
Ni	3	0.792326	0.332127	0.102641
Ni	4	0.130061	0.663264	0.292151
Ni	5	0.531596	0.080662	0.108044
Ni	6	0.881288	0.402960	0.290402
Ni	7	0.035896	0.082761	0.096449
Ni	8	0.382330	0.403552	0.291466
Ni	9	0.389438	0.911670	0.007147
Ni	10	0.717106	0.239469	0.193863
Ni	11	0.790567	0.073888	0.096797
Ni	12	0.124836	0.420064	0.291593
Ni	13	0.286469	0.074433	0.100912
Ni	14	0.630003	0.397854	0.287570
Ni	15	0.628901	0.919057	0.008979
Ni	16	0.957834	0.239851	0.192784
Ni	17	0.548163	0.325390	0.103063
Ni	18	0.893474	0.651843	0.289859
Ni	19	0.047567	0.325755	0.105583
Ni	20	0.374885	0.651521	0.285658
Ni	21	0.374001	0.161182	0.005172
Ni	22	0.703380	0.496925	0.199784
Ni	23	0.292353	0.826375	0.097272
Ni	24	0.640914	0.150871	0.293402
Ni	25	0.632420	0.666437	0.010743
Ni	26	0.953873	0.995299	0.193484
Ni	27	0.372411	0.416724	0.008106
Ni	28	0.695072	0.744771	0.203783
Ni	29	0.877474	0.426219	0.012665
Ni	30	0.207355	0.739544	0.191993
Ni	31	0.551933	0.577169	0.102638
Ni	32	0.895177	0.905597	0.287303
Ni	33	0.623860	0.418459	0.009635
Ni	34	0.956137	0.735111	0.189530
Ni	35	0.127911	0.412911	0.005928
Ni	36	0.450974	0.741806	0.196272
Ni	37	0.795223	0.581196	0.107337
Ni	38	0.134516	0.907579	0.283739
Ni	39	0.379648	0.664625	0.003593
Ni	40	0.706635	0.992776	0.198347
Ni	41	0.881316	0.671904	0.008039
Ni	42	0.197389	0.986244	0.187573
Ni	43	0.539370	0.825791	0.103543
Ni	44	0.883805	0.154512	0.288474

Table H-18 Final fractional coordinates for the optimised leached Ni₁₁Al₅ (111) surface slab structure after the third adsorption position

The leached Ni₁₁Al₅ (111) surface slab structure final cell contents after the third adsorption position				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.415648	0.896310	0.326035
O	1	0.446257	0.976525	0.322869
Al	1	0.295016	0.313569	0.098401
Al	2	0.602069	0.177222	0.007559
Al	3	0.949015	0.489582	0.200610
Al	4	0.865967	0.916398	-0.006645
Al	5	0.145345	0.920727	-0.001901
Al	6	0.478681	0.241663	0.203503
Al	7	0.870326	0.188707	0.006127
Al	8	0.211368	0.503013	0.203854
Al	9	0.136424	0.648567	-0.014684
Al	10	0.444475	0.986531	0.197307
Al	11	0.142805	0.162481	0.281793
Al	12	0.767883	0.839563	0.105298
Al	13	0.035938	0.574580	0.097182
Al	14	0.315049	0.579423	0.099617
Al	15	0.639155	0.912814	0.299157
Al	16	0.038510	0.844537	0.104733
Ni	1	0.122727	0.171356	0.009166
Ni	2	0.461927	0.493484	0.196312
Ni	3	0.791207	0.334415	0.104796
Ni	4	0.119178	0.666578	0.291763
Ni	5	0.528935	0.083181	0.107983
Ni	6	0.884223	0.401049	0.290883
Ni	7	0.035280	0.084309	0.100082
Ni	8	0.379326	0.402818	0.291691
Ni	9	0.384282	0.914595	0.008915
Ni	10	0.716694	0.243691	0.195573
Ni	11	0.787642	0.076554	0.099437
Ni	12	0.123470	0.416970	0.289578
Ni	13	0.283029	0.079074	0.102512
Ni	14	0.626781	0.409144	0.289200
Ni	15	0.624734	0.920284	0.009593
Ni	16	0.960807	0.241726	0.195114
Ni	17	0.545318	0.327487	0.104738
Ni	18	0.880124	0.659851	0.290327
Ni	19	0.043778	0.330288	0.106306
Ni	20	0.365447	0.653292	0.286587
Ni	21	0.369677	0.163344	0.006174
Ni	22	0.703269	0.500938	0.201123
Ni	23	0.288399	0.831397	0.099836
Ni	24	0.646276	0.163114	0.292700
Ni	25	0.627762	0.668604	0.011708
Ni	26	0.952585	0.997321	0.195493

Ni	27	0.368666	0.418982	0.008874
Ni	28	0.694162	0.748720	0.203536
Ni	29	0.872894	0.427957	0.013556
Ni	30	0.204429	0.744884	0.192900
Ni	31	0.549472	0.579833	0.104371
Ni	32	0.882006	0.909660	0.289257
Ni	33	0.620275	0.420315	0.011637
Ni	34	0.952924	0.739080	0.190490
Ni	35	0.123395	0.414913	0.006392
Ni	36	0.450300	0.742926	0.198218
Ni	37	0.791943	0.584983	0.107544
Ni	38	0.129468	0.908063	0.285895
Ni	39	0.375923	0.667316	0.004876
Ni	40	0.698996	0.996295	0.200882
Ni	41	0.877050	0.673843	0.008530
Ni	42	0.203521	0.994933	0.194398
Ni	43	0.535842	0.828607	0.104602
Ni	44	0.890234	0.155221	0.289711

Table H-19 Final fractional coordinates for the optimised leached Ni₁₁Al₅ (111) surface slab structure after the fourth adsorption position

The leached Ni₁₁Al₅ (111) surface slab structure final cell contents after the fourth adsorption position				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.636385	0.688411	0.346475
O	1	0.690667	0.747902	0.350974
Al	1	0.297882	0.310893	0.097521
Al	2	0.605323	0.175521	0.007117
Al	3	0.949059	0.487047	0.200975
Al	4	0.869035	0.914185	-0.006902
Al	5	0.148620	0.918263	-0.001942
Al	6	0.479786	0.238318	0.202849
Al	7	0.873944	0.186354	0.005661
Al	8	0.212528	0.499330	0.202469
Al	9	0.139438	0.646471	-0.015055
Al	10	0.449838	0.982717	0.196828
Al	11	0.136480	0.158212	0.282250
Al	12	0.771565	0.835674	0.104809
Al	13	0.037813	0.571128	0.096872
Al	14	0.316938	0.577172	0.099063
Al	15	0.650038	0.901901	0.298323
Al	16	0.041635	0.840401	0.104437
Ni	1	0.126631	0.168577	0.008973
Ni	2	0.462546	0.490466	0.195982
Ni	3	0.793001	0.331232	0.104270
Ni	4	0.124327	0.658692	0.290972
Ni	5	0.532221	0.080661	0.108056
Ni	6	0.884339	0.392425	0.290348
Ni	7	0.039135	0.081047	0.099899

Ni	8	0.379340	0.399004	0.291317
Ni	9	0.387553	0.912589	0.009121
Ni	10	0.717883	0.238069	0.195083
Ni	11	0.791119	0.073141	0.098604
Ni	12	0.129373	0.405500	0.287574
Ni	13	0.286257	0.076597	0.102613
Ni	14	0.628176	0.397061	0.288307
Ni	15	0.627800	0.918867	0.009456
Ni	16	0.960550	0.238569	0.194634
Ni	17	0.547619	0.325422	0.104325
Ni	18	0.887177	0.646023	0.294591
Ni	19	0.046311	0.326770	0.106273
Ni	20	0.370933	0.646835	0.287101
Ni	21	0.373278	0.161067	0.005726
Ni	22	0.703940	0.495920	0.201017
Ni	23	0.291039	0.829121	0.100287
Ni	24	0.638987	0.150703	0.294078
Ni	25	0.630744	0.666532	0.011198
Ni	26	0.957928	0.993578	0.194562
Ni	27	0.371991	0.417127	0.008265
Ni	28	0.698637	0.743915	0.201199
Ni	29	0.876571	0.425533	0.012979
Ni	30	0.207613	0.741798	0.193248
Ni	31	0.550830	0.578306	0.104502
Ni	32	0.890958	0.903703	0.287182
Ni	33	0.623181	0.419002	0.011350
Ni	34	0.956195	0.733098	0.191254
Ni	35	0.126780	0.412525	0.005901
Ni	36	0.453655	0.740324	0.199278
Ni	37	0.794533	0.580372	0.106886
Ni	38	0.133151	0.904341	0.286249
Ni	39	0.378674	0.665728	0.004760
Ni	40	0.705463	0.990648	0.200128
Ni	41	0.880187	0.671578	0.008001
Ni	42	0.208098	0.991930	0.194756
Ni	43	0.538576	0.825950	0.104048
Ni	44	0.883392	0.150813	0.288961

Table H-20 Final fractional coordinates for the optimised leached Ni₁₁Al₅ (111) surface slab structure after the fifth adsorption position

The leached Ni ₁₁ Al ₅ (111) surface slab structure final cell contents after the fifth adsorption position				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.511278	0.496702	0.397695
O	1	0.490034	0.497404	0.353062
Al	1	0.300893	0.309722	0.100573
Al	2	0.606670	0.175341	0.009567
Al	3	0.957770	0.482687	0.201763

Al	4	0.870745	0.913314	-0.005097
Al	5	0.151004	0.917109	-0.000147
Al	6	0.485457	0.237645	0.207166
Al	7	0.875857	0.185835	0.007358
Al	8	0.219604	0.499058	0.206355
Al	9	0.141293	0.645910	-0.012829
Al	10	0.455238	0.981762	0.199655
Al	11	0.143031	0.160467	0.283519
Al	12	0.774086	0.833992	0.106998
Al	13	0.041902	0.570012	0.098720
Al	14	0.320504	0.575964	0.102311
Al	15	0.664945	0.892911	0.298074
Al	16	0.045009	0.839289	0.106218
Ni	1	0.128802	0.167354	0.010493
Ni	2	0.467717	0.490557	0.198740
Ni	3	0.796112	0.330034	0.106102
Ni	4	0.128351	0.661850	0.293712
Ni	5	0.534793	0.080182	0.110621
Ni	6	0.892255	0.395912	0.292155
Ni	7	0.042307	0.079558	0.101522
Ni	8	0.386001	0.396699	0.296004
Ni	9	0.389569	0.911537	0.011442
Ni	10	0.723538	0.236303	0.197125
Ni	11	0.794798	0.071711	0.099567
Ni	12	0.136808	0.406090	0.290824
Ni	13	0.289391	0.075579	0.104552
Ni	14	0.645884	0.386983	0.291537
Ni	15	0.629558	0.918459	0.011998
Ni	16	0.965373	0.237278	0.196054
Ni	17	0.550485	0.323930	0.107272
Ni	18	0.897043	0.647437	0.291929
Ni	19	0.049227	0.325623	0.107269
Ni	20	0.371284	0.657103	0.291812
Ni	21	0.374774	0.160679	0.008149
Ni	22	0.710720	0.492303	0.202665
Ni	23	0.293812	0.827963	0.102704
Ni	24	0.653311	0.141387	0.295468
Ni	25	0.632553	0.666186	0.013803
Ni	26	0.963052	0.992139	0.196634
Ni	27	0.373208	0.416691	0.011324
Ni	28	0.701524	0.740275	0.205772
Ni	29	0.877923	0.425170	0.014940
Ni	30	0.212374	0.741744	0.196835
Ni	31	0.554364	0.577143	0.106856
Ni	32	0.898715	0.900942	0.289444
Ni	33	0.624620	0.418209	0.013706
Ni	34	0.961948	0.732666	0.191704
Ni	35	0.128733	0.411508	0.007957
Ni	36	0.457285	0.739404	0.201257
Ni	37	0.797636	0.580133	0.109362

Ni	38	0.138544	0.907678	0.288515
Ni	39	0.380600	0.664611	0.007467
Ni	40	0.712619	0.990046	0.200246
Ni	41	0.882103	0.670829	0.010195
Ni	42	0.212847	0.992000	0.196599
Ni	43	0.541114	0.825346	0.106928
Ni	44	0.894737	0.149062	0.290553

Appendix I Final fractional coordinates for leaching behaviour using Ni_8Al_8 (111) and pure Ni (111) adsorption, using OH^-

This section contains the final fractional coordinates of the for the leaching behaviour using the Ni_8Al_8 (111) bimetallic phase. The final fractional coordinates of the adsorption onto the pure Ni (111) at the top, bridge and fcc sites are also listed.

I.1 Fractional coordinates for the leaching behaviour using the Ni_8Al_8 (111) surface slab

Table I-1 Final fractional coordinates for the optimised leaching behaviour using the Ni_8Al_8 (111) surface slab structure for the top site

The leaching behaviour using the Ni_8Al_8 (111) surface slab structure final cell contents of the top site				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.312255	0.683764	0.452310
O	1	0.366346	0.615144	0.418426
Al	1	0.245800	0.335439	0.098329
Al	2	0.619921	0.631490	0.293784
Al	3	0.522004	0.198267	0.011115
Al	4	0.894628	0.514514	0.206653
Al	5	0.065749	0.191376	-0.007119
Al	6	0.441008	0.503015	0.201225
Al	7	0.168674	0.250875	0.204706
Al	8	0.792357	0.940024	0.001313
Al	9	0.968245	0.099894	0.105670
Al	10	0.348702	0.411978	0.311394
Al	11	0.072137	0.930985	-0.010514
Al	12	0.446861	0.242834	0.197484
Al	13	0.783910	0.197124	0.004706
Al	14	0.163131	0.506873	0.206845
Al	15	0.970666	0.348046	0.102749
Al	16	0.340509	0.659049	0.340375
Al	17	0.064600	0.670664	-0.009301
Al	18	0.432040	0.986775	0.195922
Al	19	0.080744	0.169407	0.318562
Al	20	0.709718	0.858602	0.112042
Al	21	0.256634	0.839732	0.100679
Al	22	0.637771	0.154594	0.301023
Al	23	0.981529	0.599216	0.103578
Al	24	0.357817	0.897341	0.305088
Al	25	0.770645	0.452526	0.003516
Al	26	0.158085	0.757211	0.211888
Al	27	0.262137	0.584244	0.097763
Al	28	0.639226	0.889565	0.299677
Al	29	0.358101	0.154280	0.308734
Al	30	0.979696	0.847155	0.105835
Al	31	0.155915	0.004019	0.206870
Al	32	0.778295	0.694938	-0.002033
Ni	1	0.737358	0.342402	0.101961

Ni	2	0.108112	0.653423	0.299048
Ni	3	0.473825	0.097953	0.108139
Ni	4	0.855607	0.399094	0.292049
Ni	5	0.298400	0.944986	0.011736
Ni	6	0.680845	0.247655	0.197519
Ni	7	0.733085	0.086950	0.102992
Ni	8	0.111936	0.395029	0.296764
Ni	9	0.213436	0.101668	0.111987
Ni	10	0.591871	0.409656	0.292498
Ni	11	0.554372	0.940247	0.013301
Ni	12	0.933685	0.249859	0.195757
Ni	13	0.490165	0.343780	0.107630
Ni	14	0.863596	0.648238	0.296675
Ni	15	0.296531	0.183474	0.012997
Ni	16	0.673036	0.498226	0.195643
Ni	17	0.541305	0.696308	0.011931
Ni	18	0.920809	-0.003390	0.196853
Ni	19	0.290296	0.439779	0.009589
Ni	20	0.659800	0.751516	0.202584
Ni	21	0.493883	0.593449	0.104901
Ni	22	0.867846	0.904168	0.291947
Ni	23	0.542305	0.435878	0.012574
Ni	24	0.916419	0.746909	0.197901
Ni	25	0.025079	0.448541	0.013537
Ni	26	0.403174	0.760281	0.200156
Ni	27	0.746128	0.596623	0.102300
Ni	28	0.114919	0.908109	0.300245
Ni	29	0.297710	0.690424	0.007987
Ni	30	0.668562	0.002388	0.205112
Ni	31	0.486466	0.842950	0.104273
Ni	32	0.866134	0.154673	0.286935

Table I-2 Final fractional coordinates for the optimised leaching behaviour using the Ni₈Al₈ (111) surface slab structure for the fcc site

The leaching behaviour using the Ni₈Al₈ (111) surface slab structure final cell contents of the fcc site				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.546982	0.582966	0.402606
O	1	0.499310	0.658033	0.369614
Al	1	0.246920	0.333914	0.099220
Al	2	0.634812	0.628464	0.300317
Al	3	0.520925	0.197874	0.011034
Al	4	0.893943	0.516285	0.207075
Al	5	0.065275	0.190562	-0.006631
Al	6	0.441897	0.499026	0.200416
Al	7	0.167195	0.251746	0.206211
Al	8	0.790743	0.939293	0.001870
Al	9	0.967220	0.100583	0.105596
Al	10	0.350875	0.411290	0.313655

Al	11	0.070927	0.931149	-0.009745
Al	12	0.448176	0.242203	0.198046
Al	13	0.781883	0.198141	0.005621
Al	14	0.163147	0.506311	0.208617
Al	15	0.971387	0.348188	0.102879
Al	16	0.346781	0.658663	0.317232
Al	17	0.064303	0.670465	-0.008906
Al	18	0.431707	0.989801	0.196410
Al	19	0.081305	0.169969	0.320657
Al	20	0.708625	0.855644	0.113792
Al	21	0.256094	0.838275	0.102811
Al	22	0.641470	0.150826	0.301410
Al	23	0.982344	0.597688	0.103984
Al	24	0.354012	0.915725	0.304312
Al	25	0.770511	0.452590	0.004681
Al	26	0.154360	0.756866	0.209943
Al	27	0.262595	0.583147	0.098179
Al	28	0.642860	0.891161	0.301215
Al	29	0.358890	0.158651	0.310235
Al	30	0.978939	0.845924	0.105478
Al	31	0.154826	0.006309	0.206034
Al	32	0.778451	0.693861	-0.000656
Ni	1	0.736338	0.345334	0.103240
Ni	2	0.110861	0.654462	0.301243
Ni	3	0.475018	0.096843	0.108393
Ni	4	0.860474	0.395957	0.291732
Ni	5	0.297321	0.944239	0.013549
Ni	6	0.683973	0.243689	0.196241
Ni	7	0.733581	0.084626	0.102804
Ni	8	0.113499	0.395882	0.298081
Ni	9	0.213237	0.102254	0.112620
Ni	10	0.597460	0.396439	0.289889
Ni	11	0.553229	0.937868	0.015288
Ni	12	0.932345	0.251343	0.195245
Ni	13	0.491121	0.342088	0.107545
Ni	14	0.866422	0.648173	0.298186
Ni	15	0.296043	0.182686	0.013610
Ni	16	0.671532	0.500326	0.199370
Ni	17	0.540938	0.696298	0.014308
Ni	18	0.922209	-0.004648	0.196419
Ni	19	0.289474	0.439308	0.010348
Ni	20	0.656441	0.753056	0.205898
Ni	21	0.492288	0.595493	0.108085
Ni	22	0.871828	0.903272	0.292098
Ni	23	0.541149	0.438240	0.013912
Ni	24	0.915802	0.745849	0.198374
Ni	25	0.026133	0.447358	0.013450
Ni	26	0.403912	0.755628	0.212799
Ni	27	0.744842	0.596469	0.104618
Ni	28	0.121152	0.906966	0.298225

Ni	29	0.296986	0.691329	0.009022
Ni	30	0.669650	0.001570	0.205679
Ni	31	0.484013	0.840662	0.108136
Ni	32	0.869867	0.152107	0.286587

I.2 Fractional coordinates for adsorption of OH⁻ onto the Ni (111) surface slab

Table I-3 Final fractional coordinates for the optimised Ni (111) surface slab structure after the top adsorption site

The Ni (111) surface slab structure final cell contents after the top adsorption site				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.591375	0.567037	0.412006
O	1	0.549472	0.652757	0.380265
Ni	1	0.666606	0.666266	0.096060
Ni	2	0.333462	0.332473	0.286112
Ni	3	0.833322	0.083353	-0.001408
Ni	4	0.500807	0.748375	0.192196
Ni	5	0.083474	0.833199	-0.001349
Ni	6	0.747929	0.500729	0.192556
Ni	7	0.083366	0.083170	-0.001154
Ni	8	0.750162	0.749714	0.190374
Ni	9	0.333597	0.832962	-0.000721
Ni	10	-0.000486	0.499892	0.190125
Ni	11	0.166941	0.916406	0.094947
Ni	12	0.835466	0.582210	0.286350
Ni	13	0.417122	0.666262	0.096061
Ni	14	0.084054	0.332470	0.286114
Ni	15	0.417127	0.915736	0.095438
Ni	16	0.083570	0.582864	0.286061
Ni	17	0.833154	0.333449	-0.000802
Ni	18	0.500491	0.998848	0.190567
Ni	19	0.666502	0.416985	0.095994
Ni	20	0.333357	0.083267	0.286195
Ni	21	0.916688	0.166633	0.094817
Ni	22	0.584414	0.833686	0.286967
Ni	23	0.915932	0.416881	0.095354
Ni	24	0.583695	0.082831	0.286214
Ni	25	0.166681	0.166272	0.095302
Ni	26	0.834107	0.833074	0.286044
Ni	27	0.333594	0.583263	-0.000779
Ni	28	-0.000421	0.250145	0.190175
Ni	29	0.583395	0.333450	-0.000804
Ni	30	0.250654	0.998843	0.190572
Ni	31	0.583387	0.583225	-0.000245
Ni	32	0.250123	0.249744	0.190077
Ni	33	0.833326	0.833199	-0.001347
Ni	34	0.501341	0.500729	0.192558
Ni	35	0.666648	0.916406	0.094948

Ni	36	0.332313	0.582212	0.286328
Ni	37	0.916538	0.666589	0.094883
Ni	38	0.584374	0.330656	0.286359
Ni	39	0.916673	0.916651	0.094605
Ni	40	0.584771	0.580414	0.297112
Ni	41	0.166867	0.666588	0.094879
Ni	42	0.834942	0.330654	0.286357
Ni	43	0.333488	0.083021	-0.000686
Ni	44	0.000142	0.749717	0.189833
Ni	45	0.583440	0.832961	-0.000720
Ni	46	0.250584	0.499886	0.190114
Ni	47	0.583460	0.083171	-0.001153
Ni	48	0.250118	0.749717	0.190373
Ni	49	0.666673	0.166633	0.094816
Ni	50	0.331912	0.833653	0.286990
Ni	51	0.833143	0.583261	-0.000775
Ni	52	0.500268	0.250148	0.190171
Ni	53	0.083362	0.333218	-0.000775
Ni	54	0.750060	0.999821	0.189931
Ni	55	0.083349	0.583298	-0.001152
Ni	56	0.750216	0.249559	0.190109
Ni	57	0.333412	0.333216	-0.000779
Ni	58	0.000114	0.999821	0.189933
Ni	59	0.166627	0.416731	0.095178
Ni	60	0.833976	0.082033	0.286246
Ni	61	0.417037	0.166275	0.095300
Ni	62	0.082818	0.833076	0.286047
Ni	63	0.417177	0.416880	0.095347
Ni	64	0.083464	0.082828	0.286218

Table I-4 Final fractional coordinates for the optimised Ni (111) surface slab structure after the bridge adsorption site

The Ni (111) surface slab structure final cell contents after the bridge adsorption site				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.445357	0.596953	0.398096
O	1	0.424847	0.646647	0.355920
Ni	1	0.666628	0.665913	0.095941
Ni	2	0.333489	0.329780	0.286508
Ni	3	0.833322	0.083073	-0.000987
Ni	4	0.499975	0.748633	0.191682
Ni	5	0.083516	0.832938	-0.000615
Ni	6	0.748010	0.500224	0.192361
Ni	7	0.083513	0.082812	-0.000510
Ni	8	0.750177	0.749175	0.190280
Ni	9	0.333447	0.832877	-0.000366
Ni	10	-0.000054	0.499318	0.190351
Ni	11	0.167084	0.915992	0.095708
Ni	12	0.834743	0.581981	0.286644

Ni	13	0.416659	0.666314	0.096071
Ni	14	0.083603	0.331892	0.286428
Ni	15	0.416550	0.915920	0.095788
Ni	16	0.082136	0.581965	0.286522
Ni	17	0.833100	0.333219	-0.000452
Ni	18	0.499966	0.999212	0.190265
Ni	19	0.666699	0.416635	0.095859
Ni	20	0.333616	0.082760	0.286722
Ni	21	0.916815	0.166182	0.095227
Ni	22	0.585413	0.833756	0.285729
Ni	23	0.916629	0.416246	0.095608
Ni	24	0.583785	0.081431	0.286605
Ni	25	0.166928	0.165680	0.095845
Ni	26	0.833437	0.832133	0.286628
Ni	27	0.333394	0.583143	-0.000270
Ni	28	0.000094	0.249173	0.190356
Ni	29	0.583223	0.333309	-0.000491
Ni	30	0.251432	0.996469	0.192344
Ni	31	0.583223	0.583147	-0.000219
Ni	32	0.250065	0.249122	0.190330
Ni	33	0.833371	0.832983	-0.001001
Ni	34	0.499901	0.499549	0.191278
Ni	35	0.666690	0.916228	0.095095
Ni	36	0.331195	0.578053	0.289602
Ni	37	0.916701	0.666123	0.095234
Ni	38	0.586375	0.326303	0.285276
Ni	39	0.916670	0.916245	0.095051
Ni	40	0.589534	0.577788	0.290241
Ni	41	0.166999	0.665915	0.095811
Ni	42	0.835789	0.329778	0.286624
Ni	43	0.333411	0.082794	-0.000464
Ni	44	-0.000005	0.749173	0.190204
Ni	45	0.583292	0.832920	-0.000536
Ni	46	0.250954	0.500135	0.192125
Ni	47	0.583345	0.083061	-0.000958
Ni	48	0.250600	0.748734	0.191470
Ni	49	0.666649	0.166309	0.095078
Ni	50	0.331174	0.836251	0.290383
Ni	51	0.833150	0.583053	-0.000443
Ni	52	0.499847	0.249154	0.190137
Ni	53	0.083436	0.332785	-0.000671
Ni	54	0.750050	0.999319	0.190396
Ni	55	0.083498	0.583053	-0.000494
Ni	56	0.750386	0.249155	0.190157
Ni	57	0.333414	0.333198	-0.000458
Ni	58	0.000173	0.999282	0.190212
Ni	59	0.166602	0.416195	0.095533
Ni	60	0.833843	0.081478	0.286602
Ni	61	0.416589	0.166147	0.095247
Ni	62	0.079662	0.833903	0.285613

Ni	63	0.416275	0.416623	0.095809
Ni	64	0.082622	0.082888	0.286723

Table I-5 Final fractional coordinates for the optimised Ni (111) surface slab structure after the fcc adsorption site

The Ni (111) surface slab structure final cell contents after the fcc adsorption site				
Element	Atom Number	Fractional coordinates of atoms		
		u	v	w
H	1	0.420975	0.663855	0.401347
O	1	0.417784	0.665973	0.354735
Ni	1	0.666508	0.666341	0.095843
Ni	2	0.333504	0.331597	0.286544
Ni	3	0.833377	0.083335	-0.001249
Ni	4	0.499773	0.749629	0.191756
Ni	5	0.083653	0.833166	-0.000667
Ni	6	0.747685	0.501144	0.192416
Ni	7	0.083579	0.083029	-0.000539
Ni	8	0.750166	0.749866	0.190059
Ni	9	0.333462	0.833103	-0.000257
Ni	10	0.000035	0.500070	0.190201
Ni	11	0.167202	0.916424	0.095848
Ni	12	0.835107	0.583285	0.286527
Ni	13	0.416694	0.666646	0.096251
Ni	14	0.083470	0.333247	0.286205
Ni	15	0.416409	0.916432	0.095843
Ni	16	0.081881	0.583306	0.286545
Ni	17	0.833078	0.333529	-0.000539
Ni	18	0.499977	1.000044	0.190060
Ni	19	0.666511	0.417133	0.095842
Ni	20	0.333507	0.084847	0.286547
Ni	21	0.916746	0.166667	0.095075
Ni	22	0.585818	0.835588	0.285525
Ni	23	0.916471	0.416755	0.095594
Ni	24	0.583741	0.083106	0.286388
Ni	25	0.166854	0.166343	0.095616
Ni	26	0.833347	0.833532	0.286389
Ni	27	0.333462	0.583420	-0.000255
Ni	28	0.000037	0.249868	0.190203
Ni	29	0.583212	0.333611	-0.000661
Ni	30	0.251326	0.997442	0.192467
Ni	31	0.583151	0.583418	-0.000253
Ni	32	0.250191	0.249889	0.190202
Ni	33	0.833378	0.833273	-0.001250
Ni	34	0.499776	0.500566	0.191746
Ni	35	0.666672	0.916609	0.094819
Ni	36	0.330444	0.579999	0.290831
Ni	37	0.916745	0.666569	0.095074
Ni	38	0.585829	0.328535	0.285524
Ni	39	0.916756	0.916614	0.094817

Ni	40	0.589895	0.580010	0.290673
Ni	41	0.167200	0.666359	0.095848
Ni	42	0.835119	0.331557	0.286534
Ni	43	0.333431	0.083025	-0.000538
Ni	44	0.000068	0.749879	0.190063
Ni	45	0.583212	0.833162	-0.000662
Ni	46	0.251320	0.501199	0.192457
Ni	47	0.583324	0.083331	-0.001247
Ni	48	0.250730	0.749623	0.191796
Ni	49	0.666671	0.166703	0.094820
Ni	50	0.330423	0.839514	0.290868
Ni	51	0.833079	0.583378	-0.000539
Ni	52	0.499976	0.249953	0.190060
Ni	53	0.083378	0.333302	-0.000683
Ni	54	0.750058	0.999960	0.190101
Ni	55	0.083579	0.583378	-0.000539
Ni	56	0.750170	0.249942	0.190060
Ni	57	0.333431	0.333529	-0.000538
Ni	58	0.000069	1.000029	0.190064
Ni	59	0.166851	0.416781	0.095612
Ni	60	0.833352	0.083079	0.286391
Ni	61	0.416636	0.166672	0.095075
Ni	62	0.078885	0.835539	0.285544
Ni	63	0.416407	0.417140	0.095841
Ni	64	0.081879	0.084775	0.286553

