

Dermal exposure and surface contamination associated with the use of a cobalt-chrome alloy during additive manufacturing

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PREFACE

This dissertation is submitted in article format and written in accordance with the guidelines outlined for the journal *Annals of Work Exposures and Health*. The content of the dissertation is, therefore, referenced in Harvard style of abbreviation and punctuation. Reference lists are provided at the end of each chapter and in alphabetical order by the first name of the author. The dissertation is written according to the United Kingdom English spelling which is kept consistent throughout with exceptions on names or references used.

This dissertation comprises four chapters which are outlined as follows:

- Chapter 1: In this chapter, the general introduction and problem statement related to dermal exposure and surface contamination associated with the use of a cobalt-chrome (CoCr) alloy during additive manufacturing is provided. This chapter also introduces the aims, objectives, and hypotheses of the dissertation.
- Chapter 2: In this chapter, a literature study on topics relevant to this dissertation is provided. This includes an overview of additive manufacturing (AM), its process categories, processing phases, and feedstock powders used in AM, with a specific focus on CoCr alloy feedstock powders. Occupational exposure to metal feedstock powders is discussed, including the exposure routes with a focus on dermal exposure. A brief overview of dermal absorption and the factors influencing dermal absorption of metals in CO-538 feedstock powders are provided. Literature regarding the potential health effects of exposure, legislation regarding dermal exposure, and methodologies to assess dermal exposure are discussed.
- Chapter 3: In this chapter, an article on the topic “Dermal exposure and surface contamination associated with the use of a CoCr alloy during additive manufacturing” is provided and set out in accordance with guidelines for the journal *Annals of Work Exposures and Health*.
- Chapter 4: In this final chapter, the conclusion of the main findings of the dissertation according to the aims, objectives, and hypotheses, along with the limitations, recommendations, and potential future studies are discussed. Recommendations based on the findings of this study as well as recommendations regarding necessary control measures to eliminate or reduce dermal metal exposure and surface contamination within the AM facility are made. Limitations of this study are addressed, and potential future studies are suggested.
- Annexure A: In Annexure A, the ethics approval letter for this dissertation is provided.
- Annexure B: In Annexure B, proof of language editing of this dissertation is provided.

AUTHORS' CONTRIBUTIONS

| Author | Contribution | Consent |
|---------------------------|---|---------|
| Ms LM Paulse | <ul style="list-style-type: none">• Study planning and design• Preparation of ethics application• Conducting literature research• Conducting data collection• Data analysis and result interpretation• Writing of dissertation• Formulating recommendations | |
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The following is a statement from the authors that confirms each individual's role in this study:

By providing my signature above I declare that I have approved the manuscript and that my role in the study as indicated is representative of my actual contribution. By providing my signature above I give my consent that this manuscript may be published as part of the MHS_c (Occupational Hygiene) dissertation of Ms L.M. Paulse.

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ABSTRACT

Introduction: Additive Manufacturing (AM) is a layered-based technology that is used to manufacture three-dimensional products from computer-aided design. AM offers many advantages over traditional methods of manufacturing which have led to an increase in the application of the technology in many industries, homes, and schools.

Metal powders such as cobalt-chrome (CoCr) alloys can be used as feedstock materials for the powder bed fusion (PBF) AM processes. During the activities that form part of the three processing phases of AM (pre-processing, processing, and post-processing), dermal exposure may occur when the AM operators come into direct contact with the feedstock powders, or when the powder particles become airborne and settle onto their skin or onto surfaces within the workplace with which they have contact.

Dermal exposure is often overlooked due to the perception that respiratory exposure is the main route of concern. To date, only one study has assessed dermal exposure during AM. This study found detectable concentrations of nickel (Ni), Co, and Cr on the index fingers of AM operators. Metals such as Ni, Co, and Cr are known dermal sensitizers that may lead to adverse health effects following dermal exposure.

Due to the limited amount of information available, and the adverse health effects associated with dermal exposure to metals such as Co and Cr, there is a need for further investigation into dermal exposure during metal AM. This study, therefore, aimed to expand on the information available by characterising virgin and used samples of a CoCr alloy feedstock powder (CO-538) in terms of its particle size, shape, and elemental composition, and by assessing dermal exposure and workplace surface contamination when the CoCr alloy feedstock powder was used during PBF.

Method: To establish the particle size distribution (PSD) and shape of the virgin (new) and used CO-538 feedstock powder, static image analysis (Malvern Morphologi G3) and scanning electron microscopy (SEM) analysis were used. Inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis was used to establish the elemental composition of the virgin and used CO-538 feedstock powder samples. A removal wipe sampling method using Ghostwipes™ was used to assess dermal exposure and surface contamination when the CO-538 feedstock powder was used during PBF. All AM operators at the facility (n=2) volunteered to participate in this study which was conducted over a period of eleven days during which six of the same products were manufactured. Anatomical areas such as the index finger, palm, wrist, back of the hand, and neck were sampled before and after each AM processing phase (7 pre-processing, 5 processing, and

7 post-processing phases). Operating (AM) and non-operating (non-AM) workplace surfaces were sampled before and after each shift to quantify surface contamination (35 samples). All dermal and surface wipe samples were analysed using ICP-mass spectrometry (ICP-MS).

Results: The PSD analysis indicated a statistically significant difference ($p \leq 0.05$) at $d(0.1)$ between virgin and used powder with the used powder particles generally smaller in size than those of virgin powder particles based on the mean. Statistically significant differences ($p \leq 0.05$) were also observed in the mean circularity and convexity of virgin and used powders, indicating that the used powders consisted of more particles that were irregularly shaped and less smooth-surfaced than the virgin powder particles. Co, Cr, molybdenum, aluminium, iron, and Ni were detected in the new and used CO-538 feedstock powder. Dermal exposure to CO-538 constituents occurred during all three processing phases, on all the sampled anatomical areas, with the highest total metal concentration detected on the index finger during the post-processing phase of AM with a geometric mean (GM) and 95% lower and upper confidence intervals (CI) of $3.160 \mu\text{g}/\text{cm}^2$ (CI: $0.703\text{-}14.210 \mu\text{g}/\text{cm}^2$). The metal with the highest detected concentration was Co, with a GM of $1.224 \mu\text{g}/\text{cm}^2$ (CI: $0.280\text{-}5.336 \mu\text{g}/\text{cm}^2$) on the finger during the pre-processing phase. The highest full shift GM concentration of each metal was detected on the finger and followed a trend of $\text{Co} > \text{Cr} > \text{Fe} > \text{Al} > \text{Mo} > \text{Ni}$. Surface contamination was detected on all AM and non-AM operating sampling areas with concentrations ranging from $0.106 \mu\text{g}/\text{cm}^2$ on operator 2's office desk to $19.695 \mu\text{g}/\text{cm}^2$ on workbench 1.

Conclusion: When CO-538 feedstock powder are used during AM, dermal exposure to metals such as Co, Cr and Ni, which are known dermal sensitizers, does occur. Therefore, a risk of developing adverse dermal health effects following exposure during AM does exist. Furthermore, it is shown that cross-contamination between AM and non-AM areas occurs, and, therefore, all sampled surfaces may act as a secondary source of exposure. There is thus a need for control measures to be implemented in AM facilities to eliminate or reduce dermal exposure and to limit the spread of contaminants within the facility. Comprehensive standard operating procedures regarding housekeeping and personal protective equipment should be developed and implemented in AM facilities. Furthermore, controls such as local extraction ventilation should be used during manual handling activities, and high-risk activities such as using compressed air should be prohibited.

Word count: 827

Key terms: Powder Bed Fusion, 3D printing, skin, cobalt, chromium, molybdenum, CO-538.

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LIST OF UNITS AND SYMBOLS

| | |
|--------------------|---------------------------------|
| \leq | less than or equal to |
| \geq | greater than or equal to |
| $<$ | less than |
| $>$ | greater than |
| \pm | plus-minus |
| ® | registered trademark |
| ™ | unregistered trademark |
| % | percentage |
| °C | degrees Celsius |
| cm | centimetre |
| cm ² | square centimetre |
| g | gram |
| mm ³ | cubic millimetre |
| nm | nanometre |
| µg | microgram |
| µg/cm ² | microgram per square centimetre |
| µm | micrometre |

LIST OF ABBREVIATIONS

| | |
|--------------|---|
| 3D | three-dimensional |
| ACGIH | American Conference of Governmental Industrial Hygienists |
| Ag | silver |
| Al | aluminium |
| AM | additive manufacturing |
| AMF | Additive Manufacturing Format |
| ANOVA | Analysis of Variation |
| ASTM | American Society for Testing and Materials |
| BDL | below detection limit |
| CAD | computer-aided design |
| CE | Circle Equivalent |
| CI | confidence interval |
| Co | cobalt |
| CoCr | cobalt-chrome |
| Cr | chromium |
| Cr(III) | trivalent chromium |
| Cr(VI) | hexavalent chromium |
| Cu | copper |
| D | decontamination |
| d(0.1) | indicates 10% of particles are smaller than the given diameter |
| d(0.5) | indicates 50% of particles are smaller than the given diameter |
| d(0.9) | indicates 90% of particles are smaller than the given diameter |
| DMLS | direct metal laser sintering |
| DMR | Department of Minerals and Resources, South Africa |
| DOEL | Department of Employment and Labour, South Africa |
| Dp | deposition |
| DSEN | Dermal sensitisation notation |
| E | emission |
| eds. | editors |
| <i>et al</i> | <i>et alii</i> (and others) |
| Fe | iron |
| FeNi | iron-nickel |
| FFP3 | filtering face piece 3 |
| GHS | Globally Harmonised System of Classification and Labelling of Chemicals |

| | |
|------------------|--|
| GM | geometric mean |
| H ₂ O | water |
| HCA | hazardous chemical agent |
| HEPA | high-efficiency particulate absorbing |
| IARC | International Agency for Research on Cancer |
| ICMM | International Council on Mining & Metals |
| ICP-AES | using Inductively Coupled Argon Plasma-Atomic Emission Spectroscopy |
| ICP-MS | inductively coupled plasma-mass spectrometry |
| ICP-OES | inductively coupled plasma-optical emission spectroscopy |
| ISO | International Organization for Standardizations |
| ISO/ASTM | International Organization for Standardization/ American Society for Testing and Materials |
| ISO/TR | International Organization for Standardization/Technical Report |
| L | resuspension or evaporation |
| LEV | local extraction ventilation |
| LOD | limit of detection |
| LPS | liquid-phase sintering |
| Ltd | limited liability company |
| Mg | magnesium |
| MHS | Mine Health and Safety |
| m/m | mass/mass |
| Mn | manganese |
| Mo | molybdenum |
| n | number |
| Ni | nickel |
| NiCo | nickel-cobalt |
| NIOSH | National Institute for Occupational Health and Safety |
| NPs | nanoparticles |
| OEL | occupational exposure limit |
| OHHRI | Occupational Hygiene and Health Research Initiative |
| OHS | Occupational Health and Safety |
| OSHA | Occupational Safety and Health Administration, USA |
| P | penetration and permeation |
| PBF | powder bed fusion |
| PPE | personal protective equipment |
| PSD | particle size distribution |

| | |
|-------|---|
| Pt | platinum |
| R | removal |
| Rd | redistribution |
| RHCA | Regulations for Hazardous Chemical Agents |
| RSEN | Respiratory sensitisation notation |
| SANAS | South African National Accreditation System |
| SDS | safety data sheet |
| SDSs | safety data sheets |
| SEM | scanning electron microscopy |
| Sen | sensitisation notation |
| Sk | skin notation |
| SOPs | standard operating procedures |
| STL | derived from stereolithography |
| T | transfer |
| Ti | tin |
| UK | United Kingdom |
| UN | United Nations |
| USA | United States of America |
| W | tungsten |
| WHO | World Health Organisation |
| Zn | zinc |

CHAPTER 1 GENERAL INTRODUCTION

1.1 Introduction and problem statement

Additive Manufacturing (AM) refers to the process of creating three-dimensional (3D) products from computer-aided design (CAD) by using techniques that involve adding and fusing consecutive layers of material (ISO/ASTM: 2021; Ljunggren *et al.*, 2019). The increased application and continued relevance of AM in various industries are attributed to the advantages it offers over traditional manufacturing methods (Alimi and Meijboom, 2021; Campbell *et al.*, 2012; Gibson *et al.*, 2021). These advantages include the ability to design and manufacture complex and customised products at a faster pace, with fewer processing steps, while utilising materials more sustainably by using smaller amounts thereof and reusing leftover materials (Attaran 2017; Campbell *et al.*, 2012; Gibson *et al.*, 2021).

There are seven types of AM process categories described by the American Society for Testing and Materials International (ASTM), namely binder jetting, directed energy deposition, material extrusion, material jetting, powder bed fusion (PBF), sheet lamination and vat photopolymerisation (ISO/ASTM: 2021). These AM process categories differ from each other regarding the feedstock material that is used and the method by which these feedstock materials are deposited (Monzón *et al.*, 2015). According to Matthews *et al.* (2016), the leading AM process category used to produce 3D products from metal feedstock powder is PBF. The feedstock powder that is not fused can be collected after the build and reused for future builds (Contaldi *et al.*, 2019; Tang *et al.*, 2015).

There are several different metal and alloy feedstock powders that can be applied in PBF AM (Mutchler, 2019; Qian, 2015). Metal alloys are often preferred over pure metals due to the individual characteristics of the alloy components that provide desirable properties to the end product (UN, 2019; Renneboog, 2016). Cobalt-chrome (CoCr) is often used due to it being a strong alloy that is resistant to heat, corrosion, and discolouration (Al Jabbari, 2014).

AM can be divided into three processing phases namely pre-processing, processing, and post-processing. During the pre-processing phase, the desired 3D product is designed, the AM machine is set up and loaded with feedstock powders, and the baseplate is levelled. During the processing phase, the 3D product is manufactured within the enclosed chamber of the AM machine. During the post-processing phase, the manufactured 3D product is removed from the AM machine and the AM machine along with the manufactured product is cleaned (Gibson *et al.*, 2015). During these activities, especially where manual handling of the powders is required (pre- and post-processing), feedstock powders can be released into the workplace environment

where operators may potentially become exposed (Afshar-Mohajer *et al.*, 2015; Graff *et al.*, 2017; Ljunggren *et al.*, 2019).

Most exposure studies that have been conducted within AM have focussed only on respiratory exposure and, therefore, limited information is available regarding alternative routes of exposure. Dermal exposure can occur through three typical pathways namely the deposition of substances from the air directly onto the skin, the immersion of the body into the substance, or direct contact with surfaces or clothing that have been contaminated by the substance (Schneider *et al.*, 1999). To date, only one study has investigated dermal exposure to metal feedstock powder during AM. This study found measurable concentrations of Nickel (Ni), Co and Cr at the end of a workweek on the index fingers of AM operators who worked with Hastelloy® X Ni-based feedstock powders (Hayenes International, Idaho, USA) during PBF (Ljunggren *et al.*, 2019). Three cases of occupational allergic contact dermatitis caused by dermal exposure to epoxy resin compounds that were used during vat photopolymerisation and another unspecified AM process have been reported (Creytens *et al.*, 2017; Chang *et al.*, 2004). In the first case, the patient's symptoms presented on the wrist, hands, and forearms, and spread further to the face, neck, ears, legs, and abdomen. In the second case, the symptoms presented on the back of the hands and spread to the forearms, axillae, and abdomen (Creytens *et al.*, 2017). The third case presented on both sides of the hands including the finger tips (Chang *et al.*, 2004).

When exposure to metal powders occurs, the adverse health effects associated with the exposure depend on factors such as particle size, shape, and elemental composition (Chen *et al.*, 2020). Several AM feedstock powder's safety data sheets (SDSs) which should contain information on these characteristics have failed to disclose sufficient information regarding particle size characterisation, and elemental composition (du Preez *et al.*, 2018; Mellin *et al.*, 2016). Since reusing powders may alter the chemical and physical characteristics of the feedstock powders both virgin (new) and used feedstock powders should be characterised according to size, shape, and elemental composition (Tang *et al.*, 2015).

CO-538 is a commercially available CoCr alloy feedstock powder that was investigated in this study. According to its SDS, this alloy consists of 50-70% Co, 20-50% Cr, 5-20% molybdenum, and less than 1% of both nickel (Ni) and carbon (Praxair Surface Technologies, 2015). When dermal exposure to metal alloys occurs, exposure to the individual alloying elements (metals) or a combination of metals may occur (Julander *et al.*, 2009). *In vitro*, Co and Cr can permeate through the intact skin (Larese Filon *et al.*, 2004; Larese Filon *et al.*, 2008). Co and Cr are known sensitisers that can cause adverse dermal health effects such as allergic contact dermatitis (Tokar *et al.*, 2013). When simultaneous dermal exposure to Co, Cr, Ni, or a combination of these metals occurs, sensitisation may occur more frequently than it would when exposure to the individual

metals occurs (Ruff and Belsito, 2006). It is, therefore, important to assess dermal exposure to CoCr alloy powders used in AM, and to establish the elemental composition and physical characteristics (shape and size) thereof, in order to understand the potential risk of adverse dermal health effects developing.

Removal wipe sampling methods with commercially available Ghostwipes™ have successfully been used to assess dermal exposure and surface contamination of metals including Al, Co, Cr, Ni, platinum, and other platinum group metals (du Plessis *et al.*, 2010; du Plessis *et al.*, 2013; Gorman Ng *et al.*, 2017; Linde *et al.*, 2018; Linde *et al.*, 2021; OSHA, 2002). Removal wipe sampling can be defined as the removal of substances from the skin (or workplace surface) by applying a force with a sampling medium that is equal to or larger than the adhesion force of the substance on the surface (Brouwer *et al.*, 2000; ISO/TR, 2011). Dermal wipe sampling indicates the exposure concentration detected on an anatomical area at the time of sampling (ISO/TR, 2011).

Dermal wipe sampling is an effective tool in determining full shift exposure as well as distinguishing between the exposure potential of different activities. Assessment of dermal exposure can also assist in identifying processes that may lead to exposure, identifying exposure pathways, and determining the effectiveness of or need for control measures. Surface wipe sampling also serves many purposes within occupational hygiene, including the ability to evaluate the effectiveness of control measures, to indicate the potential of a surface to act as a secondary source of exposure, and to determine the effectiveness of housekeeping (Ashley *et al.*, 2011).

The limited available information regarding dermal exposure during AM and the reported occurrence of adverse dermal health effects following exposure during AM as well as the adverse health effects associated with dermal exposure to Co and Cr, highlight the need for further investigation into dermal exposure during metal AM. This study provides much-needed information regarding the dermal exposure concentrations on different anatomical areas during each AM processing phase. This study also identifies potential workplace surfaces within AM facilities that may act as secondary sources of exposure. This information could assist in establishing operating procedures and control measures that need to be implemented to protect AM operators' health within the AM industry in the future.

1.2 Research aims and objectives

1.2.1 Research aims

The first aim of this study was to characterise virgin and used samples of a CO-538 alloy feedstock powder in terms of its particle size, shape, and elemental composition. The second aim of this study was to assess dermal exposure of AM operators as well as workplace surface contamination when the CO-538 alloy powder was used during PBF.

1.2.2 Specific research objectives

The objectives of this study were:

1. To perform static image analysis using the Malvern Morphologi G3 (Malvern Instruments Ltd, UK) and scanning electron microscopy (SEM) to establish the particle size distribution (PSD) and shape of the virgin and used CO-538 alloy powder particles.
2. To utilise Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) to establish the elemental composition of the virgin and used CO-538 alloy powders.
3. To utilise a removal wipe sampling method using Ghostwipes™ to assess dermal exposure of AM operators and contamination of workplace surfaces when the CO-538 alloy powder is used during AM.

1.3 Hypotheses

1. The elemental composition and physical characteristics of the metal alloy feedstock powder are important when assessing the potentially harmful effects that the feedstock powder may have on the health of AM operators (Chen *et al.*, 2020). SDSs of AM feedstock powders, which should contain information on these characteristics, have in several instances failed to completely disclose particle size and elemental composition (du Preez *et al.*, 2018; Mellin *et al.*, 2016).

It is hypothesised (Hypothesis 1) that the SDS of the CO-538 metal feedstock powder does not disclose all the necessary information regarding particle size and elemental composition which is essential to evaluate the potential risk of dermal exposure and health of AM operators.

2. The AM facility investigated in this study uses a CoCr alloy feedstock powder (CO-538) in a PBF AM process. PBF AM consists of three processing phases, namely pre-processing, processing, and post-processing. Activities during these three phases can lead to powder

particles being released into the work environment. Two studies that investigated metal particle emissions during PBF found that the highest rate of particle emissions during PBF was during activities that form part of the pre- and post-processing phases (Graff *et al.*, 2017; Ljunggren *et al.*, 2019). Dermal exposure may occur when powder particles emitted into the air due to different processing phases settle on the skin of AM operators, when the particles settle on surfaces with which the AM operators come into contact, or when AM operators come into direct contact with the feedstock powders during manual handling activities. To date, only one study has investigated dermal exposure to metals during AM, and found measurable concentrations of Co, Cr and Ni on the index fingers of AM operators who worked with a Hastelloy® X Ni-based feedstock powders (Hayenes International, ID, USA) (Ljunggren *et al.*, 2019).

It is hypothesised (Hypothesis 2) that measurable concentrations of metals are detected on dermal surfaces such as the wrist, palm, back of the hand, finger and neck, with the highest total metal concentrations being detected during the pre- and post-processing phases where the majority of manual handling activities take place. Furthermore, it is hypothesised (Hypothesis 3) that measurable concentrations of total metals are detected on surfaces within the AM facility indicating surface contamination during the AM process.

1.4 References

- Afshar-Mohajer N, Wu C, Ladun T, Rajon DA. (2015) Characterization of particulate matters and total VOC emissions from a binder jetting 3D printer. *Build Environ*; 93: 293-301.
- Al Jabbari YS. (2014) Physico-mechanical properties and prosthodontic applications of Co-Cr dental alloys: a review of the literature. *J Adv Prosthodont*; 6: 138-145.
- Alimi OA, Meijboom R. (2021) Current and future trends of additive manufacturing for chemistry applications: a review. *J. Mater. Sci*; 56: 16824-16850.
- Ashley K, Brisson MJ, White KT. (2011) Review of standards for surface and dermal sampling. *J. ASTM Int*; 8: 1-9.
- Attaran M. (2017) The rise of 3-D printing: The advantages of additive manufacturing over traditional manufacturing. *Bus. Horiz*; 60: 677-688.
- Brouwer DH, Boeniger MF, van Hemmen J. (2000) Hand wash and manual skin wipes. *Ann Occup Hyg*; 44: 501-510.

Campbell I, Bouwell D, Gibson I. (2012) Additive manufacturing: rapid prototyping comes of age. *Rapid Prototyp. J*; 18: 255-258.

Chang TY, Lee LJ, Wang JD, Shie RH, Chan CC. (2004) Occupational risk assessment on allergic contact dermatitis in a resin model making process. *J. Occup. Health*; 46: 148-152.

Chen R, Yin H, Cole IS, Shen S, Zhou X, Wang Y, Tang S. (2020) Exposure, assessment and health hazards of particulate matter in additive manufacturing: A review. *Chemosphere*; 259: 1-17.

Contaldi V, Del Re F, Palumbo B, Squillace A, Corrado P, Di Petta P. (2019) Mechanical characteristics of stainless steel parts produced by direct metal laser sintering with virgin and reused powder. *J. Adv. Manuf. Technol*; 105: 3337-3351.

Creytens K, Gilissen L, Huygens S, Goossens A. (2017) A new application for epoxy resins resulting in occupational allergic contact dermatitis: the three-dimensional printing industry. *Contact Derm*; 77: 349-351.

du Plessis JL, Eloff FC, Badenhorst CJ, Olivier J, Laubscher PJ, van Aarde MN, Franken A. (2010) Assessment of dermal exposure and skin condition of workers exposed to nickel at a South African base metal refinery. *Ann Occup Hyg*; 54: 23-30.

du Plessis JL, Eloff FC, Engelbrecht S, Laubscher PL, van Aarde MN, Franken A. (2013) Dermal exposure and changes in skin barrier function of base metal refinery workers co-exposed to cobalt and nickel. *Occup. Health South. Afr*; 19: 6-12.

du Preez S, de Beer DJ, du Plessis JL. (2018) Titanium powders used in powder bed fusion: their relevance to respiratory health. *South African J. Ind. Eng*; 29: 94-102.

Gibson I, Rosen D, Stucker B. (2015) *Additive manufacturing technologies: 3D Printing, Rapid Prototyping to Direct Digital Manufacturing*. 2nd ed. New York, NY: Springer. Available from Springer eBook Collection: <https://link.springer.com/book/10.1007/978-1-4939-2113-3#toc> (accessed 16 Feb 2021).

Gibson I, Rosen D, Stucker B, Khorasani M. (2021) *Additive manufacturing technologies*. 3d ed. Cham: Springer Nature. ISBN: 978-3-030-56126-0.

Gorman Ng M, MacCalman L, Semple S, van Tongeren M. (2017) Field measurements of inadvertent ingestion exposure to metals. *Ann. Work Expo. Health*; 61: 1097-1107.

Graff P, Stahlbom B, Nordenberg E, Graichen A, Johansson P, Karlsson H. (2017) Evaluating measuring techniques for occupational exposure during additive manufacturing of metals. *J. Ind. Ecol*; 21: 120-129.

ISO/ASTM (International Organization for Standardization/American Society of Testing Materials). (2021) ISO/ASTM 52900: 2021. Additive manufacturing - general principles - fundamentals and vocabulary. Available from: <https://www.iso.org/obp/ui/#iso:std:iso-astm:52900:ed-2:v1:en> (accessed 19 November 2022).

ISO/TR (International Organization for Standardization/Technical Report). (2011) ISO/TR 14294: 2011. Workplace atmospheres - measurement of dermal exposure - principles and methods. Geneva: International Organisation for Standardisation/Technical Report.

Julander A, Hindsén M, Skare L, Lidén C. (2009) Cobalt-containing alloys and their ability to release cobalt and cause dermatitis. *Contact Derm*; 60: 165-170.

Larese Filon F, D'Agostin F, Crosera M, Adami G, Bovenzi M, Maina G. (2008) In vitro percutaneous absorption of chromium powder and the effect of skin cleanser. *Toxicol In Vitro*; 22: 1562-1567.

Larese Filon F, Maina G, Adami G, Venier M, Coceani N, Bussani R, Massiccio M, Barbieri P, Spinelli P. (2004) In vitro percutaneous absorption of cobalt. *Int Arch Occup Environ Health*; 77: 85-89.

Linde SJL, Franken A, du Plessis JL. (2018) Urinary excretion of platinum (Pt) following skin and respiratory exposure to soluble Pt at South African precious metals refineries. *Int Arch Occup Environ Health*; 221: 868-875.

Linde SJL, Franken A, du Plessis JL. (2021) Skin and respiratory exposure to platinum group metals at two South African precious metals refineries. *Int Arch Occup Environ Health*; 94: 1073-1083.

Ljunggren SA, Karlsson H, Ståhlbom B, Krapf B, Fornander L, Karlsson LE, Bergström B, Nordenberg E, Ervik TK, Graff P. (2019) Biomonitoring of metal exposure during additive manufacturing (3D printing). *Saf Health Work*; 10: 518-526.

Matthews MJ, Guss G, Khairallah SA, Rubenchik AM, Depond PJ, King WE. (2016) Denudation of metal powder layers in laser powder bed fusion processes. *Acta Mater*; 114: 33-42.

- Mellin P, Jonsson C, Åkermo M, Fernberg P, Nordenberg E, Hrodin H, Strondl A. (2016) Nano-sized by-products from metal 3D printing, composite manufacturing and fabric production. *J. Clean. Prod.*; 139: 1224-1233.
- Monzón MD, Ortega Z, Martínez A, Ortega F. (2015) Standardization in additive manufacturing: activities carried out by international organizations and projects. *J. Adv. Manuf. Technol.*; 76: 1111-1121.
- Mutchler E. (2019) Trends watch: Metal additive manufacturing: Metal 3D printing is expanding manufacturing possibilities by enabling new designs and improved outcomes. *Adv. Mater. Process.*; 177: 28-29.
- OSHA (Occupational Safety and Health Administration). (2002) OSHA ID-125G: Metal and metalloid particulates in workplace atmosphere (ICP Analysis). Salt Lake City, UT: Occupational Safety and Health Administration. Available from: <https://www.osha.gov/sites/default/files/methods/id125g.pdf> (accessed 25 Jan 2022).
- Praxair Surface Technologies. (2015) Safety data sheet CO-538 products. Available from <https://www.praxairsurfacetechologies.com/-/media/corporate/praxairsurface/us/documents/sds/powders/co/co538s.pdf?la=en> (accessed 14 Oct 2021). p. 1-11.
- Qian M. (2015) Metal powder for additive manufacturing. *JOM*; 67: 536-537.
- Renneboog RM. (2016) Alloys and Intermetallics. In: Franceschetti DR. eds. *Principles of Chemistry*. Ipswich, MA: Salem Press, Grey House Publishing. p. 52-55. Available from: <https://eds-a-ebSCOhost-com.nwulib.nwu.ac.za/eds/ebookviewer/ebook/bmxlYmtfXzEyMzA0NDVfX0FO0?sid=3307e9ba-081e-4db2-8d49-db744470fa54@sessionmgr4008&vid=2&format=EB&rid=14> (accessed 30 June 2021).
- Ruff CA, Belsito, DV. (2006) The impact of various patient factors on contact allergy to nickel, cobalt, and chromate. *J. Am. Acad. Dermatol.*; 55: 32-39.
- Schneider T, Vermeulen R, Brouwer DH, Cherrie JW, Kromhout H, Fogh CL. (1999) Conceptual model for assessment of dermal exposure. *Occup. Environ. Med.*; 56: 765-773.
- Tang HP, Qian M, Liu N, Zhang XZ, Yang GY, Wang, J. (2015) Effect of powder reuse times on additive manufacturing of Ti-6Al-4V by selective electron melting. *JOM*; 67: 555-563.

Tokar EJ, Boyd WA, Freedman JH, Waalkes P. (2013) Toxic effects of metals. In: Klaason CD, eds. *Casarett & Doull's toxicology the basic science of poisons*. 8th ed. New York: McGraw-Hill Education. p. 982-1030.

UN (United Nations). (2019) ST/SG/AC.10/30/Rev.8. Globally harmonized system of classification and labelling of chemicals (GHS). 8th revised ed. New York: United Nations. ISBN: 978-92-1-117199-0.

CHAPTER 2 LITERATURE STUDY

2.1 Introduction

In this chapter literature relevant to this study is discussed. This includes an overview of AM, its process categories, processing phases, and feedstock powders used in AM, with a specific focus on CoCr alloy feedstock powders. Occupational exposure to metal feedstock powders is discussed, including the exposure routes with the focus on dermal exposure. A brief overview of dermal absorption and the factors influencing dermal absorption of metals in CO-538 feedstock powders are provided. Literature regarding the potential health effects of exposure, legislation regarding dermal exposure, and methodologies to assess dermal exposure are discussed.

2.2 Additive Manufacturing

Additive manufacturing (AM), three-dimensional (3D) printing, rapid prototyping, layer-based manufacturing, stereolithography, automated fabrication, freeform fabrication, and solid freeform fabrication are all terms that have been used interchangeably when describing a similar technology. As this technology has grown and evolved, many of these terms have fallen short of describing this technology sufficiently. In 2014 a technical committee (Committee F42 on Additive Manufacturing Technologies) within the American Society for Testing and Materials (ASTM) International recognised the need for new and standardised terminology when referring to this technology (Gibson *et al.*, 2015). The committee then developed an international standard (ISO/ASTM 52900) in which AM is used as the official term when referring to the technology and process where computer-aided design (CAD) is used to create 3D products by adding and fusing consecutive layers of material (ISO/ASTM: 2021).

2.2.1 Advantages and application of AM

AM technology offers many advantages over traditional methods of manufacturing that have led to the use of AM technologies in a vast range of manufacturing industries (Campbell *et al.*, 2012). The advantages of AM include, amongst others, speed, fewer processing steps and fewer resources required, accurate data and design interpretation, the ability to produce individually customised and complex designs, as well as the ability to utilise materials sustainably by using smaller amounts of material and reusing leftover materials (Attaran 2017: 682-683; Campbell *et al.*, 2012; Gibson *et al.*, 2021).

AM offers the advantage of a fast turnaround time in terms of the pace at which new products can be developed and manufactured (Gibson *et al.*, 2015; Gibson *et al.*, 2021). This has appealed to many automotive manufacturing industries that strive to get new products into the market faster

with reduced time and lowered development costs (Campbell *et al.*, 2012). The production volume of parts in automotive industries is extremely high, which makes the use of AM less cost-effective when compared to traditional manufacturing. However, AM is still used widely within this industry for the design and manufacturing of prototypes, jigs, fixtures, tooling, and other highly specialised applications (Gibson *et al.*, 2021).

One of the first industries to implement the use of AM technology was the aerospace industry. This industry took interest in AM due to its ability to create lightweight, mechanically functional, and complex structures (Campbell *et al.*, 2012). By adopting AM technology, the aerospace industry gained the ability to produce components from specifically tailored materials that can withstand high temperature variations and that have high strength-to-weight ratios. In contrast with the automotive industries, the production volume in the aerospace industries is very low. Low-volume production manufacturing is more cost-effective when using AM, and it removes the need for complicated design and production of moulds, fixtures, and dies that would be required in traditional manufacturing. Furthermore, AM eliminates the need to store large spares over the long lifespan of an aircraft by digitally storing the designs of spare parts that can be manufactured on demand (Gibson *et al.*, 2021).

AM is also being applied in medical industries due to its ability to create customised prosthetics and dental equipment to suit the needs of individual patients (Campbell *et al.*, 2012; Dutta and Froes, 2017). The medical industry has used AM to produce models of human bodies and organs, sometimes specific to certain patients, that may be used as a visual aid in diagnostics and surgical procedure planning. CAD software from AM has also been used in dentistry to create 3D imaging that can be measured and used to determine locations for implants, to produce surgical and drill guides, and to assist in the design of dental prosthetics. Furthermore, extensive research in tissue manufacturing and organ printing is also being done with a focus on combining AM with the use of living cells, proteins, bone tissues, and other materials that may assist in the manufacturing of tissue structures (Gibson *et al.*, 2021).

2.2.2 AM process categories

AM processes can be categorised according to the type of material that is used, the method by which these materials are deposited, and the manner in which the materials are fused together (Monzón *et al.*, 2015). The ASTM International terminology describes the seven different types of AM process categories as binder jetting, directed energy deposition, material extrusion, material jetting, powder bed fusion (PBF), sheet lamination, and vat photopolymerisation (ISO/ASTM: 2021). For the purpose of this study, the focus is placed on the PBF process category.

2.2.2.1 Powder bed fusion (PBF)

PBF was one of the first AM processes to be developed and commercialised and has been described as the leading AM process category when it comes to producing 3D products from metal feedstock powder (Gibson *et al.*, 2021; Matthews *et al.*, 2016). PBF can utilise just about any powdered feedstock material as long as it can return to a solid state after being melted. Materials such as polymers, metals, and ceramics are, therefore, often used in PBF (Gibson *et al.*, 2015; Gibson *et al.*, 2021).

PBF works on the layered-based principles of AM. The PBF build process starts with fixing a thin layer of powdered material onto the baseplate. Consecutive layers of the feedstock powder are then added and levelled over the previous layer. After each layer has been added, one or more thermal energy source, either in the form of a laser or electron beam, is used to melt and fuse specific areas of the layered feedstock powders. Powders that aren't fused remain loose around the product being manufactured and act as support for the following layers of feedstock powders (Dutta and Froes, 2017; Gibson *et al.*, 2015). The excess loose powders left over after the build can be collected and reused in future builds (Contaldi *et al.*, 2019). The thin layers of powders, small beam sizes, and the support from the powder bed, allow PBF technologies to accurately create complex 3D products (Dutta and Froes, 2017).

Many different PBF technologies have been developed, and while they share the basic set of principles that classify them as PBF, they all differ from each other in some way. These differences between the technologies arise from the modification of the PBF process to either enhance the efficiency of the machine, to focus on utilising specific materials more efficiently, and/or due to avoiding the use of patented features of other technologies (Gibson *et al.*, 2015; Gibson *et al.*, 2021). The different PBF technologies include direct metal laser sintering (DMLS), electron beam melting, selective heat sintering, selective laser melting, and selective laser sintering (Herzog *et al.*, 2016; Sing *et al.*, 2016). For this study, the focus is placed on DMLS.

2.2.2.1.1 Direct metal laser sintering (DMLS)

DMLS is the terminology used by the manufacturer (EOS GmbH Electro Optical Systems) to describe the metal laser sintering technology used in their AM machines. DMLS is a PBF technology that uses only metal powders as feedstock material. Fibre lasers are used in DMLS as a thermal energy source offering advantages such as being compact, having low initial and maintenance costs, being energy efficient, and having better beam quality than other laser types (Gibson *et al.*, 2015). DMLS machines use a fusion mechanism called “partial melting” or liquid-phase sintering (LPS). LPS refers to the fusion that occurs between powder particles when a heat source is applied that causes a certain portion of the constituents to become molten and act as

an adhesion agent to bind the remaining portion of solid particles together. With metal alloys used in DMLS, areas with higher concentrations of low-melting-point constituents melt first and therefore, fuse the solid high-melting-point constituents together (Gibson *et al.*, 2015; Kruth *et al.*, 2005).

2.2.3 AM processing phases

According to Gibson *et al* (2015), there are eight basic steps in the AM process chain. These steps can further also be divided into three processing phases, namely, pre-processing, processing, and post-processing (see Figure 2-1).

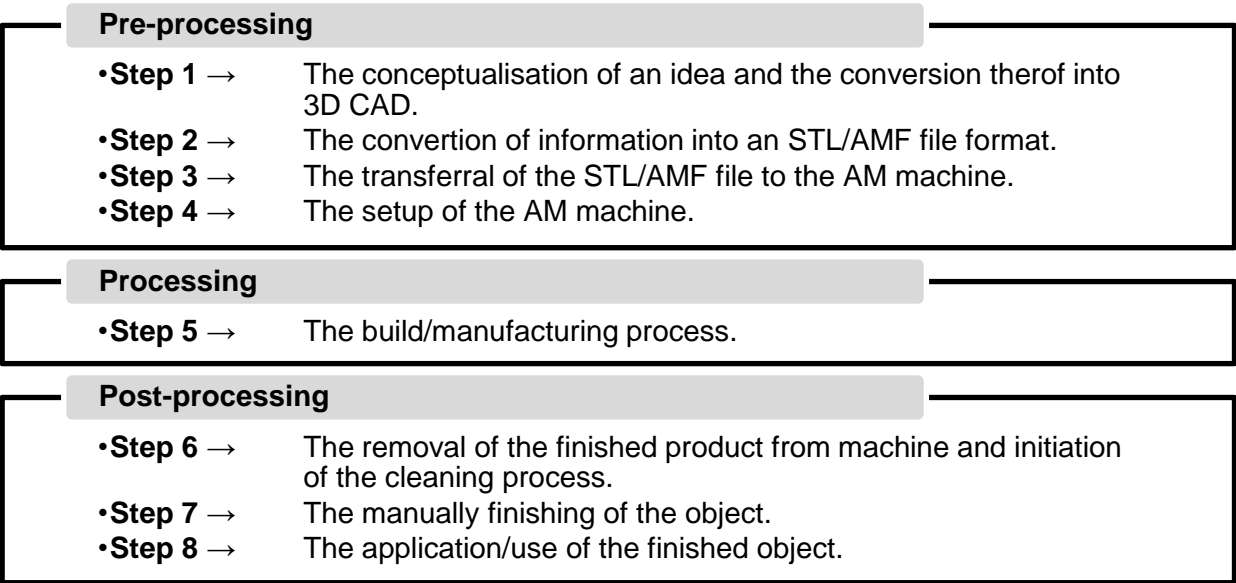


Figure 2-1: The eight basic steps of AM, as described by Gibson *et al* (2015) and grouped into the three processing phases (du Preez, 2019).

2.2.3.1 Pre-processing phase

The pre-processing phase consists of the first four steps as described by Gibson *et al* (2015). The first step in the pre-processing phase is conceptualising an idea of what the manufactured product should look like and how it should function. This idea must then be converted into 3D CAD information; either by designing the product using 3D CAD software, or by 3D scanning an already existing product, or by using a combination of these methods. The second step in this phase is to convert the 3D CAD information into either an STL (derived from stereolithography) or AMF (Additive Manufacturing Format) file format. This step is usually automated within the CAD system. The third step is the transferring of the STL/AMF file to the AM machine. The final step in the pre-processing phase is setting up the AM machine to print the desired part. During this step, the AM operator must manually sift the feedstock powders, load sufficient amounts of feedstock powder into the AM machine, and level the base plate (Gibson *et al.*, 2015).

2.2.3.2 Processing phase

The processing phase consists of the fifth step as described by Gibson *et al* (2015). This is an enclosed, computer-automated step where the actual manufacturing of the 3D product takes place within the AM machine. During manufacturing, consecutive layers of material are added and fused to form the product (Gibson *et al.*, 2015).

2.2.3.3 Post-processing phase

The post-processing phase consists of all the tasks performed after the completion of the build in order to achieve the desired properties in the final manufactured product (ISO/ASTM: 2021). The post-processing phase consists of the last three steps (steps 6-8) as described by Gibson *et al* (2015). The first step in the post-processing phase is the removal of the manufactured product from the AM machine, the removal of the excess feedstock material from the product, and the removal of support structures (Gibson *et al.*, 2015). The second step in the post-processing phase is the manual finishing of the manufactured product. This may include, but is not limited to, activities such as abrasive finishing, polishing, sanding, surface coating, and chemical or thermal treatments. The post-processing phase may also include the final cleaning of the AM machine, the manufactured product, and the workplace. The final step is the application or use of the manufactured product (Gibson *et al.*, 2015).

2.2.4 AM feedstock materials

AM feedstock material is defined as the bulk raw material that is introduced into the AM building process from which the product is manufactured. The feedstock material is available in various forms (powder, liquid, filaments, sheets, etc.) depending on the AM process that it is used for (ISO/ASTM: 2021). AM technology was originally developed for the production of paper laminates, waxes and polymeric materials, but as the technology developed, materials such as metals, ceramics, and composites have been introduced (Gibson *et al.*, 2021). This study focuses on PBF DMLS and, therefore, only metal feedstock material in powdered form is discussed.

2.2.4.1 Metal feedstock powders

Several different metal feedstock powders can be applied in PBF. These metals include, but are not limited to, stainless steel, tool steel, precious metals such as platinum, palladium, gold and silver, as well as alloys such as nickel-cobalt (NiCo), iron-nickel (FeNi), and cobalt-chrome (CoCr) (Mutchler, 2019; Qian, 2015). An alloy is a metallic material consisting of a mixture of two or more metals (which may include non-metallic elements) that can't be separated from one another through mechanical processes. Metal alloys are often used instead of pure metals due to their individual component characteristics that give the alloy the desirable properties (UN, 2019;

Renneboog, 2016). In this study, the focus is placed on CoCr alloys that are used as feedstock powders.

2.2.4.2 CoCr alloy feedstock powders

CoCr alloys are known to be strong materials and are often reinforced even more by the addition of other elements such as molybdenum (Mo) and tungsten. CoCr alloys also possess characteristics such as being non-magnetic and resistant to heat, wear, corrosion, and discolouration (Al Jabbari, 2014). These characteristics make CoCr(Mo) alloys biocompatible (Al Jabbari, 2014; Mordas *et al.*, 2020), and it has, therefore, been used to replace less biocompatible Ni-based alloys. The biocompatibility of CoCr alloys has made it highly favourable within medical industries such as orthopaedics where it is applied to construct shoulder, knee, and hip replacements, and in dentistry where it is used to produce removable partial denture framework (Al Jabbari, 2014). Even though medical products manufactured from CoCr alloys are considered biocompatible, the CoCr alloy feedstock powder from which it is manufactured, may not be biocompatible. The potential risk to health associated with exposure to the alloy in solid form (implants and dental frameworks) may differ from the risk to health associated with the alloy in powdered form (Wang *et al.*, 2019). Health risks associated with occupational exposure to CoCr alloys are discussed in Section 2.7.4 of this chapter.

2.3 Occupational exposure during AM

As AM technology has expanded, it has become increasingly accessible and has made its way into more workplaces, schools, and homes. The wide use of AM technology has led to the potential exposure of not only the AM workforce but also general users (Bours *et al.*, 2017). This has elevated the importance of information being made available regarding the health risks associated with the use of AM.

Occupational exposure during AM can occur during activities that form part of the three processing phases of AM (as discussed in Section 2.2.3). These activities may lead to the release of the feedstock powders into the workplace environment where AM operators may come into contact with them.

2.3.1 Routes of exposure

Occupational exposure can occur through inhalation, ingestion, or dermal contact. The main focus within occupational hygiene has predominantly been on inhalation as it is perceived to be the most important route (Schneider *et al.*, 2000). This perception has led to the bulk of exposure studies within AM focussing on respiratory exposure.

Currently, there are only two published studies that report on dermal health effects due to AM (Chang *et al.*, 2004; Creytens *et al.*, 2017). Chang *et al.* (2004) described one case of contact dermatitis that presented on both sides of the hands and the fingertips following exposure to epoxy resin compounds used in a vat photopolymerisation AM process. Similarly, Creytens *et al.* (2017) described two cases where dermal exposure to epoxy resins used in an unspecified AM process resulted in allergic contact dermatitis. In the first case, the patient's symptoms presented on the wrist, hands and forearms, and spread further to the face, neck, ears, legs and abdomen. In the second case, the symptoms presented on the back of the hands and spread to the forearms, axillae, and abdomen. This study concluded that there is a need for the use of non-sensitising materials in AM and a need for improved protective measures (Creytens *et al.*, 2017).

There is currently only one published study that reports on dermal exposure following AM. This study, conducted by Ljunggren *et al.* (2019), focussed on biomonitoring of exposure to metals during PBF AM. Dermal exposure, amongst other exposures of AM operators, was measured at an AM facility on two separate occasions, one year apart, before and after control measures had been implemented. The control measures included the requirement of wearing personal protective equipment (PPE) during the manual handling of metal feedstock powders. The required PPE included nitrile gloves, overalls, shoe covers, and full-face powered air-purifying respirators with P3-rated filters (filtering at least 99.95% of airborne particles). Restrictions were also implemented prohibiting the removal of manufactured products from the facility before post-processing and cleaning activities had been carried out. The study found that AM operators had measurable concentrations of Co, Cr, and Ni on the index fingers of their dominant hands on the first occasion of sampling, and no measurable concentrations on the second occasion after control measures had been implemented. The study concluded that the control measures reduced operators' exposure, which indicated the need for cautious design and control measures to be implemented at AM facilities (Ljunggren *et al.*, 2019). The dermal exposures identified in these studies highlight the need to further investigate dermal exposure in AM.

2.4 The basic structure of the skin

With a surface area of approximately 1.8 m², the skin is the largest organ of the human body (WHO, 2006). The skin consists of two layers: the underlying dermis and the outer epidermis. The dermis is the inner layer of the skin and consists of two main layers, the papillary layer which contains the capillaries, lymphatic vessels, and sensory nerves, and the reticular layer which contains the connective tissue that binds the skin to the deeper subcutaneous layers. The epidermis is the outermost layer of the skin and consists of four or five layers depending on the anatomical area. The layers of the epidermis are the stratum basale, stratum spinosum, stratum

granulosum, stratum lucidum (only found in anatomical areas with thick skin), and the stratum corneum (Martini *et al.*, 2018). The stratum corneum is the outermost layer of the epidermis and consists of metabolically dead cells named corneocytes that are held tightly together by desmosomes (Martini *et al.*, 2018; WHO, 2006). The tightly joined corneocytes provide chemical and mechanical protection (Proksch *et al.*, 2008).

The skin functions as a barrier, keeping the inside in and the outside out. The inside barrier regulates transepidermal water loss, while the outside barrier prevents the penetration of substances from the outside environment (Proksch *et al.*, 2008). The stratum corneum plays a vital role as the main physical protective barrier against the absorption of chemical and microbiological substances into the skin (Proksch *et al.*, 2008; WHO, 2006). The skin, however, is not an impenetrable barrier. When the barrier function of the skin is compromised, penetration, permeation, and absorption of substances through the skin may readily occur. The large surface area of the skin also allows for a greater probability of exposure and permeation of substances, making the skin a significant route of exposure (WHO, 2006).

2.5 Dermal exposure

Dermal exposure can occur through three typical pathways namely the deposition of substances from the air directly onto the skin, the immersion of the body or parts of the body into the substances, or direct contact with surfaces that are contaminated with the substance (Schneider *et al.*, 1999). With consideration of the conceptual model for the assessment of dermal exposure as developed by Schneider *et al.* (1999), it is possible to anticipate the pathways through which dermal exposure in the metal AM industry can occur (see Figure 2-2).

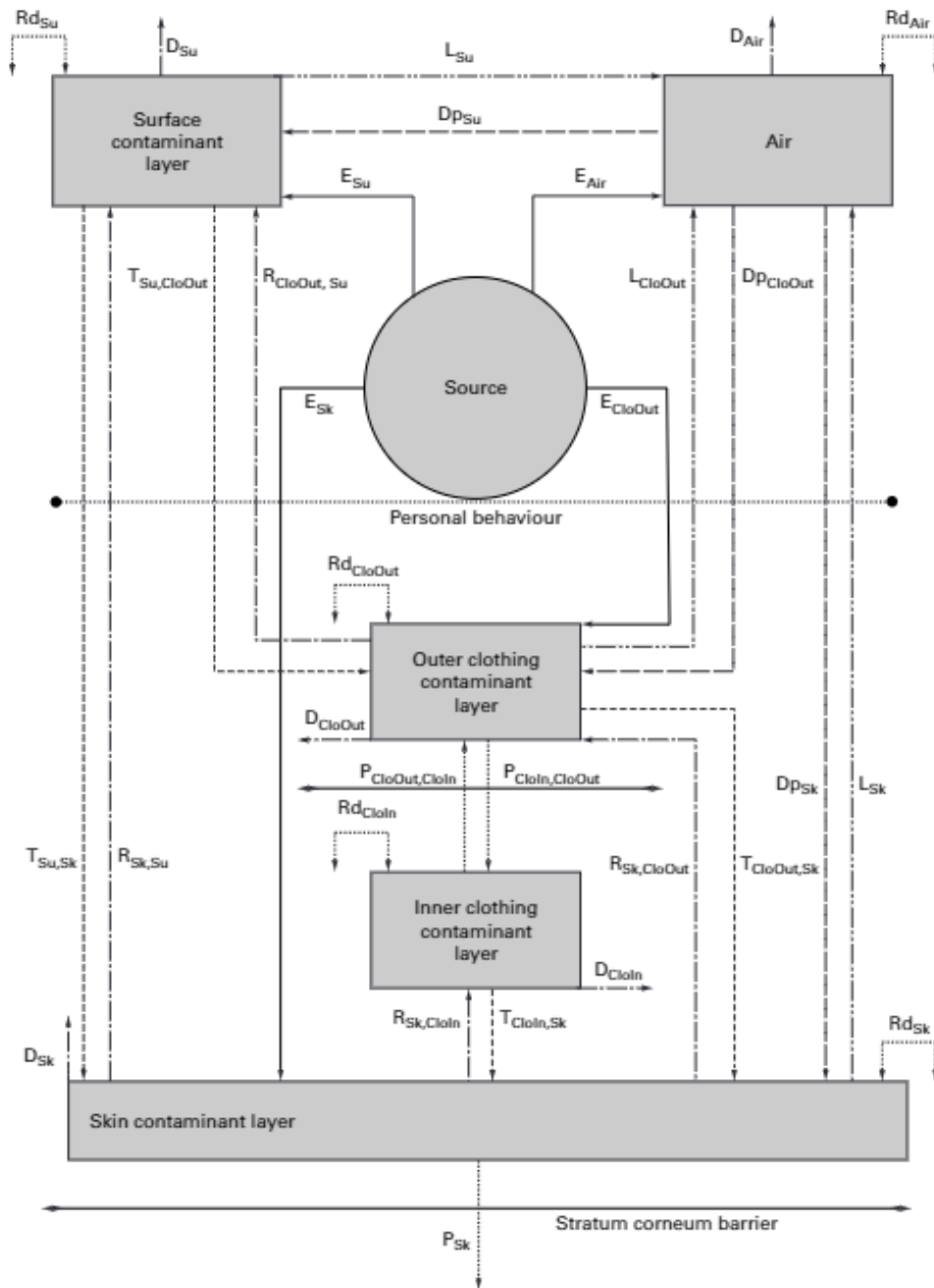


Figure 2-2: The conceptual model for assessment of dermal exposure as developed by Schneider *et al* (1999).

Abbreviations used to indicate dermal exposure pathways:

- E= emission;
- Dp= deposition;
- L= resuspension or evaporation;
- T= transfer;
- R= removal;
- Rd= redistribution;
- D= decontamination;
- P= penetration and permeation

Dermal exposure to metal feedstock powders can potentially occur during activities that form part of the different processing phases of AM. Studies have reported that respiratory exposure predominantly occurs during pre- and post-processing phases (Graff *et al.*, 2017; Ljunggren *et al.*, 2019), and the same can be expected for dermal exposure. During activities that form part of the pre- and post-processing phases, AM operators may come into direct contact with feedstock powders due to the manual handling thereof. Manual handling activities may include sieving powders, loading them into the AM machine, and removing excess powders from the AM machine after the build is complete (Gibson *et al.*, 2015). These manual handling activities and emissions from the AM machine during the processing phase may lead to the metal powder particles and fumes becoming airborne. When particles and fumes are airborne, it may lead to dermal exposure when they settle directly onto the skin of the AM operator, onto the clothing of the AM operator, and/or onto surfaces in the workplace with which the AM operator may come into contact with (Schneider *et al.*, 1999).

When particles settle on operating surfaces, skin surfaces, or clothing, they create a surface contaminant layer. Secondary dermal exposure can occur when AM operators come into direct contact with the surface contaminant layer or when mechanical forces disturb the surface contaminant layer causing resuspension of the particles into the air. Secondary dermal exposure may also occur when the surface contaminant layer comes into contact with and contaminates a different surface with which the AM operator may come into contact (Schneider *et al.*, 1999).

When particles settle on clothing, PPE, or dermal surfaces, exposure due to the surface contaminant layer as described above may occur, however, exposure from the contaminant layer may also occur depending on the type of material the clothing/PPE is made of. Particles are capable of permeating through some materials. When particles permeate through these materials they may come into direct contact with the skin (Schneider *et al.*, 1999). Further exposure due to the contamination layer may also occur if particles are still present on the skin or clothing after the AM operator has left the workplace. This may lead to cross-contamination of surfaces in non-operational areas. Since PPE is not required outside AM operational areas, dermal exposure may be more prevalent in such areas. When AM operators leave AM areas with contamination still present on skin or clothing, it may also lead to dermal exposure of other persons sharing facilities such as offices, kitchens, or bathrooms. Furthermore, the surface contamination layer may lead to accidental exposure via ingestion. Accidental ingestion may occur when food and drinks are consumed after being contaminated either due to contact with surface contamination layers or due to direct deposition of substances onto the food/drinks. Accidental ingestion may also occur when powders are transferred from the contamination layer on products or hands, into the mouth (Cherrie *et al.*, 2006).

2.6 Dermal absorption

Dermal absorption is defined as the transport or diffusion of a substance from the outside of the skin to the inside of the skin and/or into the inner systemic circulation (McDougal and Boeniger, 2002; WHO, 2006). Dermal absorption can be divided into three parts: penetration, permeation, and absorption. Penetration occurs when a substance enters a specific layer or structure of the skin, permeation occurs when a substance penetrates through one layer into a completely different layer, and absorption occurs when a substance has moved through the skin into the lymph or vascular system of the skin and is circulated through the body (WHO, 2006).

2.6.1 Mechanisms of dermal absorption

A substance can be transported through the skin by either the transcellular route, the intercellular route, or the appendageal route. Transcellular absorption occurs when a substance is transported through the skin by moving through the cell membranes of corneocytes. Intercellular absorption on the other hand occurs when a substance is transported through the skin by moving through the extracellular space around the corneocytes. Appendageal absorption occurs when a substance is transported through openings in the skin caused by hair follicles, sebaceous glands, or sweat glands (Scheuplein, 1965; Scheuplein, 1967; WHO, 2006).

2.6.2 Factors influencing dermal absorption

Many factors may impact a substance's ability to be absorbed through the skin. These factors can either be related to the substance itself, or to the skin, or to the manner of exposure. For the purpose of this study, a few important factors are briefly discussed, focussing on factors related to the absorption of metals relevant to this study. The reader is referred to Semple (2004) and Hostýnek *et al* (2003) for more details regarding these factors.

2.6.2.1 Skin-related factors

Skin-related factors such as the anatomical area of exposure may impact dermal absorption due to the differences in the physiological structure and function of the skin in different anatomical areas. In anatomical areas such as the soles of the feet and palms of the hands, the skin is remarkably thicker, and, therefore, absorption of substances through these areas is significantly lower than in anatomical areas with thinner skin (Larese Filon *et al.*, 2018; Semple, 2004). Hostýnek *et al* (2003) described a decreasing trend in the permeability of metals through anatomical areas in the order; "scrotum > forehead > postauricular > abdomen > forearm > leg > back", and ascribed these permeation differences to the differences in stratum corneum thickness, shunt density and intercellular lipid composition of these anatomical areas.

Another skin-related factor that influences the permeation of substances through the skin, is the condition of the skin. The permeation of substances through mechanically damaged or diseased skin may differ from the permeation through intact healthy skin. A study by Kezic and Nielsen (2009) found that larger compounds that would normally not be able to permeate the skin had the capability of permeating through damaged skin. A study done by Larese Filon *et al* (2009) investigated the *in vitro* permeation of metal powders through both intact and damaged skin. This study found that metal powders (Co, Ni, and Cr) were able to permeate through intact and damaged skin, with permeation increasing significantly for Co and Ni through damaged skin. This study also investigated the metal content of the skin and found significantly higher amounts of Co, Ni and Cr in damaged skin than in intact skin.

2.6.2.2 Exposure-related factors

Exposure-related factors such as the concentration of a substance on the skin can influence dermal absorption of the substance (Hostýnek, 2003; Semple, 2004). Several studies have indicated that a higher concentration of Cr results in increased permeation thereof through the skin (Gammelgaard *et al.*, 1992; Samitz *et al.*, 1967; Van Lierde *et al.*, 2006).

Another exposure-related factor that may influence the absorption of a substance is the use of PPE. While PPE is an important factor in controlling occupational exposure, the incorrect type of PPE and the incorrect use thereof may result in higher exposure and absorption of substances. This is because substances may break through the PPE if the incorrect type is used, it may enter the inside of the PPE if not used, donned, or doffed correctly, or the substances may already be on the skin surface before the PPE is donned. Contaminants on the inside of PPE may result in higher exposure for several reasons. Firstly, when substances are trapped inside the PPE, there is less opportunity for them to be removed from the skin through evaporation or other mechanical forces. This increases the duration that the persons are exposed to the contaminant. Secondly, wearing PPE such as gloves may result in occlusion of the skin. When this occurs, higher absorption of the substances can occur due to increased blood flow and sweating of the hands inside the gloves. Lastly, wearing PPE may grant a worker a false sense of protection when carrying out tasks. When they believe that they are protected, they will operate less cautiously than they would have without the PPE (Cherrie *et al.*, 2010; Semple, 2004).

2.6.2.3 Substance-related factors

In vitro experiments have reported that Co and Cr powders can permeate through the skin (Larese Filon *et al.*, 2004; Larese Filon *et al.*, 2008), however, many factors may influence the degree of permeation. One such factor is the valence or oxidation state of a substance (Hostýnek, 2003). Although metal Cr is inert, hexavalent Chromium [Cr(VI)] and trivalent

Chromium [Cr(III)] are capable of permeating through the skin (Firth and Rhyder, 2013; Larese Filon *et al.*, 2008). Cr(VI) ions can permeate through the skin without any difficulty however, they may be reduced to Cr(III) in the skin (Mali *et al.*, 1963; Samitz and Katz, 1964; Van Lierde *et al.*, 2006). Less Cr(III) permeates through the skin when compared to Cr(VI) due to a greater rejection of positive Cr(III) ions by the skin and Cr(III) ions' ability to bind with the dermal and epidermal structures (Gammelgaard *et al.*, 1992; Van Lierde *et al.*, 2006).

Vehicles (sweat) and the subsequent pH thereof are other substance-related factors known to influence dermal absorption. A high alkaline pH can reduce the barrier function of the stratum corneum leading to higher permeation of substances through the skin (Gammelgaard *et al.*, 1992), while a low acidic pH can cause oxidation of metal substances allowing them to permeate through the skin (Larese Filon *et al.*, 2004; Larese Filon, 2018).

A study done by Larese Filon *et al* (2004) investigated the *in vitro* percutaneous absorption of Co powders (2-5 μm in size) suspended in synthetic sweat with a pH of 6.5. The study found that synthetic sweat solution oxidised Co powder to form Co ions that were capable of permeating through the skin. Another study conducted by Larese *et al* (2007), found that metallic Cr did not oxidise in a synthetic sweat solution with a pH of 6.5. However, a follow-up study by Larese Filon *et al* (2008) investigated the *in vitro* percutaneous absorption of Cr powder (< 10 μm), and found that in a synthetic sweat solution with a pH of 4.5, the Cr powder could permeate through the skin. The permeation was due to the acidic pH that oxidised the Cr powder into soluble Cr III ions. Cr(VI), which can permeate much better than Cr(III), is also influenced by pH. At a higher pH (pH > 6) Cr(VI) exists as the small chromate ion that can permeate easier than the larger dichromate ion of Cr(VI) at a lower pH (pH 2-6). Van Lierde *et al* (2005) found that sweat constituents also play a role in the reduction of Cr(VI) to Cr(III), therefore, reducing the permeation of Cr(VI).

Particle size and shape are other factors that can influence the permeation of a substance. Even though data on the influence of particle size on permeation is limited, it can be expected that smaller particles will absorb faster than larger particles (WHO, 2006). Smaller particles have a higher surface-to-volume ratio and, therefore, ion release can occur faster, leading to higher dermal permeation (Larese Filon *et al.*, 2013). Larese Filon *et al* (2013) compared Co permeation results from different studies and found that cells exposed to Co nanoparticles (80 nm in size) had higher Co content than those exposed to larger Co powders (2 μm in size).

While particles larger than 45 nm (0.045 μm) may not be able to permeate and penetrate the skin directly (Larese Filon *et al.*, 2015), they may be able to enter into hair follicles where they can act as a long-lasting "reservoir" (Lademann *et al.*, 2015). Schaefer *et al* (1990) found that fluorescent polystyrene microbeads of approximately 7 μm were able to enter the hair follicles

(Toll *et al.*, 2004). When metals such as Ni and Cr enter hair follicles and form a reservoir, there may be an increased risk of adverse dermal health effects such as allergic contact dermatitis developing due to prolonged ion release (Lademann *et al.*, 2015; Larese Filon *et al.*, 2015)

2.7 Physical and chemical characteristics of AM feedstock powders

When occupational exposure to a particulate matter is of concern, the route of exposure and risks associated with exposure could depend on the physical and chemical characteristics of the particles such as elemental composition, particle shape, and particle size of the specific feedstock powder.

2.7.1 Particle size

The particulate size of the AM feedstock powder particles is an important characteristic when evaluating the health effects of exposure. The size of the particles will determine where in the respiratory tract system the particles will settle when respiratory exposure occurs (Pickford *et al.*, 2013). It will also determine how long a particle will remain suspended in the air, and, therefore, how far it can be dispersed before settling on surfaces in the workplace or on the skin. Lastly, the size of particles, amongst other factors, will influence the substance's ability to permeate through the skin (factors influencing absorption were discussed in more detail in Section 2.6.2) (Larese Filon *et al.*, 2013).

2.7.2 Particle shape

The particulate shape of the AM feedstock powder particles is another important characteristic when evaluating the health effects of exposure. Particles with irregular shapes have a higher surface-to-volume ratio when compared to perfectly spherical shapes (which are known to have the lowest surface-to-volume ratio) and thus may permeate the skin more readily (Lu *et al.*, 2010).

A study by Tak *et al* (2015) investigated shape-dependant skin penetration of silver (Ag) nanoparticles (NPs), (45-50 ± 10 nm) in rat skin. This study found that the *in vitro* absorption of rod-, spherical- and triangular-shaped Ag NPs after 12 hours were 1.82 µg/cm², 1.17 µg/cm², and 0.52 µg/cm² respectively. Furthermore, it was found that (after 30 hours) rod-shaped Ag NPs have penetrated to the dermal layer, while spherical-shaped Ag NPs have penetrated to the epidermal layer, and triangular-shaped Ag NPs have penetrated to the stratum corneum layers. Therefore, the particle shape of Ag NPs influences the skin penetration rates and depth of penetration into the skin.

2.7.3 Elemental composition

When dermal exposure to the metal alloy in powdered form occurs, it can lead to exposure to the individual elements of the powdered sample (Julander *et al.*, 2009). Various metal elements cause different types of health effects, and it is important to determine the elemental composition and to investigate the toxicity of the individual component elements of the feedstock powder. The AM process may also affect the composition and exposure of the feedstock powders. The sintering of metal powders can lead to the formation of metal fumes. The heating/melting of Cr-containing materials can cause oxidation and subsequent formation of and exposure to Cr(VI) (OSHA, 2008). Furthermore, different AM processes in the same area or previous AM processes that were conducted in the same area may lead to contamination of other elements in the feedstock powder being used.

2.8 Health effects associated with CO-538 metal constituents

The feedstock powder investigated in this study is a commercially available CoCr alloy powder (CO-538). The safety data sheet (SDS) for this product describes its elemental composition as 50-70% Co, 20-50% Cr, 5-20% Mo and <1% for both Ni and carbon (Praxair Surface Technologies, 2015). An overview of the health effects associated with exposure to the metal elements of the feedstock powder is described in this section.

2.8.1 Cobalt

Co is a relatively rare metal, that seems to be produced mainly as a by-product from the mining of copper and Ni. While Co in small amounts is an essential nutrient, exposure to higher concentrations thereof may lead to adverse health effects. Co is a known skin sensitiser that results in allergic contact dermatitis (Tokar *et al.*, 2013). Occupational exposure to Co has also been associated with other adverse health effects such as respiratory irritation and hard metal pneumoconiosis after respiratory exposure has occurred, cardiomyopathy and goitrogenic effects after ingestion and, elevated blood pressure, slowed respiration, nerve damage and tinnitus after intravenous exposure (Firth and Rhyder, 2013; Tokar *et al.*, 2013). In addition to this, the International Agency for Research on Cancer (IARC) has classified Co as a group 2B carcinogen (possibly carcinogenic to humans), which poses a risk of lung cancer in exposed persons (IARC, 2006).

2.8.2 Chromium

Natural occurring Cr is most commonly found in its trivalent state. Cr(III) is an essential nutrient that plays an important role in glucose metabolism (Tokar *et al.*, 2013). When exposure to Cr(III) occurs, its potential to induce adverse health effects may be considerably lower when compared

to Cr(VI) due to its lower ability to be absorbed into the body. Much higher concentrations of Cr(III), when compared to Cr(VI), are needed to elicit allergic contact dermatitis in exposed persons (Van Lierde *et al.*, 2005). Cr metal, raw chromite ore, and some Cr(III) salts are associated with skin irritation and dermatitis but are not considered carcinogenic (Firth and Rhyder, 2013). Cr(III) and metallic Cr are classified as group 3 carcinogens, indicating that there is insufficient information to classify the substances as carcinogenic or non-carcinogenic to humans (IARC, 1990).

Cr(VI) rarely exists naturally and is formed mostly due to the use of Cr in industrial processes. Cr(VI) can bring about allergic contact dermatitis in previously exposed persons (sensitivity to Cr is prevalent in 1% of the general population). Allergic contact dermatitis due to Cr(VI) can induce skin erythema, oedema, papule, pruritus, and scars (Tokar *et al.*, 2013). In addition to this, dermal exposure to Cr(VI) salts such as chromic acid and potassium dichromate can also lead to local effects such as chemical burns, dermatitis, and chrome ulcers. After being absorbed through the skin, it may also lead to systemic effects such as liver damage, renal failure, gastrointestinal bleeding, intravascular haemolysis, coma, shock, or death (Alikhan and Maibach, 2011; Anderson and Meade, 2014; Lin *et al.*, 2009; Matey *et al.*, 2000; Terrill and Gowar, 1990; Tokar *et al.*, 2013). Acute severe Cr poisoning due to dermal exposure is highly uncommon, but a case study by Lin *et al.* (2009) reported the occurrence thereof in a young man as a result of chemical burns across 15% of his body after short-term exposure to an electroplating solution containing Cr(VI). This led to symptoms such as nausea, vomiting, abdominal pain, dizziness, and dyspnoea, and later resulted in oliguria, pulmonary oedema, anaemia, and multiple organ failure. Although the patient recovered, adverse health effects of the exposure such as acute renal failure and skin chrome ulcers persisted (Alikhan and Maibach, 2011; Anderson and Meade, 2014; Lin *et al.*, 2009). IARC has classified Cr(VI) compounds as a group 1 carcinogen (carcinogenic to humans) associated with respiratory exposure (IARC, 2012a). Exposure to Cr(VI) can lead to lung cancer and may be associated with cancer of the nose and nasal sinuses (IARC, 2012a). There is also increasing evidence suggesting that due to Cr's ability to permeate through body tissues (such as the skin or lungs) it may be associated with cancers of the bones, stomach, prostate, kidney, bladder, and hematopoietic system (Tokar *et al.*, 2013).

2.8.3 Molybdenum

Mo is a metal that is used in industries to create high-temperature-resistant alloys for the manufacturing of gas turbines and jet aircraft engines. It is also used in the manufacturing of lubricants and dyes and is added in trace amounts to fertilisers to stimulate the growth of plants. Mo is an essential element that is understood to have low toxicity, however, it may cause some adverse health effects after chronic or high exposures. Respiratory exposure to metallic Mo and

Mo trioxide has been reported to cause pneumoconiosis, and high levels of environmental exposure have been associated with a gout-like syndrome (Tokar *et al.*, 2013). Mo trioxide is classified as a group 2B carcinogen (possibly carcinogenic to humans) associated with cancer due to inhalation (IARC, 2018). Limited information is available on the effects of dermal exposure to Mo, however, a recent study describes a case of allergic contact dermatitis in a 34-year-old woman after exposure to Mo-containing fibreglass dust which was present on the work clothes of the patient's husband who works in a fibreglass manufacturing plant (Navarro-Trivino *et al.*, 2021).

2.8.4 Aluminium

Al is the third most abundant element in the earth's crust and, therefore, it is not surprising that this metal has found many uses in different industries. Al is mainly used in the form of alloys in transportation, packing, construction, electrical applications, and in the beverage can industry. Occupational exposure to Al can mostly be expected to occur during mining, processing, and welding activities. Occupational exposure to Al predominantly occurs via inhalation of Al-containing dust particles which can lead to lung fibrosis. However, Al is poorly absorbed following inhalation, ingestion, and dermal exposure (Tokar *et al.*, 2013). A study by Flarend *et al.* (2001) found that Al can be absorbed following dermal application of Al chlorohydrate that is present in antiperspirants. However, the average absorption rate (0.25 μ /day) and the amount of Al (3.6 μ g) that entered the body following a single application to both underarms under occlusion was very low and did not significantly increase the body burden of Al. IARC (2012b) states that there is enough evidence that occupational exposure during Al production causes cancer of the bladder and lungs, to classify it as carcinogenic to humans (Group 1).

2.8.5 Iron

Fe is an essential metal with a potential for toxicity when too little or too much is available in the body. An Fe overload in the body generally occurs due to excess Fe ingestion, repeated blood transfusions, or due to hereditary hemochromatosis that causes an abnormal absorption of Fe from the intestines (Tokar *et al.*, 2013). In occupational settings, exposure to Fe can occur during the manufacturing and processing of Fe-containing products (Oppel *et al.*, 2022). Very little information regarding dermal exposure to Fe exists, however, studies have reported cases of occupational allergic contact dermatitis developing in enamellers, toolmakers, and steel welders who were exposed to Fe (Baer, 1973; Motolese *et al.*, 1993; Oppel *et al.*, 2022). IARC (2012) states that there is sufficient evidence that occupational exposure during iron and steel founding can cause cancer of the lung and has, therefore, classified it as carcinogenic to humans (Group 1).

2.8.6 Nickel

Ni is a strong metal that is resistant to corrosion and has high thermal and electrical resistance. These properties have made Ni a common addition to alloys such as stainless steel. Occupational exposure to Ni can occur in a variety of workplaces such as in mining, milling, and in a refinery, where Ni is produced, and in processes such as battery manufacturing, welding, electroplating, and smelting where Ni is used. Occupational exposure to Ni can occur via inhalation of airborne Ni particulates, or through dermal exposure when particulates settle on the skin, when workers come into contact with Ni-containing metal structures, or when they are exposed to Ni-containing liquid solutions. The most common health effect following exposure to Ni is contact dermatitis, which is found in 10 – 20 % of the general population (Tokar *et al.*, 2013). IARC (2012) has classified Ni compounds as a group 1 carcinogen (carcinogenic to humans).

2.9 Legislation relevant to dermal exposure

Occupational exposure limits (OELs) for various substances have been developed and implemented in different legislations and guidelines across the world. OELs are quantitative values that describe the maximum concentration of a specific substance that a person may be exposed to over a working life period without the risk of adverse health effects occurring (McDougal and Boeniger, 2002). OELs have only been developed for respiratory exposure, and limits on concentrations for dermal exposure are still non-existent. Instead, substances that may cause sensitisation are assigned sensitisation (SEN) notations, while substances that may contribute to overall exposure through dermal absorption, are assigned a skin notation (ACGIH, 2021; DOEL, 2022).

An SEN notation is a qualitative indicator used in legislation and guidelines to indicate that a substance has the ability to cause sensitisation. Substances with the potential of causing respiratory sensitisation through inhalation are assigned a RSEN or SEN notation, while substances with the ability to cause sensitisation through dermal contact are assigned a DSEN notation (ACGIH, 2021; DOEL, 2022). Skin notations are also assigned to indicate that there is a danger of dermal exposure, that dermal exposure has the potential to contribute significantly to overall exposure and that dermal contact may lead to overexposure even when airborne exposure is at or below the OEL (DOEL, 2022). A skin notation is also a qualitative indicator that is used to alert occupational hygienists and employers of the risks associated with dermal exposure and to indicate that control measures should be implemented (ACGIH, 2021; Bos *et al.*, 1998).

Table 2-1 indicates the skin and DSEN notations that have been assigned to CO-538 metal constituents in different legislation and recommendations (ACGIH, 2022; DOEL, 2022; MHSC, 2018). The American Conference of Governmental Industrial Hygienists (ACGIH) was the

first to develop skin notations (Boeniger, 2003) and exposure limits which later changed to Threshold Limit Values (TLVs) (Borak and Brosseau, 2015; ICMM, 2007). Even though limits set by the ACGIH are only recommendations and not legally binding in the USA, many countries around the world have opted to implement these recommendations in their legislation (Bos *et al.*, 1998; ICMM, 2007). The ACGIH has assigned a skin notation to Cr(VI) and a DSEN notation to Cr(VI), Cr(III) and Co. No notations have, however, been assigned to metallic Cr, Mo, Al, Ni or Fe (ACGIH, 2022).

In South Africa, legislation regarding exposure to substances in the workplace is laid out in the Regulations for Hazardous Chemical Agents, 2021 (RHCA), as promulgated under the Occupational Health and Safety Act (Act 85 of 1993) and in the Mine Health and Safety Act No.29 of 1996, Regulation 22.9, 2006. In both these regulations, skin notations are assigned to substances, however, only the RHCA assigns DSEN notations to substances with the ability to cause dermal sensitisation. In the RHCA skin notations are assigned to Cr(VI) and Ni, while no skin or DSEN notations are assigned to Co, Mo, Al, or Fe (DOEL, 2022; MHSC, 2018). In Regulation 22.9 no skin notations have been assigned to any of the CO-538 metal constituents (Table 2-1) (MHSC, 2018).

It is important to note that for many substances insufficient information on dermal absorption and toxicity exists. Therefore, the absence of a skin notation does not indicate that a substance poses no risk to health following dermal exposure, but rather that there is not enough information available to assign a skin notation to the substance (McDougal and Boeniger, 2002). Even though no legislation requires the assessment of dermal exposure, quantifying dermal exposure to substances in the workplace can give occupational hygienists and employers an indication of the effectiveness or need for control measures.

Table 2-1: Indication of skin and DSEN notations for relevant metal constituents of CO-538 in various legislation and recommendations (ACGIH, 2022; DOEL, 2022; MHSC, 2018).

| | OHS Act 85 of 1993 RHCA 2021 | MHS Act 29 of 1996 Section 22.9 | ACGIH (2022) |
|-------------------------------------|---|--|---------------------|
| <i>Cobalt (Co)</i> | - | - | DSEN |
| <i>Metallic Chromium (Cr)</i> | - | - | - |
| <i>Trivalent Chromium [Cr(III)]</i> | - | - | DSEN |
| <i>Hexavalent Chromium [Cr(VI)]</i> | Skin | - | Skin, DSEN |
| <i>Molybdenum (Mo)</i> | - | - | - |
| <i>Aluminium (Al)</i> | - | - | - |

| | | | |
|-------------|------|---|---|
| Nickel (Ni) | Skin | - | - |
| Iron (Fe) | - | - | - |

2.10 Methods for assessing dermal exposure and surface contamination

There are three categories of methods for assessing dermal exposure. They are *in situ* detection methods, interception methods, and removal methods. Each method that falls under these categories presents its advantages and disadvantages, and it is important to consider these when choosing a suitable dermal sampling method (Behroozy, 2013; du Plessis *et al.*, 2008). For the purpose of this study, removal methods are discussed with a specific focus on wipe sampling as a removal method.

2.10.1 Removal methods

Removal methods are used to establish the actual exposure of the skin to substances. During removal methods, the substances are removed from the skin either by washing, tape stripping, wiping, or by using specialised removal devices such as suction samplers. The removed substances can then be analysed to determine the actual amount that was present on the skin (Brouwer *et al.*, 2000; du Plessis *et al.*, 2008). Removal methods are most suited for substances that have low volatility as well as substances that remain on the skin for longer periods (Behroozy, 2013; du Plessis *et al.*, 2008).

2.10.1.1 Removal wipe sampling

Wipe sampling as a removal method has been proven to be effective in the detection and measurement of metals on skin and workplace surfaces (du Plessis *et al.*, 2013; Erfani *et al.*, 2015; Erfani *et al.*, 2017; Lidén *et al.*, 2006). Wipe sampling can be defined as the removal of substances from a surface by applying a force with a sampling medium (wipe) that is equal to or larger than the adhesion force of the substance on the surface (Brouwer *et al.*, 2000; ISO/TR, 2011).

Sampling media wipes can differ from each other with regard to shape, size, material, and whether it is dry or moistened. These differences make some types of wipes more suitable for specific substances and/or surfaces than others. Moistened wipes have proved to be more efficient than dry wipes when sampling metals (Ashley *et al.*, 2011; du Plessis *et al.*, 2008). Some wipe sampling media such as Ghostwipes™ are commercially available. Ghostwipes™ are individually wrapped wipes made from nonwoven polyvinyl alcohol fibre and moistened with deionised water (Boeniger, 2006; du Plessis *et al.*, 2008; OSHA, 2002). Ghostwipes™ have been validated for surface sampling of 13 different metals (OSHA, 2002). Ghostwipes™ have successfully been used for dermal sampling of metals including, amongst others, Co, Cr, Ni, Aluminium (Al),

Platinum (Pt), and other Pt group metals (du Plessis *et al.*, 2010; du Plessis *et al.*, 2013; Gorman Ng *et al.*, 2017; Linde *et al.*, 2018; Linde *et al.*, 2021).

Standardisation of wipe sampling and analysis methods is necessary to obtain consistent and comparable results. If standardisation is not achieved, results from wipe sampling and analysis performed by different persons, or at different periods or locations, may not be comparable. To achieve this standardisation, different organisations such as The Occupational Safety and Health Association (OSHA), the National Institute for Occupational Safety and Health (NIOSH) and, ASTM International, have developed standard operating procedures that describe the methodology of wipe sampling and analysis of different substances on surfaces including the skin (Ashley *et al.*, 2011; NIOSH, 2003; OSHA, 2002). OSHA developed method ID-125G for the collection and analysis of metal and metalloid particles on surfaces using Ghoswipes™ and NIOSH developed method 9102 for the collection and analysis of elements on surfaces using wipes (NIOSH, 2003; OSHA, 2002). In these methods, the standard operating procedure for the wipe sampling of a demarcated surface area with a moistened wipe, like a Ghostwipe™, is described. This procedure involves wiping a demarcated surface three times, first in a horizontal “S” shaped motion, followed by a vertical “S” shaped motion, and ending in a horizontal “S” shaped motion. After each wipe pattern, the wipe is folded with the exposed area inwards. When this procedure is done, the wipe samples are placed in a sterile sample storage vial. The samples are then analysed using Inductively Coupled Argon Plasma-Atomic Emission Spectroscopy (ICP-AES) (NIOSH, 2003; OSHA, 2002).

It should be taken into consideration that even while following these standardised methodologies, variation may still occur due to several factors. Since there is no standard description for the number of wipes per pattern or the amount of pressure that should be exerted on the surface while sampling, it is subject to the researcher’s interpretation. It is, therefore, recommended that the same operator should conduct all wipe sampling within a study to minimise inter-person variability (Behroozy, 2013; du Plessis *et al.*, 2008; Wheeler *et al.*, 1998). For comparable results, the size of the surface area that is sampled needs to be known, however, this may become problematic when irregularly shaped surfaces need to be sampled. Skin wipe sampling can be carried out on anatomical areas such as the hands, which include the palms and fingers as well as the back of the hands, the forearms, the forehead, the perioral region of the face, the chest, and the neck (du Plessis *et al.*, 2008; Hughson *et al.*, 2010). Templates with openings of defined sizes can be used to demarcate the surface areas that need to be sampled, however, it is not always possible to use a template on certain irregularly shaped surfaces. When sampling irregularly shaped dermal surfaces such as the perioral area, the area where sampling must be done can be determined by keeping within anatomical markers. When sampling irregular workplace surface areas such as door handles, handheld tools, or computer mice or keyboards,

the dimensions of the wiped surface may be difficult to determine. If possible, the area can be measured and calculated before sampling, or when not possible, sampling can be kept within physical markers (Day *et al.*, 2009; Hughson *et al.*, 2010).

It is also necessary to validate the sampling method and sampling media that are used to determine exposure to specific substances before the commencement of exposure monitoring. The validity of a method is determined by conducting removal and recovery efficiency studies in controlled laboratory environments (du Plessis *et al.*, 2008; Fenske: 1993). Removal efficiency, also referred to as sampling efficiency, is defined as the measure of how well the sampling method can collect a substance on the sampling media (ISO/TR, 2011). The removal efficiency is determined by calculating how much of a substance, that was initially deposited onto the skin (or surface), has been removed by the wipe (Galea *et al.*, 2014). Recovery efficiency is defined as the measure of how well an analytical laboratory can recover a substance from the sampling media (ISO/TR, 2011). The recovery efficiency is determined by dividing the amount (mass) of a substance that is recovered from the sampling media by the amount (mass) of the substance that was initially deposited onto the sampling media (Galea *et al.*, 2014). Recovery efficiencies between 70% and 120% with coefficients of variation of up to 20% indicate that the method is valid and that an analytical laboratory can accurately recover a substance from the sampling media (ISO/TR, 2011). OSHA (2002) indicates the validity of wipe sampling (OSHA method ID-125G) using Ghostwipes™ when sampling for 13 different substances including metals such as Co, Cr and, Mo.

2.11 Conclusion

In this chapter, an overview of AM, its process categories, processing phases, and feedstock powders was given. Occupational exposure to metal feedstock powders was discussed focusing on dermal exposure as an exposure route. A brief overview of dermal absorption and the factors influencing dermal absorption was provided, and literature regarding exposure to metal constituents of CO-538 including the potential health effects, legislation, and methodologies to assess dermal exposure was discussed.

Following the review of literature relevant to this study it is clear that amidst the rapidly emerging AM industry, not enough attention has been given to dermal exposure. The limited available information regarding dermal exposure during AM, the occurrence of adverse health effects following dermal exposure during AM, and the adverse health effects associated with dermal exposure to CO-538 metal constituents, highlight the need for further investigation into dermal exposure during AM.

2.12 References

- Alikhan FS, Maibach H. (2011) Topical absorption and systemic toxicity. *Cutan. Ocul. Toxicol*; 30: 175-186.
- Al Jabbari YS. (2014) Physico-mechanical properties and prosthodontic applications of Co-Cr dental alloys: a review of the literature. *J. Adv. Prosthodont*; 6: 138-145.
- ACGIH (American Conference of Governmental Industrial Hygienists). (2021) TLVs® and BEIs® based on the documentation of the threshold limit values for chemical substances and physical agents & biological exposure indices. Cincinnati, OH: ACGIH. ISBN: 978-1-607261-45-2.
- ACGIH (American Conference of Governmental Industrial Hygienists). (2022) TLVs® and BEIs® based on the documentation of the threshold limit values for chemical substances and physical agents & biological exposure indices. Cincinnati, OH: ACGIH. ISBN-13: 978-1607261520.
- Anderson SE, Meade BJ. (2014) Potential health effects associated with dermal exposure to occupational chemicals. *Environ. Health Insights*; 8: 51-62.
- Ashley K, Brisson MJ, White KT. (2011) Review of standards for surface and dermal sampling. *J. ASTM Int*; 8: 1-9.
- Attaran M. (2017) The rise of 3-D printing: The advantages of additive manufacturing over traditional manufacturing. *Bus. Horiz*; 60: 677-688.
- Baer RL. (1973) Allergic contact sensitization to iron. *J. Allergy Clin. Immunol*; 51: 35-38.
- Behroozy A. (2013) On dermal exposure assessment. *J. Occup. Environ. Med*; 4: 113-127.
- Boeniger MF. (2003) The significance of skin exposure. *Ann Occup Hyg*; 47: 591-593.
- Boeniger M. (2006) A Comparison of surface wipe media for sampling lead on hands. *J. Occup. Environ. Hyg*; 3: 428-434.
- Borak J, Brosseau LM. (2015) The past and future of occupational exposure limits. *J. Occup. Environ. Hyg*; 12: S1-S3. <https://doi.org/10.1080/15459624.2015.1091263>
- Bos PMJ, Brouwer DH, Stevenson H, Boogaard PJ, de Kort WLAM, van Hemmen JJ. (1998) Proposal for the assessment of quantitative dermal exposure limits in occupational environments: part 1. Development of a concept to derive a quantitative dermal occupational exposure limit. *J. Occup. Environ. Med*; 55: 795-804.

Bours J, Adzima A, Gladwin S, Cabral J, Mau S. (2017) Addressing hazardous implications of additive manufacturing: Complementing life cycle assessment with a framework for evaluating direct human health and environmental impacts. *J. Ind. Ecol*; 21: 25-36.

Brouwer DH, Boeniger MF, van Hemmen J. (2000) Hand wash and manual skin wipes. *Ann Occup Hyg*; 44: 501-510.

Campbell I, Bouwell D, Gibson I. (2012) Additive manufacturing: rapid prototyping comes of age. *Rapid Prototyp. J*; 18: 255-258.

Chang TY, Lee LJ, Wang JD, Shie RH, Chan CC. (2004) Occupational risk assessment on allergic contact dermatitis in a resin model making process. *J. Occup. Health*; 46: 148-152.

Cherrie JW, Semple S, Christopher Y, Saleem A, Hughson GW, Philips A. (2006) How important is inadvertent ingestion of hazardous substances at work? *Ann Occup Hyg*; 50: 693-704.

Cherrie JW, Howie RM, Semple S. (2010) *Monitoring for health hazards at work*. 4th ed. West Sussex, UK: Wiley-Blackwell. ISBN: 978-1-4051-5962-3

Contaldi V, Del Re F, Palumbo B, Squillace A, Corrado P, Di Petta P. (2019) Mechanical characteristics of stainless steel parts produced by direct metal laser sintering with virgin and reused powder. *J. Adv. Manuf. Technol*; 105: 3337-3351.

Creytens K, Gilissen L, Huygens S, Goossens A. (2017) A new application for epoxy resins resulting in occupational allergic contact dermatitis: the three-dimensional printing industry. *Contact Derm*; 77: 349-351.

Day G A, Virji M A, Stefaniak AB. (2009) Characterization of exposures among cemented tungsten carbide workers. Part II: Assessment of surface contamination and skin exposures to cobalt, chromium and nickel. *J Expo Sci Environ Epidemiol*; 19: 423-434.

DOEL (Department of Employment and Labour). (2022) Occupational health and safety act no 85 of 1993 and regulations. 23rd rev ed. Johannesburg, South-Africa: LexisNexis. ISBN: 978 1 776 17555 0.

du Plessis JL, Eloff FC, Badenhorst CJ, Booyesen R, van Aarde MN, Laubscher PJ. (2008) Dermal exposure sampling methods: an overview. *Occup. Health South. Afr*; 14: 4-11.

du Plessis JL, Eloff FC, Badenhorst CJ, Olivier J, Laubscher PJ, van Aarde MN, Franken A. (2010) Assessment of dermal exposure and skin condition of workers exposed to nickel at a South African base metal refinery. *Ann Occup Hyg*; 54: 23-30.

du Plessis JL, Eloff FC, Engelbrecht S, Laubscher PL, van Aarde MN, Franken A. (2013) Dermal exposure and changes in skin barrier function of base metal refinery workers co-exposed to cobalt and nickel. *Occup. Health South. Afr*; 19: 6-12.

du Preez S. (2019) Emissions of and exposure to hazardous chemical substances from selected additive manufacturing technologies. Potchefstroom: North-West University. (Thesis – PhD).

Dutta B, Froes FH. (2017) The Additive Manufacturing (AM) of titanium alloys. *Met. Powder Rep*; 72: 97-106.

Erfani B, Lidén C, Midander K. (2015) Short and frequent skin contact with nickel. *Contact Derm*; 73: 222-230.

Erfani B, Midander K, Lidén C, Julander A. (2017) Development, validation and testing of a skin sampling method for assessment of metal exposure. *Contact Derm*; 77: 17-24.

Fenske RA. (1993) Dermal exposure assessment techniques [Abstract]. *Ann Occup Hyg*; 37: 687-706.

Firth I, Rhyder G. (2013) Metals in the workplace. In: Reed S, Pisaniello D, Benke G, Burton K. eds. *Principles of Occupational Health & Hygiene*. 2nd ed. Crows Nest, Australia: Allen & Unwin. p. 188-220.

Flarend R, Bin T, Elmore D, Hem SL. (2001) A preliminary study of the dermal absorption of aluminium from antiperspirants using aluminium-26. *Food Chem. Toxicol*; 39: 163-168.

Galea KS, McGonagle C, Sleenwenhoek A, Todd D, Jiménez AC. (2014) Validation and comparison of two sampling methods to assess dermal exposure to drilling fluids and crude oil. *Ann Occup Hyg*; 58: 591-600.

Gammelgaard B, Fullerton A, Avnstorp C, Menné T. (1992) Permeation of chromium salts through human skin in vitro. *Contact Derm*; 27: 302-310.

Gibson I, Rosen D, Stucker B. (2015) *Additive manufacturing technologies: 3D Printing, Rapid Prototyping to Direct Digital Manufacturing*. 2nd ed. New York, NY: Springer. Available from

Springer eBook Collection: <https://link.springer.com/book/10.1007/978-1-4939-2113-3#toc>
(accessed 16 Feb 2021).

Gibson I, Rosen D, Stucker B, Khorasani M. (2021) *Additive manufacturing technologies*. 3d ed. Cham: Springer Nature. ISBN: 978-3-030-56126-0.

Graff P, Stahlbom B, Nordenberg E, Graichen A, Johansson P, Karlsson H. (2017) Evaluating measuring techniques for occupational exposure during additive manufacturing of metals. *J. Ind. Ecol*; 21: 120-129.

Herzog D, Seyda V, Wycisk E, Emmelmann C. (2016) Additive manufacturing of metals. *Acta Mater*; 117: 371-392.

Hostýnek JJ. (2003) Factors determining percutaneous metal absorption. *Food Chem. Toxicol*; 41: 327-345.

Hughson GW, Galea KS, Heim KE. (2010) Characterization and assessment of dermal and inhalable nickel exposures in nickel production and primary user industries. *Ann Occup Hyg*; 54: 8-22.

IARC (International Agency for Research on Cancer). (2006) IARC monographs on the evaluation of carcinogenic risks to humans. Vol. 68. Cobalt in hard metals and cobalt sulfate, gallium arsenide, indium phosphide and vanadium pentoxide. Lyon, France: IARC. ISBN: 92 832 1286 X.

IARC (International Agency for Research on Cancer). (1990) IARC monographs on the evaluation of carcinogenic risks to humans. Vol. 49. Chromium, nickel and welding. In IARC monographs on the evaluation of carcinogenic risks to humans. Vol. 49. Lyon, France: IARC. ISBN: 92 832 1249 5

IARC (International Agency for Research on Cancer). (2012a) IARC monographs on the evaluation of carcinogenic risks to humans. Vol. 100C. Arsenic, metals, fibres, and dusts. In Monographs on the evaluation of carcinogenic risks to humans. Lyon, France: IARC. ISBN: 978-92-832-0135-9.

IARC (International Agency for Research on Cancer). (2012b) IARC monographs on the evaluation of carcinogenic risks to humans. Vol. 100F. Chemical agents and related occupations. Lyon, France: IARC. ISBN: 978-92-832-0138-0.

IARC (International Agency for Research on Cancer). (2018) IARC monographs on the evaluation of carcinogenic risks to humans. Vol. 118. Welding, molybdenum trioxide, and indium tin oxide. Lyon, France: IARC. ISBN: 978-92-832-0185-4.

ICMM (International Council on Mining & Metals). (2007) The setting and use of occupational exposure limits: current practice. London, UK. Available from: https://www.icmm.com/website/publications/pdfs/health-and-safety/2007/research_setting-and-use-of-oels.pdf (accessed 8 July 2021).

ISO/ASTM (International Organization for Standardization/American Society of Testing Materials). (2021) ISO/ASTM 52900: 2021. Additive manufacturing - general principles - fundamentals and vocabulary. Available from: <https://www.iso.org/obp/ui/#iso:std:iso-astm:52900:ed-2:v1:en> (accessed 19 November 2022).

ISO/TR (International Organization for Standardization/Technical Report). (2011) ISO/TR 14294: 2011. Workplace atmospheres - measurement of dermal exposure - principles and methods. Geneva: International Organisation for Standardisation/Technical Report.

Julander A, Hindsén M, Skare L, Lidén C. (2009) Cobalt-containing alloys and their ability to release cobalt and cause dermatitis. *Contact Derm*; 60: 165-170.

Kezic S, Nielsen JB. (2009) Absorption of chemicals through compromised skin. *Int Arch Occup Environ Health*; 82: 677-688.

Kruth JP, Mercelis P, Van Vaerenbergh J, Froyen L, Rombouts M. (2005) Binding mechanisms in selective laser sintering and selective laser melting. *Rapid Prototyp. J*; 11: 26-36.

Lademann J, Knorr F, Richter H, Jung S, Meinke MC, Rühl E, Alexiev U, Calderon M, Patzelt A. (2015) Hair follicles as a target structure for nanoparticles. *J. Innov. Opt. Health Sci*; 8: 1530004-1 - 1530004-8. DOI: 10.1142/S1793545815300049

Larese Filon F. (2018) Penetration of metals through the skin barrier. In: Chen JK, Thyssen JP. eds. *Metal allergy: from dermatitis to implant and device failure*. Cham: Springer. p. 67-74.

Larese Filon F, Crosera M, Timeus E, Adami G, Bovenzi M, Ponti J, Maina G. (2013) Human skin penetration of cobalt nanoparticles through intact damaged skin. *Toxicol In Vitro*; 27: 121-127.

Larese F, Gianpietro A, Venier M, Maina G, Renzi N. (2007) In vitro percutaneous absorption of metal compounds. *Toxicol. Lett*; 170: 49-56.

- Larese Filon F, D'Agostin F, Crosera M, Adami G, Bovenzi M, Maina G. (2008) In vitro percutaneous absorption of chromium powder and the effect of skin cleanser. *Toxicol In Vitro*; 22: 1562-1567.
- Larese Filon F, D'Agostin F, Crosera M, Adami G, Bovenzi M, Maina G. (2009) In vitro absorption of metal powders through intact and damaged human skin. *Toxicol In Vitro*; 23: 574-579.
- Larese Filon F, Maina G, Adami G, Venier M, Coceani N, Bussani R, Massiccio M, Barbieri P, Spinelli P. (2004) In vitro percutaneous absorption of cobalt. *Int Arch Occup Environ Health*; 77: 85-89.
- Lidén C, Skare L, Lind B, Nise G, Vahter M. (2006) Assessment of skin exposure to nickel, chromium and cobalt by acid wipe sampling and ICP-MS. *Contact dermat*; 54: 233-238.
- Lin CC, Wu ML, Yang CC, Ger J, Tsai WJ, Deng JF. (2009) Acute severe chromium poisoning after dermal exposure to hexavalent chromium [Abstract]. *J Chin Med Assoc*, 72: 219-221.
- Linde SJL, Franken A, du Plessis JL. (2018) Urinary excretion of platinum (Pt) following skin and respiratory exposure to soluble Pt at South African precious metals refineries. *Int Arch Occup Environ Health*; 221: 868-875.
- Linde SJL, Franken A, du Plessis JL. (2021) Skin and respiratory exposure to platinum group metals at two South African precious metals refineries. *Int Arch Occup Environ Health*; 94: 1073-1083.
- Ljunggren SA, Karlsson H, Ståhlbom B, Krapf B, Fornander L, Karlsson LE, Bergström B, Nordenberg E, Ervik TK, Graff P. (2019) Biomonitoring of metal exposure during additive manufacturing (3D printing). *Saf Health Work*; 10: 518-526.
- Lu H, Ip E, Scott J, Foster P, Vickers M, Baxter LL. (2010) Effects of particle shape and size on devolatilization of biomass particle. *Fuel*; 89: 1156-1168.
- Mali JWH, Van Kooten WJ, Van Neer FCJ. (1963) Some aspects of the behaviour of chromium compounds in the skin. *The Journal of Investigative Dermatology*, 41: 111-122.
- Martini F, Nath J, Bartholomew E. (2018) *Fundamentals of Anatomy and Physiology*. 11th ed. Harlow: Pearson Education Limited. Available from ProQuest EBook Central: <https://www.proquest.com/ebooks-central>

[//ebookcentral.proquest.com/lib/northwu-ebooks/detail.action?docID=5186130#goto_toc](http://ebookcentral.proquest.com/lib/northwu-ebooks/detail.action?docID=5186130#goto_toc)
(accessed 2 Jun 2021).

Matey P, Allison KP, Sheehan TMT, Gowar JP. Chromic acid burns: early aggressive excision is the best method to prevent systemic toxicity. *J. Burn Care Rehabil*; 21: 241-245.

Matthews MJ, Guss G, Khairallah SA, Rubenchik AM, Depond PJ, King WE. (2016) Denudation of metal powder layers in laser powder bed fusion processes. *Acta Mater*; 114: 33-42.

McDougal JN, Boeniger MF. (2002) Methods for assessing risks of dermal exposure in the workplace. *Critical Reviews in Toxicology*, 32: 291-327.

MHSC (Mine Health and Safety Council). (2018) Mine Health and Safety Act No. 29 of 1996 and Regulations.

https://mhsc.org.za/sites/default/files/public/legislation_document/Mine%20Health%20and%20Safety%20Act%2029%20of%201996%20and%20Regulations%20Final%20Booklet.pdf

(accessed 31 Oct 2022).

Monzón MD, Ortega Z, Martínez A, Ortega F. (2015) Standardization in additive manufacturing: activities carried out by international organizations and projects. *J. Adv. Manuf. Technol*; 76: 1111-1121.

Mordas G, Jasulaitienė V, Steponavičiūtė A, Gaspariūnas M, Petkevič R, Selskienė A, Juškėnas R, Paul DF, Mann JE, Remeikis V, Račiukaitis G. (2020) Characterisation of CoCrMo powder for additive manufacturing. *J. Adv. Manuf. Technol*; 111: 3083-3093.

Motolese A, Truzzi M, Giannini A, Seidenari S. (1993) Contact dermatitis and contact sensitization among enamellers and decorators in the ceramics industry [Abstract]. *Contact Derm*; 28: 59-62.

Mutchler E. (2019) Trends watch: Metal additive manufacturing: Metal 3D printing is expanding manufacturing possibilities by enabling new designs and improved outcomes. *Adv. Mater. Process*; 177: 28-29.

NIOSH (National Institute for Occupational Safety and Health). (2003) Elements on wipes: Method 9102. <https://www.cdc.gov/niosh/docs/2003-154/pdfs/9102.pdf> (accessed 25 Feb 2020).

Navarro-Triviño FJ, Cassini Gómez de Cádiz VA, Ruiz-Villaverde R. (2021) Allergic conjugal contact dermatitis caused by molybdenum from fiberglass. *International Journal of Dermatology*, 60: e80-e119. doi: 10.1111/ijd.15117

OSHA (Occupational Safety and Health Administration). (2002) OSHA ID-125G: Metal and metalloid particulates in workplace atmosphere (ICP Analysis). Salt Lake City, UT: Occupational Safety and Health Administration. Available from: <https://www.osha.gov/sites/default/files/methods/id125g.pdf> (accessed 25 Jan 2022).

OSHA (Occupational Safety and Health Administration). (2008) Guidance for the identification and control of safety and health hazards in metal scrap recycling. <https://www.osha.gov/Publications/OSHA3348-metal-scrap-recycling.pdf> (accessed 28 Feb 2020).

Oppel E, Kapp F, Böhm A, Pohl R, Thomas P, Summer B. (2022) Contact sensitization to iron: A potentially underestimated metal allergen and elicitor of complications in patients with metal implants. *Contact Derm*; 86: 531-538.

Pickford G, Davies B, Apthorpe L. (2013) Aerosols. In: Reed S, Pisaniello D, Benke G, Burton K. eds. *Principles of Occupational Health & Hygiene*. 2nd ed. Crows Nest, Australia: Allen & Unwin. p. 141-186.

Praxair Surface Technologies. (2015) Safety data sheet CO-538 products. Available from <https://www.praxairsurfacetech.com/-/media/corporate/praxairsurface/us/documents/sds/powders/co/co538s.pdf?la=en> (accessed 14 Oct 2021). p. 1-11.

Proksch E, Brander JM, Jensen J. (2008) The skin: an indispensable barrier. *Experimental Dermatology*, 17: 1063-1072.

Qian M. (2015) Metal powder for additive manufacturing. *JOM*; 67: 536-537.

Renneboog RM. (2016) Alloys and Intermetallics. In: Franceschetti DR, eds. *Principles of Chemistry*. Ipswich, MA: Salem Press, Grey House Publishing. p. 52-55. Available from: <https://eds-a-ebSCOhost-com.nwulib.nwu.ac.za/eds/ebookviewer/ebook/bmxlYmtfXzEyMzA0NDVfX0FO0?sid=3307e9ba-081e-4db2-8d49-db744470fa54@sessionmgr4008&vid=2&format=EB&rid=14> (accessed 30 June 2021).

Samitz MH, Katz S. (1964) A study of the chemical reactions between chromium and skin. *Journal of Investigative Dermatology*, 43: 35-42.

Samitz MH, Katz S, Shrager JD. (1967) Studies of the diffusion of chromium compounds through skin. *The Journal of Investigative Dermatology*, 48: 514-520.

- Scheuplein RJ. (1965). Mechanism of percutaneous adsorption. I. Routes of penetration and the influence of solubility. *The Journal of Investigative Dermatology*, 48: 334-346.
- Scheuplein RJ. (1967) Mechanism of percutaneous absorption. II. Transient diffusion and the relative importance of various routes of skin penetration. *The Journal of Investigative Dermatology*, 48: 79-88.
- Schneider T, Cherrie JW, Vermeulen R, Kromhout H. (2000) Dermal exposure assessment. *Ann Occup Hyg*; 44: 493-499.
- Schneider T, Vermeulen R, Brouwer DH, Cherrie JW, Kromhout H, Fogh CL. (1999) Conceptual model for assessment of dermal exposure. *Occup. Environ. Med*; 56: 765-773.
- Semple S. (2004) Dermal exposure to chemicals in the workplace: just how important is skin absorption? *Occupational and Environmental Medicine*, 61: 376- 382.
- Sing SL, An J, Yeong WY, Wiria FE. (2016) Laser and electron-beam powder-bed additive manufacturing of metallic implants: a review on processes, materials and designs. *J. Orthop. Res*; 34:369-385.
- Tak KT, Pal S, Naoghare PK, Rangasamy S, Song JM. (2015) Shape-dependant skin penetration of silver nanoparticles: Does it really matter? *Sci. Rep*; 5: 1-11.
- Terrill PJ; Gowar JP. (1990) Chromic acid burns; beware, be aggressive, be watchful [Abstract]. *Br. J. Plast. Surg*; 43: 699-701.
- Tokar EJ, Boyd WA, Freedman JH, Waalkes P. (2013) Toxic effects of metals. In: Klaason CD, eds. *Casarett & Doull's toxicology the basic science of poisons*. 8th ed. New York: McGraw-Hill Education. p. 982-1030.
- Toll R, Jacobi U, Richter U, Lademann J, Schaefer H, Blume-Peytavi U. (2004) Penetration Profile of Microspheres in Follicular Targeting of Terminal Hair Follicles. *J Invest Dermatol*; 123: 168-176. DOI:<https://doi.org/10.1111/j.0022-202X.2004.22717.x>
- UN (United Nations). (2019) ST/SG/AC.10/30/Rev.8. Globally harmonized system of classification and labelling of chemicals (GHS). 8th revised ed. New York: United Nations. ISBN: 978-92-1-117199-0
- Van Lierde V, Chéry CC, Moens L, Vanhaecke F. (2005) Capillary electrophoresis hyphenated to inductively coupled plasma-sector field-mass spectrometry for the detection of chromium species after incubation of chromium in simulated sweat. *Electrophoresis*, 26: 1703-1711.

Van Lierde V, Chéry CC, Roche N, Monstrey S, Moens L, Vanhaecke F. (2006) In vitro permeation of chromium species through porcine and human skin as determined by capillary electrophoresis-inductively coupled plasma-sector field mass spectrometry. *Anal. Bioanal. Chem*; 384: 378-384.

Wang X, Herting G, Wei Z, Wallinder IO, Hedberg Y. (2019) Bioaccessibility of nickel and cobalt in powders and massive forms of stainless steel, nickel- or cobalt-based alloys, and nickel and cobalt metals in artificial sweat. *Regul. Toxicol. Pharmacol*; 106: 15-26.

Wheeler JP, Stancliffe JD. (1998) Comparison of methods for monitoring solid particulate surface contamination in the workplace. *Ann Occup Hyg*; 42: 477-488.

WHO (World Health Organisation). (2006) Environmental health criteria 235: dermal absorption. <https://incem.org/documents/ehc/ehc/ehc235.pdf> (accessed 26 May 2021).

CHAPTER 3 ARTICLE

3.1 Guidelines for authors

3.1.1 Annals of Work Exposures and Health

Annals of Work Exposures and Health publishes original research and development material that helps reduce risk of ill-health resulting from work, and welcomes submissions in these areas.

Language. Manuscripts must be in English and authors should try to write in a way which is simple and clear. British or American styles and spelling may be used, but should be used consistently, and words or phrases which might be unclear in other parts of the world should be avoided or clearly explained. It is the authors' responsibility to provide a text in good English, and authors whose first language is not English should seek help from a native speaker or competent translator. This must be done before first submission to ensure a thorough peer review.

Brevity. The necessary length of a paper depends on the subject, but any submission must be as brief as possible consistent with clarity. The number of words, excluding the abstract, references, tables and figs, must be stated as a message to the Editor at the time of submission. Section 2 details the word count for each category. If this length is more than 5000 words, a statement must be included justifying the extra length.

Title, abstract and keywords. These are important because most readers find papers by internet search of subjects, not by browsing the journal. Titles should be constructed to succinctly describe the major issue or question examined by the paper and should not assert the research findings as a truth. Recognisable, searchable terms and keywords must be included to enable readers to more effectively find your paper. To optimise the visibility of your paper we advise you to make a list of the 10 most likely search terms (words and phrases) that your intended readers will use to find your work, and to ensure that these appear in your title, the abstract and the keywords. The 'number one' search term from your list should appear somewhere in the paper's title. This will usually not be just a single word; rather a short phrase summarising the main subject of the paper. The 'top 5' search terms (including 'number one') should each appear at least once in the abstract, with the 'top 3' appearing more than once if possible. It is important that your abstract is written in a naturalistic and engaging style that will encourage readers to follow up by reading the full paper. The 'bottom 5' search terms can then be added as keywords. It is important to include variants of the 'top 5' here if they exist, e.g. alternative names for chemicals or processes.

Structure of paper. Papers should generally conform to the pattern: Introduction, Methods, Results, Discussion, and Conclusions, unless these are clearly inappropriate. A paper must be

prefaced by an abstract of the argument and findings, which may also be arranged under the same headings. As with many other journals, we are unable to publish footnotes to the text. Please therefore incorporate this sort of material into the body of the paper, in brackets if appropriate.

Design and analysis. The quality of the data and analysis must always be good enough to justify the inferences and conclusions drawn. Particular attention should be given to design of sampling surveys, which should be planned using modern statistical principles, and to the treatment of results below the limit of detection (see this page).

Units and symbols. SI units must be used, though their equivalent in other systems may be given as well.

Figures. These include photographs, diagrams and charts. The first submission should include good quality low resolution copies of Figures, and may be incorporated into the text or at the end of the manuscript.

Tables. Tables should be numbered consecutively and given a suitable caption. As with Figures, it is helpful to incorporate them into the text of the first submission, but in the revised version each table should be presented on a separate page. Footnotes to tables should be provided below the table and should be referred to by superscript lowercase letters.

References. References should only be included which are essential to the development of an argument or hypothesis, or which describe methods for which the original account is too long to be reproduced. References in the text should be in the form Jones (1995), or Jones and Brown (1995), or Jones *et al.* (1995) if there are more than two authors, and they should be incorporated naturally into the text.

For example:

Jones and Brown (1995) and Hospath *et al.* (2006) observed total breakdown of control..., or

Total breakdown of control has sometimes been observed (Jones and Brown, 1995; Hospath *et al.*, 2006).

Papers whose references are not properly arranged may be returned for revision without review. At the end of the paper, references should be listed in alphabetical order by name of first author, using the Harvard Style of abbreviation and punctuation. ISBNs should be given for books and other publications where appropriate. Material unobtainable by readers should not be cited. Personal Communications, if essential, should be cited in the text (e.g., Professor O.H. Poobah, Institute for Dusty Sciences). Internet material can be referred to if it is likely to be permanently

available; the date on which it was last accessed should be given. References will not be checked editorially, and their accuracy is the responsibility of authors.

For example:

Simpson AT, Groves JA, Unwin J, Piney M. (2000) Mineral oil metal working fluids (MWFs)—Development of practical criteria for mist sampling. *Ann Occup Hyg*; 44: 165–72.

Vincent JH. (1989) *Aerosol sampling: science and practice*. Chichester, UK: John Wiley. ISBN: 0 471 92175 0.

Swift DL, Cheng Y-S, Su Y-F, Yeh H-C. (1994) Ultrafine aerosol deposition in the human nasal and oral passages. In Dodgson J, McCallum RI, eds. *Inhaled Particles VII*. Oxford: Elsevier Science. p. 77–81. ISBN: 0 08 040841 9 H.

British Standards Institution. (1986). BS 6691: 1986. Fume from welding and allied processes. Part 1. Guide to methods for the sampling and analysis of particulate matter. London: British Standards Institution.

Morse SS. (1995) Factors in the emergence of infectious diseases. *Emerg Infect Dis* [serial online] 1995 Jan–Mar;1(1). Available from: URL: <http://www.cdc.gov/ncidod/EID/eid.htm> (accessed 25 Oct 2010).

Dermal exposure and surface contamination associated with the use of a cobalt-chrome alloy during additive manufacturing

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3.2 Abstract

Background: Amidst the rapidly emerging Additive Manufacturing (AM) industry, not enough attention has been paid to dermal exposure, with only one study that has investigated dermal exposure to metals when a nickel (Ni) based alloy was used. This study aimed to characterise a cobalt (Co) – chrome (Cr) alloy feedstock powder (CO-538) in terms of particle size, shape, and elemental composition, and assess dermal exposure and workplace surface contamination when the CO-538 feedstock powder was used during powder bed fusion (PBF) AM.

Methods: Particle size distribution (PSD) and shape of the virgin (new) and used feedstock powder was established using static image analysis (Malvern Morphologi G3) and scanning electron microscopy (SEM) analysis. The elemental composition of powders was established using inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis. A removal wipe sampling method using Ghostwipes™ was used. All AM operators at the facility participated (two in total), and metals were removed from the index finger, palm, wrist, back of the hand, and neck, before and after each AM processing phase (7 pre-processing, 5 processing, and 7 post-processing phases). Operating (AM) and non-operating (non-AM) workplace surfaces were wiped before and after each shift to quantify surface contamination (35 samples). All dermal and surface wipe samples were analysed using ICP-mass spectrometry (ICP-MS).

Results: PSD analysis indicated a statistically significant difference ($p \leq 0.05$) at $d(0.1)$ between virgin and used powder with the used powder particles generally smaller in size than that of virgin powder particles based on the mean. Statistically significant differences ($p \leq 0.05$) were also observed in the mean circularity and convexity of virgin and used powders, indicating that the used powder particles were more irregularly shaped and less smooth-surfaced than that of virgin powders. Co, Cr, molybdenum, aluminium, iron, and Ni were detected in the CO-538 feedstock powder. These metals were also detected on the skin of AM operators and on surfaces within the AM and non-AM areas of the facility. Dermal exposure occurred on all the anatomical areas, with the highest total metal concentration detected on the index finger during the post-processing phase of AM with a geometric mean and 95% lower and upper confidence intervals (CI) of $3.160 \mu\text{g}/\text{cm}^2$ (CI: $0.703\text{-}14.210 \mu\text{g}/\text{cm}^2$). The highest full shift GM concentration of each metal was detected on the finger and followed a trend of $\text{Co} > \text{Cr} > \text{Fe} > \text{Al} > \text{Mo} > \text{Ni}$. Surface contamination occurred on all AM and non-AM sampling areas after a full shift with metal concentrations ranging from $0.106 \mu\text{g}/\text{cm}^2$ on operator 2's office desk to $19.695 \mu\text{g}/\text{cm}^2$ on workbench 1.

Conclusion: Dermal exposure to all CO-538 metal constituents occurred on all sampled anatomical areas during all three processing phases. This finding indicates that a risk of adverse dermal health effects following exposure during metal AM exists. Measurable concentrations of

metals that were detected on all sampled surfaces indicate that cross-contamination between AM and non-AM areas occur and that these surfaces may act as a secondary source of exposure. There is thus a need for control measures to be implemented in AM facilities to eliminate or reduce surface metal contamination and dermal exposure.

3.3 Introduction

Additive Manufacturing (AM) is the term used to describe the technology where three-dimensional products are created from computer-aided design (CAD) by adding and fusing consecutive layers of feedstock material (ISO/ASTM: 2021; Ljunggren *et al.*, 2019). Powder Bed Fusion (PBF) has been described as the leading AM process category in industries where metal products are manufactured (Matthews *et al.*, 2016). PBF makes use of an increasing number of different metals and metal alloy powders as feedstock materials (Mutchler, 2019; Qian, 2015). During PBF consecutive layers of these metal feedstock powders are added and predetermined areas are fused using either lasers or electron beams (Dutta and Froes, 2017; Gibson *et al.*, 2015).

AM can be divided into three processing phases, namely pre-processing, processing, and post-processing. During the pre-processing phase, the desired product is designed using a CAD system and the AM machine is set up, loaded with feedstock powders and the baseplate is levelled. During the processing phase, the actual manufacturing of the designed product takes place within the enclosed chamber of the AM machine. During the post-processing phase, the product is manually removed from the AM machine and the AM machine along with the manufactured product is cleaned (Gibson *et al.*, 2015).

When considering the conceptual model for the assessment of dermal exposure, dermal exposure due to PBF AM using metal feedstock powder can be anticipated to occur when AM operators come into direct contact with feedstock powders during manual handling activities of the pre- and post-processing phases (Schneider *et al.*, 1999). Powder particles may also become airborne during the different processing phases, leading to dermal exposure when airborne particles settle directly onto the skin. Airborne particles may also settle onto surfaces within the workplace creating a surface contaminant layer. Furthermore, dermal exposure may occur when AM operators come into contact with the surface contaminant layer, or when mechanical forces cause settled particles to become re-suspended into the workplace environment.

To date, only one study has assessed dermal exposure during AM when a nickel (Ni) based alloy Hastelloy® X (Haynes International, ID, USA) was used. The study found measurable concentrations of Ni, cobalt (Co), and chrome (Cr) on the index fingers of AM operators (Ljunggren *et al.*, 2019). Three cases of occupational allergic contact dermatitis have been reported following dermal exposure to epoxy resin compounds that were used during a vat

photopolymerisation AM process (Chang *et al.*, 2004) and another unspecified AM process (Creytens *et al.*, 2017). The limited available information and the occurrence of adverse health effects following dermal exposure highlight the need for further investigation into dermal exposure during AM.

The adverse health effects associated with exposure to metal feedstock powders depend on factors such as particle size, shape, and elemental composition (Chen *et al.*, 2020). Safety data sheets (SDSs) should contain information on these characteristics. However, several SDSs of different AM feedstock powders have failed to disclose this information adequately (du Preez *et al.*, 2018; Mellin *et al.*, 2016). Furthermore, the information provided in SDSs only applies to virgin feedstock powders. When leftover feedstock powders are reused, the chemical and physical characteristics of the feedstock powders may be altered (Tang *et al.*, 2015). Therefore, when assessing the potential adverse health effects associated with exposure to AM feedstock powders, it is necessary to characterise both virgin and used feedstock powders according to size, shape, and elemental composition.

The feedstock powder investigated in this study was a commercially available Cobalt-Chrome (CoCr) alloy powder (CO-538) that, according to its SDS, consists of 50-70% Co, 20-50% Cr, 5-20% Molybdenum (Mo) and <1% for both Ni and carbon (Praxair Surface Technologies, 2015). CoCr alloys are often used as feedstock powders due to it being a biocompatible alloy that is strong and resistant to heat, corrosion, and discolouration. These characteristics of CoCr alloys make it ideal for use in biomedical industries such as orthopaedic prostheses and dentistry where the application of AM is rapidly increasing (Al Jabbari, 2014). Although products manufactured from CoCr alloys are considered biocompatible, exposure to the individual constituents of the alloy in powdered form may pose risks to the health of AM operators. *In vitro* permeation of Co and Cr through human skin has been described (Larese Filon *et al.*, 2004; Larese Filon *et al.*, 2008) and dermal exposure to Co and Cr may cause allergic contact dermatitis (Tokar *et al.*, 2013).

This study aims to expand the information available on the health risks associated with metal AM by characterising virgin and used CO-538 feedstock powder according to size, shape, and elemental composition and assessing dermal exposure and surface contamination when the CO-538 powder was used during PBF AM.

3.4 Method

This study was conducted at a South African AM facility where CO-538 alloy feedstock powders are used during the process of PBF using an ORLAS CREATOR (O.R. Lasertechnologie GmbH) AM machine. A schematic layout of the AM and non-AM operating areas within the facility is

provided in Section 3.11 Supplementary information (Figure S3-4). Ethics approval for this study was obtained from the North-West University Health Research Ethics Committee (NWU-00152-21-A1). The two AM operators volunteered and provided informed consent to participate in this study which was conducted over a period of eleven days. During this period, six of the same products were manufactured and the print duration (the processing phase) of each product ranged between 11 hours 41 minutes and 13 hours 47 minutes.

Each manufacturing process was divided into three processing phases: pre-processing, processing, and post-processing. During the pre-processing phase, the AM operator loaded used feedstock material into the AM machine and where necessary topped it up with virgin feedstock powder. The AM operator then levelled the baseplate and set the height of the powder scraper. The AM operator then closed the AM machine and started the print using the computer located on top of the AM machine. During the processing phase, the AM operator left the AM area and monitored the print virtually via a camera mounted on the AM machine's window. The AM operator returned to the AM area occasionally for the remainder of the work shift to monitor the progress or to make minor adjustments using the computer. In other instances, the AM operator only returned for the post-processing phase. During the post-processing phase, the excess powder around the manufactured product was removed, and then the manufactured product was removed from the AM machine. Next, the AM machine and product were cleaned using a vacuum cleaner and leftover (used) powder was sifted to be re-used in the following prints. The sieve was cleaned when necessary, using compressed air to remove excess particles.

In total, seven pre-processing phases, five processing phases, and seven post-processing phases were monitored. Operator 1 carried out five of the pre-processing phases, one processing phase, and three post-processing phases, and the remainder of the phases was carried out by Operator 2. The uneven number of the different processing phases was due to unplanned breakdowns or maintenance and AM operators not returning during the processing phase.

Personal protective equipment (PPE) available to the AM operators included full-face respirators that cover the eyes, nose, and mouth, with reusable filtering face piece 3 (FFP3) particulate filters as well as standard disposable nitrile gloves and laboratory coats. During all pre- and post-processing phases both AM operators wore respirators, but nitrile gloves were worn inconsistently depending on the AM operator and the activity being carried out. During the processing phase, no PPE was worn by either of the AM operators and laboratory coats weren't worn during any of the processing phases.

3.4.1 Powder size, shape, and elemental composition

Samples of both virgin and used CO-538 feedstock powder along with the relevant SDS were collected from the AM facility. Static image analysis was used to determine the particle size and shape of both the virgin and used CO-538 feedstock powders using a Malvern Morphologi G3 instrument (Malvern Instruments Ltd, United Kingdom). The particle size distribution (PSD) was based on the Circle Equivalent (CE) diameter of each particle as measured by the Malvern Morphologi G3. The shape of the powder particles was based on the circularity (measurement of how close the particle shape is to that of a perfect circle) and convexity (measurement of particle edge roughness) of all particles as calculated by the Malvern Morphologi G3 software (Malvern Panalytical, 2021). A sample of 5 mm³ feedstock powder was dispersed onto the microscope slide and scanned by the instrument using 10x, 20x, and 50x optics. Images of representative particles in each sample were captured and analysed by the instrument. All samples were analysed a minimum of five times, however, due to variation in d(0.1) of virgin powders a further three repeats of virgin powder analysis were conducted.

Scanning electron microscopy (SEM) analysis was conducted on both virgin and used CO-538 samples using a Phenom pro-desktop (Phenom Pro Desktop SEM, Phenom-world B., Eindhoven, Netherlands) SEM instrument. A sample of 3 - 5 mm³ of CO-538 powder was applied onto one side of double-sided adhesive carbon tape and loaded into the SEM sample chamber. Representative images of each sample were taken at different magnifications to visualise particles at 1950x and 590x magnification (du Preez *et al.*, 2018). Images of the powders were used as a qualitative indication of particle size, shape, and surface characteristics.

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) analysis was conducted on two powder samples (one virgin and one used) using a Spectro Arcos (AMETEK, Inc. Materials Analysis Division, USA) ICP spectrometer. The powder samples were prepared using microwave digestion and injected into the instrument's burner from where they entered, as fine-droplet aerosols, into the plasma. The plasma within the ICP instrument is heated to extremely high temperatures (approximately 10000°C) and causes elements to emit light of characteristic wavelengths. The light emitted was captured by light sensors and used to analyse the concentration of the elements in the samples (Worden, 2005).

3.4.2 Dermal exposure

Dermal exposure samples were collected by means of a removal wipe sampling method using commercially available Ghostwipes™ (SKC, Eighty-Four, Pennsylvania, USA). Ghostwipes™ are individually wrapped and moistened (with deionised H₂O) sampling media that have been validated for surface sampling of 13 different metals (OSHA, 2002). Ghostwipes™ have

successfully been used for dermal sampling of metals including, amongst others, Co, Cr, Ni, Aluminium (Al), Platinum (Pt), and other Pt group metals (du Plessis *et al.*, 2010; du Plessis *et al.*, 2013; Gorman Ng *et al.*, 2017; Linde *et al.*, 2018; Linde *et al.*, 2021). When one AM operator carried out a full shift, samples were collected before the shift and subsequently after each processing phase. However, when different AM operators carried out different processing phases within a shift, samples were also collected before each processing phase. For example, if operator 1 started the shift with the pre-processing phase, but then operator 2 conducted the processing phase, samples were collected before the shift and after the pre-processing phase from operator 1, and before and after the processing phase from operator 2.

Samples were collected from the wrist, palm, back of the hand and ventral side of the index finger of the dominant hand and the right-hand side of the neck. A clean acetate template with a defined rectangular opening of 24 cm² (6 x 4 cm) was used to ensure that a constant surface area was sampled. For the index finger, the ventral side of the finger was sampled. The sampled surface area of the index finger was calculated in accordance with the method used by du Plessis *et al.* (2010). A trace of the operator's index finger along with a trace of a 1 cm² reference area was made on paper, cut out, and weighed repeatedly (n = 5) on a Sartorius microbalance to determine the average mass of each. The surface area of the index finger was then calculated by dividing the mass of the finger trace by the calculated mass of the 1 cm² paper.

The researcher wore a clean pair of gloves, removed the wipe from its packaging and used it to wipe the dermal surface area while keeping within the perimeters of the template or predetermined anatomical markers. Each surface area was wiped three times consecutively, first in a horizontal "S" shaped motion, followed by a vertical "S" shaped motion, and ending again in a horizontal "S" shaped motion. After each wipe pattern, the wipe was folded with the exposed area inward. After this procedure, each wipe sample was placed in a separate clean and labelled hard-walled vial where it was stored and sent to a South African National Accreditation System (SANAS) accredited laboratory for analysis using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in accordance with OSHA method ID-125G (OSHA, 2002). Each wipe sample was prepared using acid digestion and introduced into the ICP-MS instrument. The ICP-MS instrument uses an inductively coupled plasma as describe above for ICP-OES, however, in ICP-MS it is used to convert elements into ions. These ions then enter a high vacuum chamber within the mass spectrometer where ions are separated by mass. This allows for elements in a sample to be separated and concentrations determined (Worden, 2005).

Four field-blanks (unexposed wipes that were removed from their packaging and placed into separate hard-walled vials) and two media-blanks (unopened wipes) were stored and analysed as described for dermal wipe samples.

3.4.3 Workplace surface contamination

The workplace area was observed before sampling commenced to identify surfaces that the AM operator came into contact with most often and, therefore, had the highest potential risk of leading to dermal exposure. Ten workplace surfaces were identified for sampling, namely 1) the door handle of the AM machine; 2) the tablet computer mounted on the front of the AM machine; 3) the computer mouse located on top of the AM machine; 4) the general workbench where most post-processing activities took place (Workbench 1); 5) the general workbench next to the AM machine (Workbench 2); 6) the sieve used to sift leftover powders before they are reused; 7) the door handle between the non-AM and AM area; 8) the door handle between the non-AM area and the corridor leading to the operators' offices; 9) the desk area in front of the computer in Operator 1's office, and; 10) the desk area in front of the computer in Operator 2's office (Figure S3-4 in Section 3.11 Supplementary information).

Samples were collected before the shift on the first day and thereafter after each post-processing phase. The wiping procedure was carried out as described for dermal wipe sampling. For flat surfaces, a clean pair of gloves and a clean acetate template with a defined opening of 100 cm² (10 x 10 cm) were used to ensure that a constant surface area was sampled. Irregularly shaped surfaces were sampled in a similar manner but without the use of a template. All samples were stored and selected samples (n=17 after shift samples and n=18 before shift samples) were analysed as described for dermal wipe samples.

3.5 Data analysis

All data sets obtained during this study were statistically analysed using GraphPad Prism, Version 8.0 (GraphPad Software Inc., San Diego, California, USA). All p values ≤ 0.05 were considered to be statistically significant.

Basic descriptive statistics were used to analyse data sets obtained from the results of PSD and shape analysis. Data sets of PSD and shape of virgin and used powders were normally distributed. Due to the normal distribution and the unequal number of repeats of virgin and used data, the data sets were compared using unpaired t-tests with Welch's correction.

Wipe samples mass were blank corrected for each metal by subtracting the average mass of each metal found on the blanks from the mass of the metal on the specific wipe. The concentration in $\mu\text{g}/\text{cm}^2$ was calculated by dividing the mass of the metal powders detected on each sample by the area sampled. Samples containing less than 1 μg , the limit of detection (LOD) mass of the metals, as well as samples that had negative (-) mass after being blank corrected, were reported as below the detection limit (BDL). For statistical analysis, all BDL values were substituted using NDExpo version 1.0 (ExpoStats Bayesian Calculator, Montreal, Canada). The total metal

concentration was calculated as the sum of all metals that were detected in 20% or more of the samples which included Co, Cr, Mo, Al, Iron (Fe) and Ni. Metals that were detected in less than 20% of the samples and/or were not detected or SDS reported in the feedstock powders, were excluded from the results. Detected metals that are not reported include Copper (Cu), Magnesium (Mg), Manganese (Mn), Titanium (Ti), Tungsten (W), and Zinc (Zn).

Dermal metal concentration data was not normally distributed and was log-transformed for statistical analysis. Concentrations of Co, Cr, Mo, Al, Fe and Ni were summed to calculate the total metal concentration on each wipe. The geometric mean (GM) and 95% lower and upper confidence intervals (CI) concentrations were calculated for total metal concentration on each anatomical area during each processing phase. A one-way ANOVA with Tukey's multiple comparison test was performed to determine statistically significant differences in exposure on anatomical areas during the different processing phases. The GM and 95% lower and upper CI for each metal's concentration on each anatomical area were calculated for all three processing phases. The full shift GM concentration for each metal on each anatomical area was calculated as the sum of the GM concentrations of each processing phase.

For workplace surface contamination, the total metal concentration was calculated as the sum of the metal elements (Co, Cr, Mo, Al, Fe and Ni) that were detected on each surface. Metals that were detected but are not included in the results for reasons as stated for dermal wipe analysis are Cu, Mg, W, and Zn. Where the sampling area was known, results are reported in $\mu\text{g}/\text{cm}^2$, however, for irregularly shaped surfaces such as the computer mouse and door handles, the surface area could not be calculated, and total metal contamination is, therefore, reported as $\mu\text{g}/\text{sample}$.

3.6 Results

3.6.1 PSD and shape analysis

The particle size distribution (PSD) and shape analysis of virgin and used CO-538 powders are presented and compared in Table 3-1. No information regarding the PSD or shape of the virgin powder was reported in the SDS (Praxair Surface Technologies, 2015). Results from the PSD, circularity, convexity and SEM could, therefore, not be compared to the SDS.

The median $d(0.5)$ diameter (\pm SD) of the virgin and used powder particles were $23.710 \pm 1.560 \mu\text{m}$ and $17.270 \pm 4.068 \mu\text{m}$ respectively. For virgin powders, 10% of the particles [$d(0.1)$] had diameters smaller than $4.844 \pm 4.909 \mu\text{m}$. Virgin powders contained no particles larger than $119.530 \mu\text{m}$. For the used powder, 10% of the particles had diameters smaller than $0.242 \pm 0.018 \mu\text{m}$. Used powders had no particles larger than $111.250 \mu\text{m}$. At $d(0.1)$ the mean particle size of the used powders was significantly smaller than that of the virgin powders ($p \leq 0.05$).

SEM images (Figure 3-1; A-F) gave a visual representation of the size and shape of the virgin and used CO-538 powder particles. SEM, circularity and convexity results indicated that the CO-538 powder particles consisted of a mixture of spherical particles with smooth surfaces, and irregularly shaped particles with less smooth surfaces. Statistically significant differences were observed between the mean circularity of the virgin and used powders and between the mean convexity of virgin and used powders. This indicates that the used powders consisted of more irregularly shaped and less smooth surfaced particles than the virgin powders.

Table 3-1: PSD and shape of virgin and used CO-538 powder reported as mean \pm standard deviation.

| Powder | n | PSD (μm) | | | Circularity | Convexity |
|---------------|----------|---------------------------------------|--------------------|--------------------|--------------------------------|--------------------------------|
| | | d(0.1) | d(0.5) | d(0.9) | | |
| <i>Virgin</i> | 8 | 4.844 \pm 4.909 ^a | 23.780 \pm 1.306 | 39.690 \pm 1.288 | 0.874 \pm 0.017 ^b | 0.981 \pm 0.002 ^c |
| <i>Used</i> | 5 | 0.242 \pm 0.018 ^a | 19.720 \pm 3.441 | 36.400 \pm 2.904 | 0.808 \pm 0.045 ^b | 0.973 \pm 0.006 ^c |

d(0.1) indicates 10% of particles are smaller than the given diameter; d(0.5) indicates 50% of particles are smaller than the given diameter; d(0.9) indicates 90% of particles are smaller than the given diameter. a-c indicates statistically significant differences where $p \leq 0.05$. Circularity is the ratio of the perimeter of a circle with an area equivalent to the particle, divided by the actual particle perimeter. A circularity of 1 represents a perfect circle. Convexity is the measurement of particle edge roughness. A convexity of 1 represents a smooth surface.

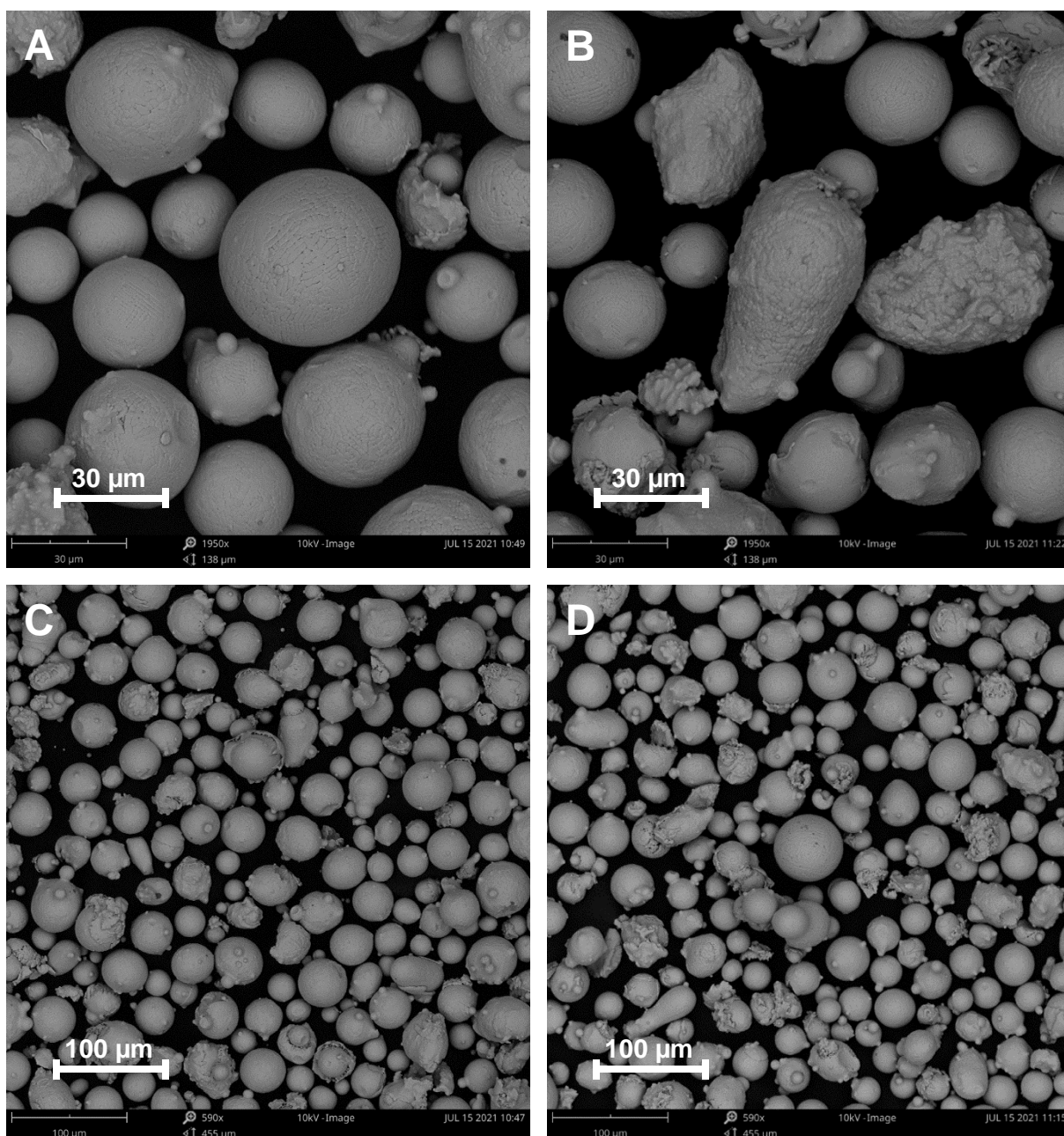


Figure 3-1: SEM images of virgin (A & C) and used (B & D) CO-538 powders at 590x (A & B) and 1950x (C & D) magnification.

3.6.2 Elemental composition

Table 3-2 presents the elemental composition of virgin and used samples as detected through ICP-OES analysis and the elemental composition ranges as reported in the standard and SDS for the CO-538 feedstock powder (ASTM, 2019; Praxair Surface Technologies, 2015). All elements that were detected through ICP-OES fell within the percentage ranges as reported in ASTM standard and SDS for the CO-538 feedstock powder, except for Mo which was detected at slightly lower concentrations in the used powder sample. The SDS, however, failed to report the presence of metals such as Mn, Fe, Ni and Al which were detected through ICP-OES. ICP-

OES analyses for virgin and used CO-538 were similar, with all metals detected in the virgin powder, also detected in the used powder samples.

Table 3-2: Elemental composition of virgin and used CO-538 feedstock powders.

| Elements | | Reported in ASTM % (m/m) | Reported in SDS % | Analysed by ICP-OES % (m/m) | |
|------------------|-------------------|-------------------------------------|------------------------------|--|-------------|
| | | <i>Maximum</i> | | <i>Virgin</i> | <i>Used</i> |
| Metal | <i>Cobalt</i> | Balance | 50-75 | 64.10 | 65.00 |
| | <i>Chrome</i> | 27-30 | 20-50 | 28.50 | 28.70 |
| | <i>Molybdenum</i> | 5-7 | 5-20 | 6.39 | 4.97 |
| | <i>Manganese</i> | 1.00 | - | 0.12 | 0.12 |
| | <i>Iron</i> | 0.75 | - | 0.35 | 0.57 |
| | <i>Nickel</i> | 0.50 | - | 0.21 | 0.21 |
| | <i>Aluminium</i> | 0.10 | - | 0.06 | <0.05 |
| | <i>Tungsten</i> | 0.20 | - | - | - |
| | <i>Titanium</i> | 0.10 | - | - | - |
| Non-metal | <i>Silicon</i> | 1.00 | - | 0.27 | 0.36 |
| | <i>Carbon</i> | 0.35 | <1 | - | - |
| | <i>Nitrogen</i> | 0.25 | <1 | - | - |
| | <i>Phosphorus</i> | 0.02 | - | - | - |
| | <i>Boron</i> | 0.01 | - | - | - |
| | <i>Sulphur</i> | 0.01 | - | - | - |

% (m/m) = Composition, % (Mass/Mass); Balance is the difference of 100% and the sum of the percentage of other elements specified.

3.6.3 Dermal exposure

Measurable concentrations of metals were detected on all the anatomical areas during all the processing phases. Figure 3-2 indicates the GM and 95% lower and upper CI of total metal (Co, Cr, Mo, Al, Fe and Ni) exposure during each processing phase.

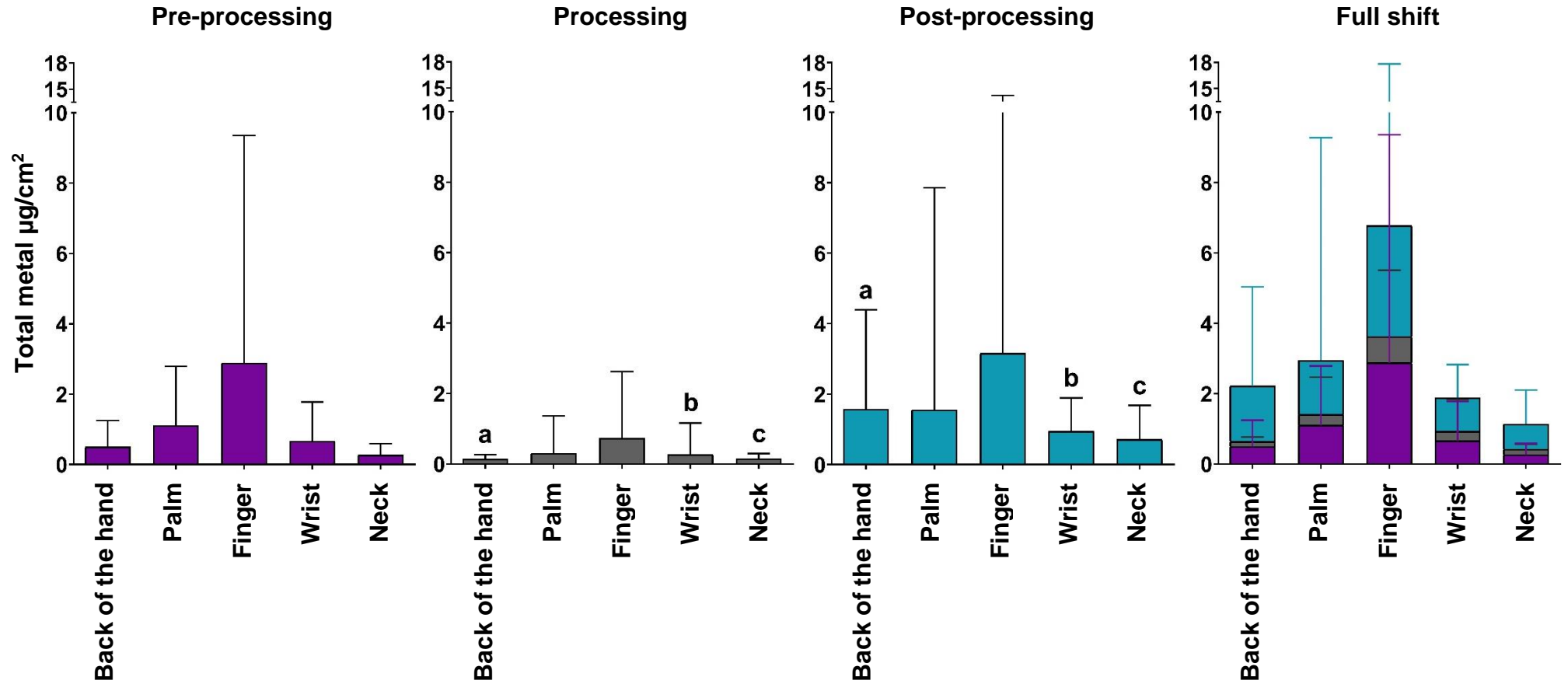


Figure 3-2: GM \pm 95% CI of total metal concentration ($\mu\text{g}/\text{cm}^2$) on different anatomical areas after pre-processing ($n = 7$) processing ($n = 5$) and post-processing ($n = 7$) phases of AM, and the full shift total metal concentration as the sum of the GMs of all three processing phases. a-c Indicates statistically significant differences ($p \leq 0.05$).

After the pre-processing phase, measurable total metal concentrations were detected on all anatomical areas with a GM of 0.503 $\mu\text{g}/\text{cm}^2$ and 95% lower and upper CI of 0.203-1.247 $\mu\text{g}/\text{cm}^2$ on the back of the hand. On the palm the total metal concentration detected was 1.108 $\mu\text{g}/\text{cm}^2$ (CI: 0.440-2.788 $\mu\text{g}/\text{cm}^2$), 2.884 $\mu\text{g}/\text{cm}^2$ (CI: 0.889-9.359 $\mu\text{g}/\text{cm}^2$); on the finger, 0.665 $\mu\text{g}/\text{cm}^2$ (CI: 0.249-1.776 $\mu\text{g}/\text{cm}^2$); on the wrist, and 0.271 $\mu\text{g}/\text{cm}^2$ (CI: 0.125-0.586 $\mu\text{g}/\text{cm}^2$); on the neck.

After the processing phase, total metal concentrations were detected on all anatomical areas with 0.145 $\mu\text{g}/\text{cm}^2$ (CI: 0.080-0.264 $\mu\text{g}/\text{cm}^2$) on the back of the hand; 0.306 $\mu\text{g}/\text{cm}^2$ (CI: 0.069-1.362 $\mu\text{g}/\text{cm}^2$) on the palm; 0.735 $\mu\text{g}/\text{cm}^2$ (CI: 0.206-2.623 $\mu\text{g}/\text{cm}^2$) on the finger; 0.273 $\mu\text{g}/\text{cm}^2$ (CI: 0.064-1.161 $\mu\text{g}/\text{cm}^2$) on the wrist; and 0.155 $\mu\text{g}/\text{cm}^2$ (CI: 0.081-0.296 $\mu\text{g}/\text{cm}^2$) on the neck.

Metals were detected on all anatomical areas after the post-processing phase with total metal concentrations of 1.577 $\mu\text{g}/\text{cm}^2$ (CI: 0.566-4.394 $\mu\text{g}/\text{cm}^2$) on the back of the hand, 1.533 $\mu\text{g}/\text{cm}^2$ (CI: 0.307-7.858 $\mu\text{g}/\text{cm}^2$) on the palm; 3.160 $\mu\text{g}/\text{cm}^2$ (CI: 0.703-14.210 $\mu\text{g}/\text{cm}^2$) on the finger; 0.940 $\mu\text{g}/\text{cm}^2$ (CI: 0.471-1.890 $\mu\text{g}/\text{cm}^2$) on the wrist, and 0.717 $\mu\text{g}/\text{cm}^2$ (CI: 0.306-1.679 $\mu\text{g}/\text{cm}^2$) on the neck.

Statistically significant differences were found between the total metal concentrations after the processing and post-processing phases on the back of the hand, wrist and neck indicating that GM total metal concentrations were significantly higher during the post-processing phase when compared to the processing phase. In Figure 3-2 the full shift total metal concentration is indicated as the sum of the GMs of all three processing phases. The anatomical areas with the highest full shift exposure were the finger > palm > back of the hand > wrist > neck.

Figure 3-3 indicates the full shift GM concentrations (sum of GM of each processing phase) of each of the metals on the different anatomical areas. The highest full shift GM concentration of each metal was detected on the finger and followed a trend of Co > Cr > Fe > Al > Mo > Ni. The lowest GM full shift concentration of Co, Cr, Al and Fe was detected on the neck and the lowest GM full shift concentration of Mo and Ni was detected on the wrist.

For all metals, the highest GM (and 95% lower and upper CI) concentrations were detected on the finger. The highest concentration detected was that of Co with a GM of 1.224 $\mu\text{g}/\text{cm}^2$ (CI: 0.280-5.336 $\mu\text{g}/\text{cm}^2$) on the finger during the pre-processing phase and the lowest concentration detected was Ni, with a GM of <0.001 $\mu\text{g}/\text{cm}^2$ (CI: 0.0002-0.0007 $\mu\text{g}/\text{cm}^2$) during the pre-processing phase on the wrist.

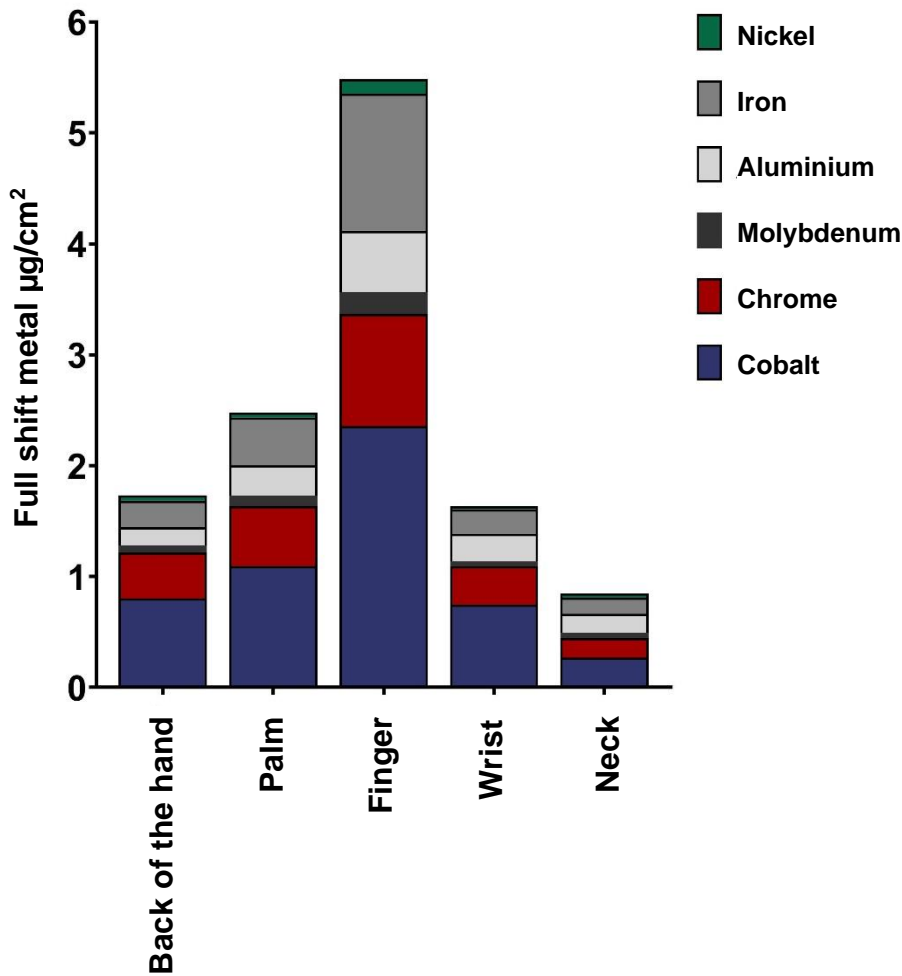


Figure 3-3: GM of full shift dermal exposure concentration ($\mu\text{g}/\text{cm}^2$) of each metal on different anatomical areas.

3.6.4 Workplace surface contamination

The surface areas where wipe samples were collected in the AM and non-AM areas are indicated Figure S3-4 in Section 3.11, Supplementary information. Measurable concentrations of metals were detected on all surfaces sampled in AM and non-AM areas (Table 3-3). Total metal concentrations detected before shift on the first day of sampling ranged from $0.002 \mu\text{g}/\text{cm}^2$ (printer tablet) to $45.060 \mu\text{g}/\text{cm}^2$ (Workbench 2) (data not shown). Total metal concentrations detected after a full shift ranged between $0.106 \mu\text{g}/\text{cm}^2$ (Office: Operator 2) to $19.695 \mu\text{g}/\text{cm}^2$ (Workbench 1). Total metal concentrations detected on irregularly shaped surfaces ranged from $1.739 \mu\text{g}/\text{sample}$ on door handle 2 (non-AM area) to $59.027 \mu\text{g}/\text{sample}$ on door handle 1 (AM area).

Table 3-3: Total metal concentration ($\mu\text{g}/\text{cm}^2$) detected after shift on workplace surfaces (n=17 samples).

| Workplace surfaces | Total metal concentration after shift ($\mu\text{g}/\text{cm}^2$) |
|--|---|
| <i>Workbench 1</i> | 4.733 - 19.695 |
| <i>Workbench 2</i> | 4.043 - 8.435 |
| <i>Printer door</i> | 0.188 - 0.275 |
| <i>Printer tablet screen</i> | 0.159 |
| <i>Sieve</i> | 2.826 |
| <i>Office desk: Operator 1*</i> | 0.138 - 0.367 |
| <i>Office desk: Operator 2*</i> | 0.106 - 0.245 |
| Irregularly shaped workplace surfaces | Total metal concentration after shift ($\mu\text{g}/\text{sample}$) |
| <i>Computer mouse</i> | 25.933 - 40.886 |
| <i>Door handle 1</i> | 42.087 - 59.027 |
| <i>Door handle 2*</i> | 1.739 |

* indicates the surface is in a non-AM area.

3.7 Discussion

While the application of AM is rapidly expanding and new AM materials are being developed, information regarding the risk to the health of AM operators remain limited (Chen *et al.*, 2020; Roth *et al.*, 2019: 321). This study aims to expand on the information available regarding the health risks associated with metal AM by characterising a CO-538 feedstock powder according to its particle size, shape and elemental composition and by assessing dermal exposure and surface contamination when the CO-538 powder is used during PBF AM.

Virgin and used powder particle sizes corresponded with one another at $d(0.5)$ and $d(0.9)$, however, at $d(0.1)$ the used powder particles mean was statistically significantly smaller than that of the virgin powders (Table 1). These findings are in agreement with that of Mellin *et al* (2016) who reported the presence of smaller particles in used samples of Inconel 939 (IN939) feedstock powder and suggested that these smaller powder particles detached from larger powder particles during manual handling of the powders, or due to the heat during the processing phase (Mellin *et al.*, 2016). A statistically significant difference was observed between the mean circularity and convexity of the virgin and used powders (Table 3-1). This indicated that the used powders consisted of more irregularly shaped and less smooth surfaced particles than the virgin powders. These findings are in agreement with that of Tang *et al* (2015) who investigated the effect that the

number of times a feedstock powder is reused, would have on its physical characteristics and found that titanium feedstock powder (Ti-6Al-4V) particles became less spherical and less smooth after each reuse.

There is limited information available regarding the effect of physical characteristics such as particle size and shape on dermal exposure. However, it is known that a larger surface-to-volume ratio of certain metal particles such as Co and Cr allows for increased oxidation (in the presence of sweat) and subsequent release of soluble ions that can permeate through the skin (Larese Filon *et al.*, 2013; WHO, 2006). Particles with irregular shapes have a higher surface-to-volume ratio when compared to perfectly spherical shapes (which are known to have the lowest surface-to-volume ratio) and thus may permeate the skin more readily (Lu *et al.*, 2010). Similarly, smaller particles have a higher surface-to-volume ratio when compared to larger particles and, therefore, they may be able to permeate the skin more readily.

Nano-sized particles may be able to enter the skin, however, particles larger than 45 nm (0.045 μm) are not capable of permeating or penetrating through the skin (Larese Filon *et al.*, 2015). Larger particles may, however, be able to enter into hair follicles where they can act as a long-lasting “reservoir” (Lademann *et al.*, 2015). Schaefer *et al.* (1990) found that fluorescent polystyrene microbeads of approximately 7 μm were able to enter the hair follicles (Toll *et al.*, 2004). When metals such as Ni and Cr form a reservoir inside the hair follicles there may be an increased risk of adverse dermal health effects such as allergic contact dermatitis developing due to its prolonged ion release (Lademann *et al.*, 2015; Larese Filon *et al.*, 2015)

The size of the particles may further affect the duration that particles remain suspended in the air and, therefore, how far they can disperse before settling on workplace or dermal surfaces (Pickford *et al.*, 2013). Small particles may remain suspended in the air for a longer duration allowing them to disperse further before settling. This may lead to dermal exposure and surface contamination occurring further away from the source.

Knowledge of the elemental composition, size, and shape of the metal alloy feedstock powder is important when assessing the potentially harmful effects that the feedstock powder may have on the health of AM operators (Chen *et al.*, 2020). SDSs which should contain information on these characteristics of feedstock powders have, in several instances, failed to disclose the particle size and elemental composition sufficiently (du Preez *et al.*, 2018; Mellin *et al.*, 2016). The same was found for the SDS of CO-538 which contained no information on the particle size and only limited information on the elemental composition of the CO-538 feedstock powder (Table 3-2). ICP-OES analysis indicated the presence of Co, Cr, Mo, Ni, Fe, Al, Mn, and Si in virgin and used samples of CO-538 powders. The elemental composition for Co, Cr, and Mo of the virgin powder sample, corresponded with the information given in the SDS of CO-538. However, the SDS failed to report

the presence of metals such as Mn, Fe, Ni, and Al which were detected through ICP-OES. When insufficient information is provided in SDSs of AM feedstock powders, AM operators may be unaware of the risks to health associated with the use of the feedstock powder leading to a false sense of protection (du Preez *et al.*, 2018).

There was variability in dermal exposure concentrations within the three processing phases on all anatomical areas which is consistent with variability reported in other dermal exposure studies (du Plessis *et al.*, 2010; du Plessis *et al.*, 2013; Hughson *et al.*, 2010; Julander *et al.*, 2010). The variability may be due to AM operators wearing PPE inconsistently and/or the variety of activities carried out during the processing phases (Hughson *et al.*, 2010).

Measurable concentrations of metals were detected on the skin of AM operators on all the anatomical areas during all of the processing phases. Statistically significant higher total metal concentrations were detected on the back of the hand, wrist, and neck during the post-processing phase when compared to the processing phase (Figure 3-2). The higher dermal exposure during the post-processing phase corresponds with the findings of Graff *et al.* (2017) and Ljunggren *et al.* (2019) who reported that particle emissions during PBF were highest during the manual handling activities that generally form part of the pre- and post-processing phases. The total metal concentrations during the pre-processing phase, however, did not differ significantly from the concentrations during the other processing phases. This may be due to fewer manual handling activities that were carried out during the pre-processing phase.

The anatomical area with the highest full shift dermal exposure was the finger followed by the palm > back of the hand > wrist > neck (Figure 3-2). Most manual handling activities occurred during the post-processing phase, which included removing excess powder around the manufactured product, removing the manufactured product and cleaning it, cleaning the AM machine of all leftover feedstock powder, sieving the used powders as well as cleaning the sieve with compressed air. The use of compressed air is not permitted in South Africa according to the Regulations for Hazardous Chemical Agents (2021) as promulgated under the Occupational Health and Safety act (Act 85 of 1993) (DOEL, 2022). During the processing phase, no gloves were worn, and during the pre- and post-processing phases, gloves were worn inconsistently. In two instances where gloves were worn during the post-processing phase, sharp edges on the manufactured product also caused the gloves to tear. These occurrences explain in part why the highest dermal exposure concentrations were detected on the hands of AM operators.

The anatomical area of exposure is a skin-related factor that influences the absorption of substances through the skin (Hostýnek *et al.*, 2003; Semple, 2004). The skin on the ventral side of the hands (palm and index finger) is thicker than the skin on the other sampled anatomical areas such as the back of the hand, the wrist, and the neck. Seen in the light of the fact that

concentrations were detected on the back of the hand, wrist, and neck, it should be noted that absorption of metals through these areas may occur more readily than in the anatomical areas with thicker skin (Larese Filon *et al.*, 2018; Semple, 2004).

In Figure 3-3 the full shift (pre-processing + processing + post-processing) GM concentrations of each metal on the different anatomical areas are illustrated. The highest full shift GM concentration of each metal was detected on the finger and followed a trend of Co > Cr > Fe > Al > Mo > Ni. Interpreting dermal exposure concentrations is challenging since no occupational exposure limits for dermal exposure exists (Naylor *et al.*, 2020: 800). Results indicate that dermal exposure to all these metals occurred and, therefore, a risk of adverse dermal health effects following exposure during metal AM exist. Co, Cr, and Ni are known dermal sensitizers, and exposure can result in allergic contact dermatitis (Tokar *et al.*, 2013). Although the concentrations of Ni exposure were low, it is known that simultaneous exposure to Ni, Co, Cr, or a combination of these metals, may result in sensitization more frequently than exposure to the individual metals would (Ruff and Belsito, 2006).

A study by Ljunggren *et al* (2019) reported dermal exposure following AM and found a mean concentration of 0.11 $\mu\text{g}/\text{cm}^2$ Co, 0.37 $\mu\text{g}/\text{cm}^2$ Cr, and 0.63 $\mu\text{g}/\text{cm}^2$ Ni at the end of a workweek on the index fingers of AM operators who worked with an alloy powder that, according to its manufacturer, consisted of 47% Ni, 22% Cr, 18% Fe, 9% Mo, 1.5% Co, and less than 15% other metals. This study used a tape-stripping sampling method and, therefore, the dermal exposure concentrations reported cannot directly be compared to the concentrations found in our study. It can, however, be noted that the GM concentration of Co [1.016 $\mu\text{g}/\text{cm}^2$ (CI: 0.140-7.357 $\mu\text{g}/\text{cm}^2$)] and Cr [0.565 $\mu\text{g}/\text{cm}^2$ (CI: 0.092- 3.470 $\mu\text{g}/\text{cm}^2$)] on the index finger following the post-processing phase was higher than the mean concentrations reported in Ljunggren *et al* (2019), whereas the Ni concentrations were lower [0.105 $\mu\text{g}/\text{cm}^2$ (CI: 0.615-0.018 $\mu\text{g}/\text{cm}^2$)]. This is most likely due to the differences in the elemental composition of the feedstock powders used.

Measurable concentrations of metals were detected on all workplace surfaces that were sampled in the AM and non-AM areas of the AM facility. The presence of metals indicates that these surfaces may act as secondary sources of exposure and that cross-contamination between AM and non-AM areas occurs. Dermal exposure may occur when AM operators come into direct contact with contaminated surfaces or when mechanical forces such as the use of compressed air cause particles to be re-suspended in the environment where they may settle on dermal surfaces. Respiratory exposure may also occur when re-suspended particles are inhaled. Furthermore, accidental ingestion may occur when food and drinks are consumed after being contaminated either due to contact with contaminated surfaces or due to the direct deposition of

substances onto the food/drinks. Accidental ingestion may also occur when powders are transferred from contaminated products or hands, into the mouth (Cherrie *et al.*, 2006).

On the first day of sampling, before the AM operators started their shift, samples were collected from all surfaces to determine the initial contamination on these surfaces. Detectable concentrations of metals were detected on all sampled surfaces. The initial contamination was expected since no routine housekeeping schedule had been implemented at the AM facility at the time of the study. Since all sampled surfaces have been identified to act as secondary sources of exposure, there is a need for them to be cleaned at regular intervals.

Ljunggren *et al* (2019) found that after stricter policies regarding PPE usage were implemented, the dermal exposure concentrations of AM operators were reduced significantly to a point where no measurable concentrations of Co were detected on the index fingers of AM operators. When considering the dermal exposure concentrations and adverse health effects associated with dermal exposure to metals such as Co, Cr, and Ni that were detected in this study, it is clear that improved control measures and standard operating procedures (SOPs) regarding PPE usage need to be implemented at the AM facility investigated (Tokar *et al.*, 2013). These control measures should include the use of an isolation or extraction cabinet when compressed air is used, the use of a local extraction ventilation (LEV) system with a movable capture hood to capture airborne particles during manual handling activities, and the implementation of a routine housekeeping schedule. PPE such as respiratory protection, gloves, and long-sleeve coveralls must be a mandatory requirement when entering the AM area, and reusable PPE should be stored in separate storage areas dedicated for clean and contaminated PPE in the non-AM area.

While a large number of samples were collected, the two AM operators did not carry out the same number of each processing phase. Therefore, the samples of the same processing phases weren't divided equally between the two AM operators. Not enough data was, therefore, available to study the variability in dermal exposure between operators during the different processing phases.

3.8 Conclusion

Information regarding dermal exposure during AM has remained limited despite the fact that cases of adverse dermal health effects developing following dermal exposure during AM have been reported (Chang *et al.*, 2004; Creytens *et al.*, 2017). Since the metal constituents of CO-538 feedstock powder such as Co and Cr are associated with dermal health effects (Tokar *et al.*, 2013), this study has provided much-needed information regarding dermal exposure when metal feedstock powders are used during AM (PBF).

Co, Cr, Mo, Fe, Al, and Ni were detected in the virgin and used samples of CO-538 feedstock powder, and these metals were also detected on sampled dermal and workplaces surfaces. The SDS of CO-538 did not report the presence of Fe, Al, and Ni, and no information regarding the physical characteristics (PSD and shape) of powder particles was provided (Praxair Surface Technologies, 2015). When AM operators are not informed of the potential health effects that are associated with exposure, it may lead to higher exposure. It is, therefore, crucial that manufacturers provide all the necessary information in SDSs.

The findings of this study have shown that dermal exposure to metal feedstock powders occurs during all three (pre-processing, processing, and post-processing) phases of AM. Dermal exposure during AM was identified on all sampled anatomical areas (the wrist, palm, back of the hand, ventral side of the index finger on the dominant hand, and the right-hand side of the neck), with the highest total metal concentration detected on the index finger during the post-processing phase. Furthermore, measurable concentrations of metals were detected on all sampled surfaces in the AM and non-AM areas. This indicates that cross-contamination between AM and non-AM areas occurs, and that these surfaces may act as an unexpected source of exposure to AM operators and other staff members working within the facility. Therefore, a need exists for control measures such as comprehensive SOPs regarding housekeeping and PPE to be developed and implemented in AM facilities to eliminate or reduce surface contamination and dermal exposure.

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3.10 References

Al Jabbari YS. (2014) Physico-mechanical properties and prosthodontic applications of Co-Cr dental alloys: a review of the literature. *J Adv Prosthodont*, 6: 138-145.

ASTM (American Society for Testing Materials) International. (2019) F75 – 18. Standard Specification for Cobalt-28 Chromium-6 Molybdenum Alloy Castings and Casting Alloy for Surgical Implants (UNS R30075)¹. West Conshohocken, PA: ASTM.

Chang TY, Lee LJ, Wang JD, Shie RH, Chan CC. (2004) Occupational risk assessment on allergic contact dermatitis in a resin model making process. *J. Occup. Health*; 46: 148-152.

Chen R, Yin H, Cole IS, Shen S, Zhou X, Wang Y, Tang S. (2020) Exposure, assessment and health hazards of particulate matter in additive manufacturing: A review. *Chemosphere*; 259: 1-17.

Cherrie JW, Semple S, Christopher Y, Saleem A, Hughson GW, Philips A. (2006) How important is inadvertent ingestion of hazardous substances at work? *Ann Occup Hyg*; 50: 693-704.

Creytens K, Gilissen L, Huygens S, Goossens A. (2017) A new application for epoxy resins resulting in occupational allergic contact dermatitis: the three-dimensional printing industry. *Contact Derm*; 77: 349-351.

du Plessis JL, Eloff FC, Badenhorst CJ, Olivier J, Laubscher PJ, van Aarde MN, Franken A. (2010) Assessment of dermal exposure and skin condition of workers exposed to nickel at a South African base metal refinery. *Ann Occup Hyg*; 54: 23-30.

du Plessis JL, Eloff FC, Engelbrecht S, Laubscher PL, van Aarde MN, Franken A. (2013) Dermal exposure and changes in skin barrier function of base metal refinery workers co-exposed to cobalt and nickel. *Occup. Health South. Afr*; 19: 6-12.

du Preez S, de Beer DJ, du Plessis JL. (2018) Titanium powders used in powder bed fusion: their relevance to respiratory health. *South African J. Ind. Eng*; 29: 94-102.

Dutta B, Froes FH. (2017) The Additive Manufacturing (AM) of titanium alloys. *Met. Powder Rep*; 72: 97-106.

DOEL (Department of Employment and Labour). (2022) Occupational health and safety act no 85 of 1993 and regulations. 23rd rev ed. Johannesburg, South-Africa: LexisNexis. ISBN: 978 1 776 17555 0.

Gibson I, Rosen D, Stucker B. (2015) *Additive manufacturing technologies: 3D Printing, Rapid Prototyping to Direct Digital Manufacturing*. 2nd ed. New York, NY: Springer. Available from Springer eBook Collection: <https://link.springer.com/book/10.1007/978-1-4939-2113-3#toc> (accessed 16 Feb 2021).

Gorman Ng M, MacCalman L, Semple S, van Tongeren M. (2017) Field measurements of inadvertent ingestion exposure to metals. *Ann. Work Expo. Health*; 61: 1097-1107.

Graff P, Stahlbom B, Nordenberg E, Graichen A, Johansson P, Karlsson H. (2017) Evaluating measuring techniques for occupational exposure during additive manufacturing of metals. *J. Ind. Ecol*; 21: 120-129.

- Hostýnek JJ. (2003) Factors determining percutaneous metal absorption. *Food Chem. Toxicol*; 41: 327-345.
- Hughson GW, Galea KS, Heim KE. (2010) Characterization and assessment of dermal and inhalable nickel exposures in nickel production and primary user industries. *Ann Occup Hyg*; 54: 8-22.
- ISO/ASTM (International Organization for Standardization/American Society of Testing Materials). (2021) ISO/ASTM 52900: 2021. Additive manufacturing - general principles - fundamentals and vocabulary. Available from: <https://www.iso.org/obp/ui/#iso:std:iso-astm:52900:ed-2:v1:en> (accessed 19 November 2022).
- Julander A, Liljedahl ER, de Paula HK, Assarsson E, Engfeldt M, Littorin M, Anto CS, Lidén C, Broberg K. (2010) Nickel penetration into stratum corneum in FLG null carriers- A human experimental study. *Contact Derm*; 87: 154-161.
- Lademann J, Knorr F, Richter H, Jung S, Meinke MC, Rühl E, Alexiev U, Calderon M, Patzelt A. (2015) Hair follicles as a target structure for nanoparticles. *J. Innov. Opt. Health Sci*; 8: 1530004-1 - 1530004-8. DOI: 10.1142/S1793545815300049
- Larese Filon F, Crosera M, Timeus E, Adami G, Bovenzi M, Ponti J, Maina G. (2013) Human skin penetration of cobalt nanoparticles through intact damaged skin. *Toxicol In Vitro*; 27: 121-127.
- Larese Filon F, D'Agostin F, Crosera M, Adami G, Bovenzi M, Maina G. (2008) In vitro percutaneous absorption of chromium powder and the effect of skin cleanser. *Toxicol In Vitro*; 22: 1562-1567.
- Larese Filon F, Maina G, Adami G, Venier M, Coceani N, Bussani R, Massiccio M, Barbieri P, Spinelli P. (2004) In vitro percutaneous absorption of cobalt. *Int Arch Occup Environ Health*; 77: 85-89.
- Larese Filon F. (2018) Penetration of metals through the skin barrier. In: Chen JK, Thyssen JP. eds. *Metal allergy: from dermatitis to implant and device failure*. Cham: Springer. p. 67-74.
- Larese Filon F, Mauro M, Adami G, Bovenzi M, Crosera M. 2015. Nanoparticles skin absorption: new aspects for a safety profile evaluation. *Regul Toxicol Pharmacol*; 72: 310-322.

Linde SJL, Franken A, du Plessis JL. (2018) Urinary excretion of platinum (Pt) following skin and respiratory exposure to soluble Pt at South African precious metals refineries. *Int Arch Occup Environ Health*; 221: 868-875.

Linde SJL, Franken A, du Plessis JL. (2021) Skin and respiratory exposure to platinum group metals at two South African precious metals refineries. *Int Arch Occup Environ Health*; 94: 1073-1083.

Ljunggren SA, Karlsson H, Ståhlbom B, Krapf B, Fornander L, Karlsson LE, Bergström B, Nordenberg E, Ervik TK, Graff P. (2019) Biomonitoring of metal exposure during additive manufacturing (3D printing). *Saf Health Work*; 10: 518-526.

Lu H, Ip E, Scott J, Foster P, Vickers M, Baxter LL. (2010) Effects of particle shape and size on devolatilization of biomass particle. *Fuel*; 89: 1156-1168.

Malvern Panalytical. (2021) Morphologi G3 user guide. Available from <https://www.malvernpanalytical.com/en/learn/knowledge-center/user-manuals/man0410en> (accessed 28 Nov 2021).

Matthews MJ, Guss G, Khairallah SA, Rubenchik AM, Depond PJ, King WE. (2016) Denudation of metal powder layers in laser powder bed fusion processes. *Acta Mater*; 114: 33-42.

Mellin P, Jonsson C, Åkermo M, Fernberg P, Nordenberg E, Hrodin H, Strondl A. (2016) Nano-sized by-products from metal 3D printing, composite manufacturing and fabric production. *J. Clean. Prod*; 139: 1224-1233.

Mutchler E. (2019) Trends watch: Metal additive manufacturing: Metal 3D printing is expanding manufacturing possibilities by enabling new designs and improved outcomes. *Adv. Mater. Process*; 177: 28-29.

Naylor CL, Davies B, Gopaldasani V. (2020) Quantitative skin exposure assessment of metals: a systematic literature review of current approaches for risk assessment using the construction industry as an exposure scenario. *Int Arch Occup Environ Health*; 93: 789-803.

OSHA (Occupational Safety and Health Administration). (2002) OSHA ID-125G: Metal and metalloid particulates in workplace atmosphere (ICP Analysis). Salt Lake City, UT: Occupational Safety and Health Administration. Available from: <https://www.osha.gov/sites/default/files/methods/id125g.pdf> (accessed 25 Jan 2022).

Pickford G, Davies B, Apthorpe L. (2013) Aerosols. In: Reed S, Pisaniello D, Benke G, Burton K. eds. *Principles of Occupational Health & Hygiene*. 2nd ed. Crows Nest, Australia: Allen & Unwin. p. 141-186.

Praxair Surface Technologies. 2015. Safety data sheet CO-538 products. Available from <https://www.praxairsurfacetechologies.com/-/media/corporate/praxairsurface/us/documents/sds/powders/co/co538s.pdf?la=en> (accessed 14 Oct 2021). p. 1-11.

Qian M. (2015) Metal powder for additive manufacturing. *JOM*; 67: 536-537.

Roth GA, Geraci CL, Stefaniak A, Murashov V, Howard J. (2019) Potential occupational hazards of additive manufacturing. *J. Occup. Environ. Hyg*; 16: 321-328.

Ruff CA, Belsito, DV. (2006) The impact of various patient factors on contact allergy to nickel, cobalt, and chromate. *J. Am. Acad. Dermatol*; 55: 32-39.

Schneider T, Vermeulen R, Brouwer DH, Cherrie JW, Kromhout H, Fogh CL. (1999) Conceptual model for assessment of dermal exposure. *Occup. Environ. Med*; 56: 765-773.

Semple S. (2004) Dermal exposure to chemicals in the workplace: just how important is skin absorption? *Occupational and Environmental Medicine*, 61: 376- 382.

Tang HP, Qian M, Liu N, Zhang XZ, Yang GY, Wang, J. (2015) Effect of powder reuse times on additive manufacturing of Ti-6Al-4V by selective electron melting. *JOM*; 67: 555-563.

Tokar EJ, Boyd WA, Freedman JH, Waalkes P. (2013) *Toxic effects of metals*. In: Klaason CD, eds. *Casarett & Doull's toxicology the basic science of poisons*. 8th ed. New York: McGraw-Hill Education. p. 982-1030.

Toll R, Jacobi U, Richter U, Lademann J, Schaefer H, Blume-Peytavi U. (2004) Penetration Profile of Microspheres in Follicular Targeting of Terminal Hair Follicles. *J Invest Dermatol*; 123: 168-176. DOI:<https://doi.org/10.1111/j.0022-202X.2004.22717.x>

WHO (World Health Organisation). (2006) Environmental health criteria 235: dermal absorption. <https://incem.org/documents/ehc/ehc/ehc235.pdf> (accessed 26 May 2021).

Worden, RH. (2005) Analytical methods: Geochemical analysis (including x-ray). In: Selley RC, Cocks LRM, Plimer IR. eds. *Encyclopedia of Geology*. Oxford: Elsevier. p. 54-76. DOI:10.1016/B0-12-369396-9/00096-4

3.11 Supplementary information

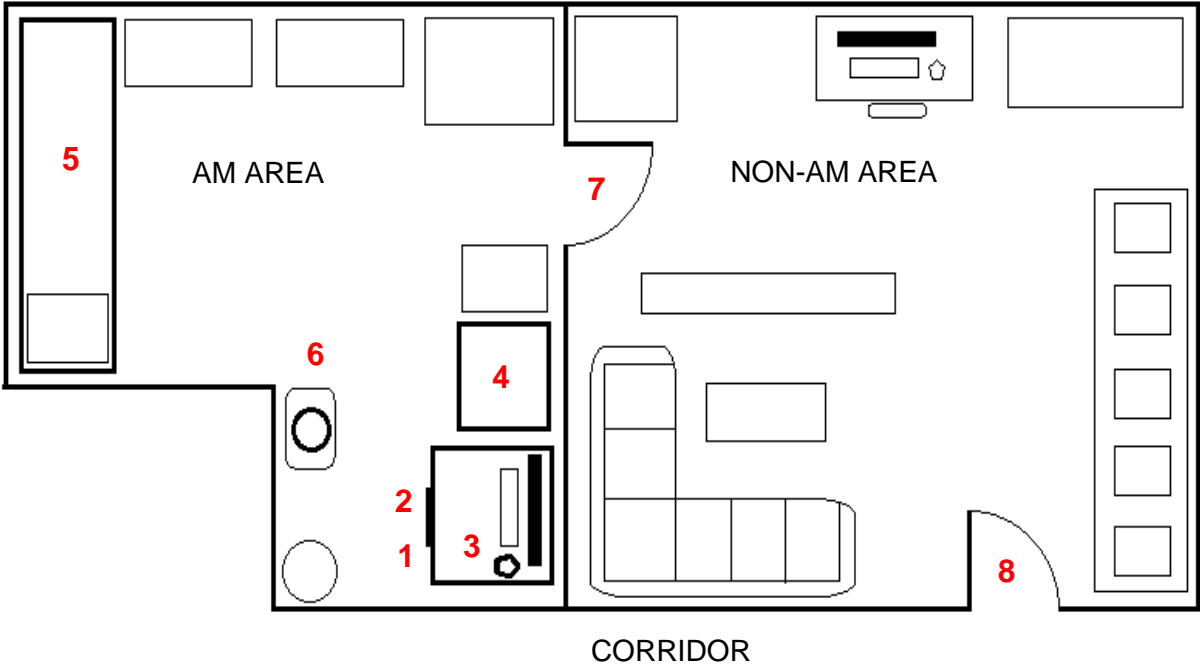


Figure S3-4: Layout of AM and non-AM operating areas where surface sampling was performed.

- 1). The door handle of the AM machine.
- 2). The tablet mounted on the front of the AM machine.
- 3). The computer mouse located on top of the AM machine.
- 4). The general workbench where most post-processing activities took place (Workbench 1).
- 5). The general workbench next to the AM machine (Workbench 2).
- 6). The sieve used to sift leftover powders.
- 7). The door handle between the non-AM and AM area.
- 8). The door handle between the non-AM area and the corridor leading to the operators' offices.

CHAPTER 4 CONCLUSIONS, RECOMMENDATIONS, LIMITATIONS, AND FUTURE STUDIES

4.1 Introduction

In this chapter, the conclusion of the main findings of the dissertation according to the aims, objectives, and hypotheses, along with the limitations, recommendations, and potential future studies are discussed. Recommendations based on the findings of this study as well as recommendations regarding necessary control measures to eliminate or reduce dermal metal exposure and surface contamination within the AM facility are made. Limitations of this study are addressed, and potential future studies are suggested.

4.2 Main findings

This study aimed to characterise virgin and used samples of a CO-538 alloy feedstock powder (CO-538) in terms of its particle size, shape, and elemental composition and assessed dermal exposure of AM operators as well as workplace surface contamination when CO-538 was used during powder bed fusion (PBF). The aims of this study were achieved through the completion of the following three objectives.

The first objective of this study was to perform static image analysis using the Malvern Morphologi G3 (Malvern Instruments Ltd, United Kingdom) and scanning electron microscopy (SEM) to establish the particle size distribution (PSD) and shape of the virgin and used CO-538 powder particles. The PSD was based on the Circle Equivalent (CE) diameter of each particle as measured by the Malvern Morphologi G3 (Chapter 3, Table 3-1). The median [d(0.5)] diameter and standard deviation of the virgin and used powder particles were $23.710 \pm 1.560 \mu\text{m}$ and $17.270 \pm 4.068 \mu\text{m}$ respectively. For virgin powder, 10% of the particles [d(0.1)] had diameters smaller than $4.844 \pm 4.909 \mu\text{m}$, and the powder contained no particles larger than $119.530 \mu\text{m}$. For the used powder, 10% of the particles had diameters smaller than $0.242 \pm 0.018 \mu\text{m}$, and the powders contained no particles larger than $111.250 \mu\text{m}$. A statistically significant difference ($p \leq 0.05$) was observed at d(0.1) between virgin and used powder with the used powder particles generally smaller than that of virgin powder particles based on the mean. SEM images (Chapter 3, Figure 3-1) along with circularity and convexity results of all particles as calculated by the Malvern Morphologi G3 software (Malvern Panalytical, 2021) (Chapter 3, Table 3-1) indicated that the CO-538 powder particles consisted of a mixture of spherical particles with smooth surfaces, and irregular particles with less smooth surfaces. Statistically significant differences ($p \leq 0.05$) were observed in the mean circularity and convexity of virgin and used powders, indicating that

the used powder particles were more irregularly shaped and less smooth-surfaced than that of virgin powder particles.

The second objective of this study was to utilise Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) to establish the elemental composition of the virgin and used CO-538 powders. Table 3-2 in Chapter 3 shows the ICP-OES analysis results of both the virgin and used powders. The composition percentage for each metal of virgin CO-538 powder followed a descending trend of Co (64.1%) > Cr (28.5%) > Mo (6.39%) > Fe (0.35%) > Ni (0.21%) > Mn (0.12%) > Al (0.06%). The same trend was found with the used CO-538 powder of Co (65%) > Cr (28.7%) > Mo (4.97%) > Fe (0.57%) > Ni (0.21%) > Mn (0.12%) > Al (<0.05%). The elemental composition as detected by ICP-OES, corresponded with the percentage ranges as reported in the American Society for Testing and Materials (ASTM) standard and safety data sheet SDS of CO-538 except for Mo which was detected at slightly lower concentrations in the used powder sample (ASTM, 2019; Praxair Surface Technologies, 2015). The SDS, however, failed to report the presence of metals such as Mn, Fe, Ni, and Al which were detected through ICP-OES.

The third objective of this study was to utilise a removal wipe sampling method using Ghostwipes™ to assess dermal exposure of AM operators as well as contamination of workplace surfaces when a CO-538 alloy powder was used during AM. All workplace surfaces in AM and non-AM areas had measurable concentrations of metals ($0.106 \mu\text{g}/\text{cm}^2$ - $19.695 \mu\text{g}/\text{cm}^2$) detected during wipe sampling. Similarly, measurable concentrations of Co, Cr, Mo, Fe, Ni, Mn, and Al were detected on all the anatomical areas and removed by wipe sampling after each of the processing phases. Statistically significant differences ($p \leq 0.05$) were found between the total metal concentrations detected after the processing and post-processing phases on the back of the hand, wrist and neck, indicating that concentrations were significantly higher during the post-processing phase when compared to the processing phase. The anatomical area with the highest GM total metal exposure during all the processing phases was the finger with $2.884 \mu\text{g}/\text{cm}^2$ (CI: 0.889 - $9.359 \mu\text{g}/\text{cm}^2$) during the pre-processing phase, $0.735 \mu\text{g}/\text{cm}^2$ (CI: 0.206 - $2.623 \mu\text{g}/\text{cm}^2$) during the processing phase and $3.160 \mu\text{g}/\text{cm}^2$ (CI: 0.703 - $14.210 \mu\text{g}/\text{cm}^2$) during the post-processing phase. The lowest total metal exposure was found on the neck during the pre-processing phase with $0.271 \mu\text{g}/\text{cm}^2$ (CI: 0.125 - $0.586 \mu\text{g}/\text{cm}^2$) and post-processing phase with $0.717 \mu\text{g}/\text{cm}^2$ (CI: 0.306 - $1.679 \mu\text{g}/\text{cm}^2$), however, during the processing phase the lowest total metal concentration was found on the back of the hand with $0.145 \mu\text{g}/\text{cm}^2$ (CI: 0.080 - $0.264 \mu\text{g}/\text{cm}^2$).

Three hypotheses were postulated for this study. The first hypothesis states that the SDS of CO-538 does not provide comprehensive information regarding particle size and elemental composition which is essential to evaluate the potential risk of dermal exposure and the health of

AM operators. This study found that the SDS for CO-538 contained no information on the particle size and only limited information regarding the elemental composition. The elemental composition for Co, Cr, and Mo of the virgin powder sample, corresponded with the information given in the SDS of CO-538. However, the SDS failed to report the presence of metals such as Mn, Fe, Ni, and Al which were detected through ICP-OES analysis (Praxair Surface Technologies, 2015). The first hypothesis of this study is, therefore, accepted.

The second hypothesis of this study states that measurable concentrations of metals are detected on dermal surfaces such as the wrist, palm, back of the hand, finger, and neck, with the highest total metal concentrations detected during the pre- and post-processing phases when the majority of manual handling activities take place. Measurable concentrations of metals were detected on all the anatomical areas during all the processing phases ranging from a GM (and 95% lower and upper CI) of 0.145 $\mu\text{g}/\text{cm}^2$ (CI: 0.080-0.264 $\mu\text{g}/\text{cm}^2$) on the back of the hand during the processing phase to 3.160 $\mu\text{g}/\text{cm}^2$ (CI: 0.703-14.210 $\mu\text{g}/\text{cm}^2$) on the finger during the post-processing phase. Statistically, significantly ($p \leq 0.05$) higher total metal concentrations were detected on the back of the hand, wrist, and neck during the post-processing phase when compared to the processing phase (Chapter 3, Figure 3-2). The total metal concentrations during the pre-processing phase did, however, not differ significantly from the concentrations during the other processing phases. This may be due to fewer manual handling activities that were carried out during the pre-processing phase when compared to the post-processing phase. This hypothesis is, therefore, partially accepted.

The third hypothesis of this study states that measurable concentrations of total metals are detected on surfaces within the AM facility indicating surface contamination during the AM process. Measurable concentrations of metals were detected on all workplace surfaces that were sampled in the AM and non-AM areas of the AM facility. The total metal concentrations detected on the workplace surfaces ranged from 0.106 $\mu\text{g}/\text{cm}^2$ on the office desk of AM operator 2 in the non-AM area to 19.695 $\mu\text{g}/\text{cm}^2$ on workbench 1 in the AM area. The presence of metals indicates that these surfaces may act as secondary sources of exposure and that cross-contamination between AM and non-AM areas occurs. This hypothesis is, therefore, accepted.

4.3 Recommendations

In Chapter 3 it is indicated that the SDS of CO-538 provides no information regarding the particle size and insufficient information regarding the elemental composition (Praxair Surface Technologies, 2015). When insufficient information is provided in SDSs, AM operators may be unaware of the potential health risks associated with the use of the feedstock materials which may lead to a false sense of protection (du Preez *et al.*, 2018). It is, therefore, recommended

(Recommendation 1) that manufacturers of AM metal feedstock powders should provide SDSs that have more comprehensive and accurate information regarding particle size and elemental composition of the powders. Where the exact elemental composition proportion is confidential for commercial reasons, the proportions may be expressed as a percentage range of the element by mass or volume as permitted and required by the Regulations for Hazardous Chemical Agents (2021) as promulgated under the Occupational Health and Safety Act (Act 85 of 1993) and internationally recommended by the Globally Harmonised System of Classification and Labelling of Chemicals (GHS) (DOEL, 2022; UN, 2019).

The results of this study as described in Chapter 3, show measurable concentrations of metals being detected on all dermal and workplace surfaces. This highlights the need for improved control measures to be implemented at the AM facility to eliminate or reduce the dermal exposure of AM operators. Control measures should be implemented following the hierarchy of controls in the order of elimination, substitution, engineering controls, administrative controls, and personal protective equipment (PPE) (HSE, 2013). Recommendations regarding control measures are, therefore, made in the said order.

1. Elimination and substitution

Elimination and substitution of the CO-538 metal feedstock powder used at the AM facility are not viable since the CO-538 powder is chosen for the physico-chemical characteristics that make it ideal for producing end products with specific qualities.

2. Engineering controls

The results of this study indicate that the highest exposure concentrations were detected during the post-processing phase. These results are in line with that of Graff *et al* (2017) and Ljunggren *et al* (2019) who reported that particle emissions during PBF are the highest during the manual handling activities that generally form part of the pre- and post-processing phases. When particles become airborne, it can lead to respiratory exposure or dermal exposure when particles settle on the skin of AM operators or on surfaces within the workplace with which the AM operators come into contact. It is, therefore, recommended (Recommendation 2) that a Local Extraction Ventilation (LEV) system with a portable capture hood is used to capture particles that become airborne during manual handling activities.

In the AM facility investigated during this study, AM operators used compressed air to remove particles from sieves. When compressed air is used, the particles become suspended in the air which may lead to exposure via inhalation or dermal contact when particles settle on the skin of AM operators or on surfaces with which the AM operators come into contact. Furthermore, the Regulations for Hazardous Chemical Agents (2021) Subregulation 13, states that no person may, as far as reasonably practicable, use compressed air or permit the use of compressed air to

remove particles of a substance from any surface or person (DOEL, 2022). It is, therefore, recommended (Recommendation 3) that alternative cleaning methods such as vacuuming by using an intrinsically safe vacuum with a high-efficiency particulate absorbing (HEPA) filter, be used instead of compressed air. However, it is recommended that where cleaning by compressed air is essential, an isolation or extraction cabinet is implemented for this task and that compressed air is used only to clean equipment such as the sieves, and never used to remove the substances from the AM operators' skin or clothing.

3. Administrative controls

The Regulations for Hazardous Chemical Agents (2021), Subregulation 6 (a) requires that adequate washing facilities are provided to employees in order to maintain good personal hygiene, control of exposure and avoid the spread of contaminants (DOEL, 2022). It is, therefore, recommended (Recommendation 4) that AM operators are provided with adequate cleansers that can be used to wash their hands after exposure. Operators should be trained on the importance of good personal hygiene practices, and the importance of washing their hands especially before eating, to prevent inadvertent ingestion exposure.

The AM facility investigated in this study has no scheduled housekeeping routine, and the effects of a lack of housekeeping were evident in the high initial concentrations of metals ($0.002 \mu\text{g}/\text{cm}^2$ - $45.060 \mu\text{g}/\text{cm}^2$) that were detected on surfaces in the AM and non-AM areas within the AM facility. Since contaminated surfaces may act as a source of exposure, it is crucial that the exposure potential is reduced by using the correct cleaning methods (as discussed later in the paragraph) and by cleaning these surfaces at regular intervals. It is, therefore, recommended (Recommendation 5) that a weekly routine cleaning schedule is set up and implemented at the AM facility when all surfaces within the AM and non-AM areas are thoroughly cleaned. It is recommended that all surfaces within the AM area should be cleaned before and after each AM print, with a specific focus on the workplace surfaces that AM operators come into contact with the most. The surfaces that AM-operators come into contact with the most were identified in this study and are indicated in Chapter 3, Supplement information. Dry cleaning methods such as sweeping or wiping surfaces with a dry cloth can cause particles to become suspended in the workplace air. It is, therefore, recommended (Recommendation 6) that cleaning methods such as using an intrinsically safe vacuum with a HEPA filter, and wet cleaning methods such as wiping surfaces with a moistened cloth, are used.

The Regulations for Hazardous Chemical Agents (2021), Subregulation 3 (1) states that an employer should provide an employee, who may be exposed to a hazardous substance, with suitable and sufficient information, instruction, and training at suitable intervals (DOEL, 2022). It

is, therefore, recommended (Recommendation 7) that all AM operators receive suitable and sufficient training at regular intervals on topics as stated in Subregulation 3 (2). This should include but is not limited to information on the substances with which the AM operators may work, including where it may be found, the risks associated with exposure, the information provided in SDSs, and the legislated OELs that are in place. Furthermore, information, training, and instruction, in the form of written standard operating procedures (SOPs), on the required PPE and the correct use thereof, the control measures that are in place, and precautions that should be taken, as well as good housekeeping practices, should be developed and implemented. It is also important that training is provided regarding the need for engineering controls, how it is used, and how to maintain them, especially when new controls such as LEV systems which are recommended in this study, are implemented (DOEL, 2022).

The Regulations for Hazardous Chemical Agents (2021), Section 12 states that an employer must ensure that (a) all control equipment and facilities are maintained in good working order, and (b) that engineering control measures are thoroughly examined and tested by an approved inspection authority at intervals not exceeding 24 months (DOEL, 2022). It is, therefore, recommended (Recommendation 8) that the LEV system is maintained in a good condition and inspected at required intervals. This can be achieved by implementing a maintenance and inspection plan and by reporting defects and having them repaired in a timely manner.

4. PPE

PPE available to the AM operators at the AM facility investigated in this study includes full-face respirators that cover the eyes, nose, and mouth, with reusable filtering face piece 3 (FFP3) particulate filters as well as standard disposable nitrile gloves and laboratory coats. During all pre- and post-processing phases both AM operators wore respirators, but nitrile gloves were worn inconsistently depending on the AM operator and the activity being carried out. During the processing phase, no PPE was worn by either of the AM operators and laboratory coats weren't worn during any of the processing phases. The results of dermal wipe sampling indicate that all dermal surfaces that were sampled in this study (wrist, palm, back of the hand, index finger, and neck) had measurable concentrations of metals and that the highest concentrations were detected on the hands of AM operators. It is, therefore, recommended (Recommendation 9) that comprehensive SOPs regarding the use of PPE are developed and implemented at the AM facility. These SOPs should include that AM operators wear all recommended PPE whenever they enter the AM area. Furthermore, it is recommended (Recommendation 10) that PPE signage is displayed at the entrance to the AM area to indicate that gloves and respiratory protection must be worn when entering the area.

Incorrect storage procedures of PPE such as laboratory coats and respirators were observed at the AM facility. Laboratory coats were stored within the AM area and respirators were removed as operators exited the AM area, and placed on open surfaces within the non-AM area. Not only can this lead to contamination of surfaces in the non-AM area, but it can also lead to contamination of the inside of the respirator. When respirators are contaminated on the inside, AM operators may be exposed when they wear the contaminated PPE. It is, therefore, recommended (Recommendation 11) that PPE is stored in non-AM areas with separate dedicated containers/facilities for clean and contaminated PPE. It is also recommended (Recommendation 12) that reusable PPE such as laboratory coats and respirators are cleaned in accordance with the product's user instructions at regular intervals to minimise further contamination (DOEL, 2022). Respirators and filters should also be inspected at regular intervals, preferably before each use to ensure that the product is in good working condition and that damaged or deteriorated parts are repaired or replaced before use.

It was observed that nitrile gloves tore on several occasions during the post-processing phase when AM operators removed the manufactured product from the AM machine. Torn gloves were removed, and a new pair of gloves were donned on potentially already exposed hands. It is, therefore, recommended (Recommendation 13) that AM operators wash their hands each time before putting on a new pair of gloves. It is also recommended (Recommendation 14) that gloves such as chemical-resistant Uvex U-Chem 3200 (Uvex, 2022a) or Uvex Profapren gloves (Uvex, 2022b) which are less prone to tearing are used during post-processing activities where AM operators remove sharp surfaced products from the AM machine.

4.4 Limitations

The following limitations were identified in this study.

1. Only two AM operators are required to work at the investigated AM facility and, therefore, the study was limited by the small sample size.
2. While a large number of samples were collected, samples of the same processing phases weren't divided equally between the AM operators. Due to the limited number of AM operators available to participate in this study and the data not being distributed equally between the AM operators, not enough data was available to study the variability in dermal exposure between operators during the different processing phases.
3. AM operators did not stay in the AM area for the full duration of the AM process. Operators would leave once the processing phase commenced, only returning periodically until the end of their shifts. Since AM operators often finished their shift whilst the processing phase was still in progress, samples had to be taken before AM operators left work. The periods that AM operators were present during the processing phase, therefore, differed significantly from day

to day. Although these factors limited the study, the results are representative of their real-world workplace exposure.

4. While dermal wipe sampling is good method to determine exposure, the results only indicate the exposure concentration detected on an anatomical area at the time of sampling (ISO/TR, 2011), and does not indicate the concentration of the substance that could have already penetrated into the skin.

4.5 Future studies

The following potential future studies were identified in this study:

1. After the implementation of recommendations regarding control measures have been completed, a follow-up study could assess dermal exposure and surface contamination to determine the effectiveness of the implemented control measures.
2. A future study where a larger number of AM operators working with metal AM are included, could be conducted to investigate the variability in dermal exposure among AM operators and/or the variability in exposure at different AM facilities.
3. A further investigation into exposure via different exposure routes including dermal, inhalation, and ingestion when the CO-538 powder is used during PBF with simultaneous biological monitoring for metals such as Co, Cr, and Ni could be conducted to determine the correlation between exposure and systemic uptake of the metals in AM operators.

4.6 References

ASTM (American Society for Testing Materials) International. (2019) F75 – 18. Standard Specification for Cobalt-28 Chromium-6 Molybdenum Alloy Castings and Casting Alloy for Surgical Implants (UNS R30075)¹. West Conshohocken, PA: ASTM.

DOEL (Department of Employment and Labour). (2022) Occupational health and safety act no 85 of 1993 and regulations. 23rd rev ed. Johannesburg, South-Africa: LexisNexis. ISBN: 978 1 776 17555 0.

du Preez S, de Beer DJ, du Plessis JL. (2018) Titanium powders used in powder bed fusion: their relevance to respiratory health. *South African J. Ind. Eng;* 29: 94-102.

Graff P, Stahlbom B, Nordenberg E, Graichen A, Johansson P, Karlsson H. (2017) Evaluating measuring techniques for occupational exposure during additive manufacturing of metals. *J. Ind. Ecol;* 21: 120-129.

Health and Safety Executive (HSE). 2013. Control of substances hazardous to health. The control of substances hazardous to health regulations 2002 (as amended). Approved code of

practice and guidance. 6th ed. Available from: <https://www.hse.gov.uk/pubns/priced/l5.pdf> (accessed 7 Feb 2021).

Ljunggren SA, Karlsson H, Ståhlbom B, Krapf B, Fornander L, Karlsson LE, Bergström B, Nordenberg E, Ervik TK, Graff P. (2019) Biomonitoring of metal exposure during additive manufacturing (3D printing). *Saf Health Work*; 10: 518-526.

Praxair Surface Technologies. 2015. Safety data sheet CO-538 products. Available from <https://www.praxairsurfacetechologies.com/-/media/corporate/praxairsurface/us/documents/sds/powders/co/co538s.pdf?la=en> (accessed 14 Oct 2021). p. 1-11.

UN (United Nations). (2019) ST/SG/AC.10/30/Rev.8. Globally harmonized system of classification and labelling of chemicals (GHS). 8th revised ed. New York: United Nations. ISBN: 978-92-1-117199-0.

Uvex. (2022a) Product data sheet for uvex profapren. Available from https://d3nan4w00fsv2d.cloudfront.net/DATASHEET/60119_PDB_EN.pdf (accessed 8 Sept 2022).

Uvex. (2022b) Product data sheet for uvex u-chem 3200. Available from https://d3nan4w00fsv2d.cloudfront.net/DATASHEET/60972_PDB_EN.pdf (accessed 8 Sept 2022).

ANNEXURE A: ETHICS APPROVAL LETTER



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studies)

20 June 2021

ETHICS APPROVAL LETTER OF STUDY

Based on approval by the North-West University Health Research Ethics Committee (NWU-HREC) on 20/06/2021, the NWU-HREC hereby approves your study as indicated below. This implies that the NWU-HREC grants its permission that, provided the general conditions specified below are met and pending any other authorisation that may be necessary, the study may be initiated, using the ethics number below.

| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|--|---|----------------|--------------|---|---|---|---|------|---|---|--------|---|---|---|---|---|-------------|--|--|--------------|--|--|--|--|------|--|--|--------|--|--|
| Study title: Dermal exposure and surface contamination associated with the use of cobalt-chrome alloys during additive manufacturing | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Principal Investigator/Study Supervisor/Researcher: Dr S du Preez | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Student: LM Paulse - 27022870 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Ethics number: | <table border="1"><tr><td>N</td><td>W</td><td>U</td><td>-</td><td>0</td><td>0</td><td>1</td><td>5</td><td>2</td><td>-</td><td>2</td><td>1</td><td>-</td><td>A</td><td>1</td></tr><tr><td colspan="3">Institution</td><td colspan="5">Study Number</td><td colspan="3">Year</td><td colspan="3">Status</td></tr></table> | N | W | U | - | 0 | 0 | 1 | 5 | 2 | - | 2 | 1 | - | A | 1 | Institution | | | Study Number | | | | | Year | | | Status | | |
| N | W | U | - | 0 | 0 | 1 | 5 | 2 | - | 2 | 1 | - | A | 1 | | | | | | | | | | | | | | | | |
| Institution | | | Study Number | | | | | Year | | | Status | | | | | | | | | | | | | | | | | | | |
| <u>Status:</u> S = Submission; R = Re-Submission; P = Provisional Authorisation; A = Authorisation | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Application Type: Single study | Risk: <table border="1"><tr><td>Minimal</td></tr></table> | Minimal | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Minimal | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Commencement date: 20/06/2021 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Expiry date: 30/06/2022 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Approval of the study is provided for a year, after which continuation of the study is dependent on receipt and review of an annual monitoring report and the concomitant issuing of a letter of continuation. A monitoring report is due at the end of June annually until completion. | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |

| |
|--|
| General conditions: |
| <i>While this ethics approval is subject to all declarations, undertakings and agreements incorporated and signed in the application form, the following general terms and conditions will apply:</i> |
| <ul style="list-style-type: none">• <i>The principal investigator/study supervisor/researcher must report in the prescribed format to the NWU-HREC:</i><ul style="list-style-type: none">- <i>annually on the monitoring of the study, whereby a letter of continuation will be provided annually, and upon completion of the study; and</i>- <i>without any delay in case of any adverse event or incident (or any matter that interrupts sound ethical principles) during the course of the study.</i>• <i>The approval applies strictly to the proposal as stipulated in the application form. Should any amendments to the proposal be deemed necessary during the course of the study, the principal investigator/study supervisor/researcher must apply for approval of these amendments at the NWU-HREC, prior to implementation. Should there be any deviations from the study proposal without the necessary approval of such amendments, the ethics approval is immediately and automatically forfeited.</i>• <i>Annually a number of studies may be randomly selected for active monitoring.</i>• <i>The date of approval indicates the first date that the study may be started.</i>• <i>In the interest of ethical responsibility, the NWU-HREC reserves the right to:</i><ul style="list-style-type: none">- <i>request access to any information or data at any time during the course or after completion of the study;</i>- <i>to ask further questions, seek additional information, require further modification or monitor the conduct of your research or the informed consent process;</i> |

- *withdraw or postpone approval if:*
 - *any unethical principles or practices of the study are revealed or suspected;*
 - *it becomes apparent that any relevant information was withheld from the NWU-HREC or that information has been false or misrepresented;*
 - *submission of the annual monitoring report, the required amendments, or reporting of adverse events or incidents was not done in a timely manner and accurately; and/or*
 - *new institutional rules, national legislation or international conventions deem it necessary.*
- *NWU-HREC can be contacted for further information via Ethics-HRECApply@nwu.ac.za or 018 299 1206*

Special conditions of the research approval due to the COVID-19 pandemic:

Please note: Due to the nature of the study i.e. (physical sampling (wipes) of surfaces and the skin of employees within additive manufacturing entities situated on university campuses), this study will be able to proceed during the current alert level, following receipt of the approval letter. No additional COVID-19 restrictions have been placed on the study, other than those as indicated under the COVID-19 risk mitigation strategy indicated by the researchers. In addition, the researcher must ensure that before proceeding with the study that all research team members have reviewed the North-West University COVID-19 Occupational Health and Safety Standard Operating Procedure.

The NWU-HREC would like to remain at your service and wishes you well with your study. Please do not hesitate to contact the NWU-HREC for any further enquiries or requests for assistance.

Yours sincerely,



Digitally signed by
Prof Petra Bester
Date: 2021.06.22
12:21:46 +02'00'

Chairperson NWU-HREC

Current details:(23239522) G:\My Drive\9. Research and Postgraduate Education\9.1.5.4 Templates\9.1.5.4.2_NWU-HREC_EAL.docm
20 August 2019
File Reference: 9.1.5.4.2

ANNEXURE B: LANGUAGE EDITTING



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28 November 2022

LANGUAGE EDITING STATEMENT

I, Jannetje Levina De Kock hereby declare that the thesis

Dermal exposure and surface contamination associated with the use of a cobalt-chrome alloy during additive manufacturing

by

L. Paulse

Student Number: 27022870

for submission to the NWU

in the Niche area Occupational Hygiene and Health Research Initiative (OHHRI)

- has been edited for language correctness and spelling.
- has been edited for consistency (repetition, long sentences, logical flow)

No changes have been made to the document's substance and structure (nature of academic content and argument in the discipline, chapter and section structure and headings, order, and balance of content, referencing style, and quality).

J L DE KOCK