



Emissions of and exposure to hazardous chemical substances from selected additive manufacturing technologies

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¹¹ For I know the plans I have for you, declares the Lord, “plans to prosper you and not to harm you, plans to give you hope and a future”.

Jeremiah 29:11

¹¹ Ek weet wat Ek vir julle beplan, sê die Here: “voorspoed en nie teenspoed nie; Ek wil vir julle ‘n toekoms gee, ‘n verwagting”.

Jeremia 29:11

“In the middle of difficulty lies opportunity.”

Albert Einstein

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ABSTRACT

Title:

Emissions of and exposure to hazardous chemical substances from selected additive manufacturing technologies.

Background:

Additive Manufacturing (AM) is the process of joining feedstock materials one layer at a time in order to produce objects from a three dimensional (3D) computer aided design (CAD). Powder bed fusion (PBF) and direct energy deposition (DED) are two widely applied powder based metal AM processes used commercially in the South African AM industry. A number of studies have investigated small desktop polymer material extrusion fused deposition modelling (FDM™) 3D printers and found that these printers are high emitters of particulate matter and volatile organic compounds. Chamber studies have been of value by contributing to a better understanding of emissions from FDM™ desktop printers. However, despite the numerous studies on particulate matter emissions from desktop FDM™ printers there is an unbridged gap to identify the hazardous chemical substance emissions from and the respiratory exposure of AM operators when utilising metal powders in AM. AM processes takes place in three distinct phases, namely the pre-processing, processing and post-processing phases, and occupational exposure may occur during each of these three phases since most tasks are manually performed by the AM operator. To date only one study has investigated particle emissions from and exposure to metals during PBF while there is no published literature on emissions or exposure from DED. PBF and DED are applied in South Africa and therefore, the investigation of particle emissions from and personal exposure of AM operators to hazardous chemical substances (metals) is needed.

Aims and objectives:

The general research aim of this thesis was to assess the emissions of and occupational exposure to hazardous chemical substances (particles and metals) associated with two metal powder based AM process categories (powder bed fusion and direct energy deposition) at three South African institutions utilising AM. The specific objectives were: (i) to establish the physico-chemical characteristics (particle size, shape and elemental composition) of virgin and used metal powders, used during powder bed fusion and direct energy deposition, and the relevance thereof to AM operators' health. (ii) to assess particle emissions and respiratory metal exposure of AM operators when using three titanium powders and maraging steel during the pre-

processing, processing and post-processing phases of AM at three AM facilities utilising PBF. (iii) to assess particle emissions and respiratory metal exposure of AM operators when using two stainless steel powders during DED at an AM facility.

Methods:

Samples of virgin and used (recycled) titanium and maraging steel as well as used stainless steel powders, along with their respective safety data sheets (SDSs) were collected from three AM facilities in South Africa utilising PBF and DED. Powder samples were characterised in terms of particle size distribution (PSD), particle shape and elemental composition. Real time monitoring devices, namely a Condensation Particle Counter (0.01 to $> 1 \mu\text{m}$) and an Airborne Particle Counter (0.30 to $10.00 \mu\text{m}$) were used to investigate particle emissions [particle number concentrations (p/m^3)] during PBF and DED process phases. The concentration of metals in the workplace air was established by means of static area monitoring according to the National Institute for Occupational Safety and Health (NIOSH) 7300 method using a closed-faced cassette (CFC). Personal (AM operator) respiratory exposure to metals used the same NIOSH method. Ethics approval for this study was obtained from the Health Research Ethics Committee of the North-West University (NWU-00004-16-A1). Researchers followed well known occupational hygiene methods, and other state of the art methods not currently used in occupational hygiene compliance monitoring. Personal exposure to metals $< 300 \text{ nm}$ in size was assessed by using a nanoparticle respiratory deposition sampler.

Results:

Only one of the three titanium powders PSD was in accordance with the SDS. From the SEM images, thoracic sized ($< 10 \mu\text{m}$) and respirable sized ($< 4 \mu\text{m}$) particles were observed in powders from all three facilities. The elemental composition analysis (XRD analysis) of the investigated powders differed from the composition stated in the respective SDSs. Particles $\leq 1 \mu\text{m}$ were present in the workplace air. Increases in particle number concentrations were observed during specific pre- and post-processing tasks such as cleaning and powder sieving which led to an increase in particle emissions with the highest particle number concentration of $6.12 \times 10^{10} \text{ p}/\text{m}^3$ (0.01 to $> 1 \mu\text{m}$) measured during the post-processing phase of PBF with titanium. Tasks such as unloading of the AM machines led to particle concentrations (0.01 to $> 1 \mu\text{m}$) as high as $5.98 \times 10^{10} \text{ p}/\text{m}^3$ during PBF with maraging steel and $5.75 \times 10^{10} \text{ p}/\text{m}^3$ during DED of stainless steel. Static area monitoring indicated low concentrations of metals in the workplace atmosphere during PBF and DED. During both PBF and DED, AM operators were exposed to detectable concentrations of metals including aluminium, chromium, copper, iron,

nickel, titanium and vanadium, including metals < 300 nm in size. Full shift metal exposure was calculated for comparisons with occupational exposure limits (OELs) of all detected metals. AM operators' personal respiratory exposure was < 1.04% of the time weighted average OELs (TWA-OELs) when using titanium powders, and < 3.60% of the respective TWA-OELs and < 9.01% of threshold limit value (TLVs®) during the use of maraging steel. Exposure to Ni, a human carcinogen, was the highest.

Conclusion:

There is a shortage of studies reporting particle emissions from and AM operators' respiratory exposure to metals resulting from use of titanium and metals powders used in PBF and DED. Inadequate information in the SDSs may mislead employers and AM operators' regarding the protection of AM operator health, and therefore, powder characterisation should form an integral part of risk assessments at each facility. During the pre-and post-processing phases of PBF and DED, particles were emitted during phase specific tasks such as cleaning, sieving, and unloading of the AM machine. When particle number concentrations during the processing phase from PBF and DED were compared to FDM™ printers, it was found that particle number concentrations emitted from FDMs™ were approximately five to nine times higher. The maximum particle number concentrations emitted from DED were 3% lower than that of PBF. Low concentrations of metals were present in the workplace atmosphere throughout the use of titanium, maraging steel and stainless steel powders. Although no OELs were exceeded, AM operators were exposed to detectable concentrations of metals, including metals < 300 nm in size. The findings of this study serve as a starting point to create awareness of AM operator exposure associated with metal AM, and to assist industrial AM facilities in identifying hazards and implementing phase and task specific control measures during PBF and DED using titanium powders and metal powders. Eleven recommendations are made for the attention of all role players including AM powder manufacturers/suppliers, employers (AM facilities) and AM operators/employees in an effort to reduce particle emissions from and AM operator's respiratory exposure to metals. Along with the recommendations, specific limitations experienced during the study were also identified along with recommendations for future studies.

Keywords:

particle characterisation, particle number concentration, respiratory exposure, titanium, powder bed fusion, direct energy deposition, metals.

PREFACE

This thesis is submitted in article format and written according to the requirements of the North-West University's Manual for Postgraduate Studies and conforms to the requirements preferred by the appropriate journals. The thesis is written according to United Kingdom English spelling, with the exception of institutional names and references that were used as is. The following three articles are included in this thesis:

- ⌘ Article I: Titanium powders used in Powder Bed Fusion: Its relevance to respiratory health.
- ⌘ Article II: Particle emissions and metal exposure during Powder Bed Fusion Additive Manufacturing using titanium powders.
- ⌘ Article III: Particle emission from and exposure to metals during Powder Bed Fusion and Direct Energy Deposition additive manufacturing using maraging steel and stainless steel powders.

For uniformity, the reference style required by *The Journal of Occupational and Environmental Hygiene* is used throughout the thesis, with the exception of Chapter 3 that is written according to the guidelines of *The South African Journal of Industrial Engineering*. Details on the requirements of the reference style can be found at the beginning of Chapters 3, 4 and 5 of this thesis.

The contributions of the listed co-authors and their consent for use in this thesis are given in Table 1. The relevant editors or publishers granted permission for the use of the published material, and proof is provided in Appendix A-C.

Table 1: Contributions of the different authors and consent for use.

Author	Contribution of co-author	Consent*
S. du Preez	Responsible for the planning of the study design and the data collection. Responsible for data collection by performing exposure monitoring studies at the respective additive manufacturing facilities. Responsible to data analysis and interpretation of the results. First author of the articles included in Chapters 3 - 5. Responsible for writing the thesis.	
Prof. J.L. du Plessis	As Promoter, supervised the design and planning of the study as well as the data collection and the writing of the thesis. Provided intellectual input on statistical analysis, interpretation of data and the writing of articles and the thesis.	
Prof. D.J. de Beer	As Co-promoter, supervised the design and planning of the study as well as the data collection and the writing of the thesis. Secured the funding for the study as well as the participation of the respective Additive Manufacturing facilities.	

*I declare that I have approved the chapter/article(s) and that my role in the study as indicated above is representative of my actual contribution, and that I hereby give my consent that it may be published as part of the thesis of Mrs. S du Preez.

The outline of the thesis is as follows:

- ⌘ Chapter 1 - General introduction with background, research aims and objectives, and hypotheses.
- ⌘ Chapter 2 - A literature study on topics relevant to this thesis.
- ⌘ Chapter 3 - Article I entitled: Titanium powders used in Powder Bed Fusion: Its relevance to respiratory health, accepted for publication in *The South African Journal of Industrial Engineering*.
- ⌘ Chapter 4 - Article II entitled: Particle emissions and metal exposure during Powder Bed Fusion Additive Manufacturing using titanium powders, submitted to *The Journal of Occupational and Environmental Hygiene*, to be considered for publication.
- ⌘ Chapter 5 - Article III entitled: Particle emission from and exposure to metals during Powder Bed Fusion and Direct Energy Deposition additive manufacturing using maraging steel and stainless steel powders, prepared for submission to *The Journal of Occupational and Environmental Hygiene*, to be considered for publication.
- ⌘ Chapter 6 - A summary of the main findings of the study is provided and conclusions are drawn. Additionally, recommendations are made, and the limitations of the study as well as recommendations for future studies are provided.
- ⌘ Appendix A: Permission to use copyright material.
- ⌘ Appendix B: Proof of acceptance of article I to the respective scientific journal.
- ⌘ Appendix C: Proof of submission of article II to the respective scientific journal.
- ⌘ Appendix D: Declaration of language editing.
- ⌘ Appendix E : Ethics certificate

The project forms part of the Qualification of Additive Manufacturing of Ti₆Al₄V for Medical Implants and Aerospace Components. This project is funded by the Department of Science and Technology (DST) with the focus area being additive manufacturing of titanium.

“Any opinion, finding, conclusion and recommendation expressed in this material is that of the author(s), and the DST does not accept any liability in this regard.”

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LIST OF UNITS

%	percentage
<	less than
>	greater than
≤	less or equal than
≥	greater or equal than
±	plus-minus
μg	micrograms
μg/m ³	microgram per cubic metre
μm	micrometre
kV	kilovolt
ℓ/min	litres per minute
m	meter
m ³	cubic metre
ml	millilitre
mg	milligrams
mg/m ³	milligram per cubic metre
mm	millimetre
mm ³	cubic millimetre
p/min	parts per minute
p/cm ³	parts per cubic centimetre
p/m ³	parts per cubic metre
ppb	parts per billion
ppm	parts per million
α	Alpha
β	Beta
n	number
nm	nanometre
™	trademark
®	registered

LIST OF ABBREVIATIONS

3D	three dimensional
ABS	acrylonitrile butadiene styrene
ACGIH	American Conference of Governmental Industrial Hygienists
Al	aluminium
AM	Additive Manufacturing
ANOVA	analysis of variance
APC	Airborne Particle Counter
ASTM	American Society of Testing and Materials
BDL	below the limit of detection
CAD	computer aided design
CFC	closed-faced cassette
Co	cobalt
CoCr	cobalt-chrome
CPC	Condensation Particle Counter
CP	co-polyester
Cr	chromium
Cr(III)	trivalent chromium
Cr(VI)	hexavalent chromium
Cu	copper
DED	direct energy deposition
DL	detection limit
DM	direct manufacturing
DMD	direct metal deposition
DMLS	direct metal laser sintering
DOL	department of labour
EBM	electron beam melting
ELPI	electrical low-pressure impactor
<i>et al.</i>	<i>et alii</i> (and others)
FDM™	fused deposition modelling
Fe	iron
FFP	filtering face piece
HCS	hazardous chemical substances
HCSR	hazardous chemical substances regulations
HIPS	high-impact polystyrene

LIST OF ABBREVIATIONS CONTINUED

IARC	International Agency for Research on Cancer
ICP-MS	inductively coupled plasma-mass spectrometry
i.e.	that is to say/in other words
Inc.	incorporated
ISO	International Standards Organisation
LBAM	laser based additive manufacturing
LENS	laser engineered net shaping
LOM	laminated object manufacturing
Ltd.	limited company
Mn	manganese
Mo	molybdenum
Ni	nickel
NIOSH	National Institute for Occupational Safety and Health
NP	nanoparticles
NRD	Nanoparticle Respiratory Deposition
OELs	occupational exposure limits
OEL-CL	occupational exposure limit – control limit
OEL-RL	occupational exposure limit – recommended limit
OSHA	Occupational Safety and Health Association
PAHs	polycyclic aromatic hydrocarbons
PBF	powder bed fusion
PC	polycarbonates
PCTPE	plasticized copolyamide thermoplastic
Pty	proprietary company
PET	polyethylene terephthalate
PLA	poly lactic acid
PMMA	polymethylmethacrylate
PPE	personal protective equipment
PSD	particle size distribution
PVA	polyvinyl alcohol
PVC	polyvinyl chloride
RAPDASA	Rapid Prototyping Product Development Association of South Africa
SANAS	South African National Accreditation System
SDS	safety data sheet
SEM	scanning electron microscopy
SLM	selective laser melting

LIST OF ABBREVIATIONS CONTINUED

SHS	selective heat sintering
SLS	selection laser sintering
SMPS	scanning mobility particle sizer
SMD	shaped metal deposition
Sn	tin
STL	stereolithography
TEM	transmission electron microscopy
Ti	titanium
TiO ₂	titanium dioxide
TLV [®]	threshold limit value
TVOCs	total volatile organic compounds
TWA	time-weighted average
UAM	Ultrasonic additive manufacturing
UFPs	ultrafine particles
UC	ultrasonic consolidation
UV	ultraviolet
V	vanadium
VDV	veiligheidsdatavel
VOCs	volatile organic compounds
WAAM	wire and arc additive manufacturing
WC	tungsten carbide
XRD	X-Ray diffraction

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Chapter 1: GENERAL INTRODUCTION

1.1 Introduction

Additive Manufacturing (AM) refers to different technologies in which three dimensional (3D) computer aided design (CAD) modelling is used to design objects where after 3D-objects are built layer-by-layer at a time by adding feedstock materials.^[1,2] According to internationally standardised terminology, there are seven standard AM process categories with prominent technologies within each process category. The seven standard process categories are powder bed fusion (PBF), direct energy deposition (DED), binder jetting, material jetting, vat photopolymerisation, material extrusion and sheet lamination. AM feedstock can be in the form of liquid, powder, or solid materials. Powder is the only feedstock material that can be recycled and reused, creating a powder blend consisting of virgin (new/unused) powder and used (recycled) powder.^[3]

AM permits the production of objects, which are difficult or even impossible to produce, using any other manufacturing method. This includes aerospace and automotive parts, customised medical implants, electronics, jewellery, toys and textiles.^[4,5] AM has also led to unanticipated product developments such as the production of concrete, furniture, food, and the rapidly emerging field of bioprinting.^[6] AM has become a leading manufacturing technology, with many leading global organisations now successfully applying AM technology for producing both industrial and consumer products and is also being applied in universities' engineering and design programmes.^[5,7] At present AM is considered to be the core technology for future development and is therefore, referred to as the "third industrial revolution".^[5,6]

Each AM process consists, in most instances, of three phases, namely pre-processing, processing and post processing phases. AM, as with any other machine operated process, requires routine or intermittent interactions between the operator and the AM machine, feedstock material, and the part being built. The first study to suggest that further research is needed to investigate the toxicity of materials used in AM was in 2006 by Drizo and Pegna.^[8] According to Drizo and Pegna^[8] this fast paced industry does not leave sufficient time for material testing or enough time to compile a database of materials used in AM. The physical size and chemical composition of AM powder are important primary considerations for the respiratory health of AM operators. The particle size of feedstock powders determines whether particles are inhaled, and if inhalable where it may be deposited in the respiratory tract.^[9,10] The

chemical composition of powder particles is important when investigating possible health effects as each metal constituent of AM powders may potentially pose a different respiratory health hazard.^[11] Safety data sheets (SDSs) previously referred to as material safety data sheets, provided with substances hazardous to health, are fundamental in evaluating the health and safety of a workplace.^[12] However, in a study of recycled Inconel 939 alloy powder Mellin *et al.*^[13] emphasised that the SDSs (as provided by the manufacturer/supplier) disclosed minimal information on the size of powder particles and in another paper Slotwinski and Garboczi^[14] reported that there is a need for proper characterisation of metal powders including size, shape and composition of AM powders.

Back in 1999 the safe work practices of AM were first mentioned as a necessity for AM work environments.^[15] This was followed by three studies that were concerned with SDSs lack of coverage of standardised health protocols, as well as health and safety guidelines for operators during all phases of the AM process.^[16-18] Although AM significantly advanced as a technology, product quality has predominantly been the focus rather than the safety or the health of the operator.^[15,17,18] In 2012 concerns were raised about inhalation exposure to raw materials and additives, and powder deposits in the eyes and onto the skin during all three phases of AM.^[19] In 2013, Stephens *et al.*^[10] established that commercially available material extrusion type desktop fused deposition modelling (FDMTM) 3D printers emitted ultrafine particles (UFPs; i.e. particles < 100 nm). Since 2013 a number of studies, many in controlled environments (chamber studies) have been published investigating particle emissions from smaller desktop FDMTM printers.^[18,20-27] In short, these studies highlighted particulate (i.e. UFPs) and volatile organic compounds (VOCs) emissions during operation.^[25,26,28] Of the seven AM process categories, PBF is the most researched technology in terms of the feedstock materials used and technology development, however, research on emissions from, exposure of AM operators and potential health risks remains limited.^[17,18] This could be ascribed to the limited number of PBF machines in operation as well as the industrial size of the machines, limiting access to study emissions, but also preventing performing studies in a controlled environment (chamber studies). Of the two studies, Mellin *et al.*^[13] found small round respirable metal particles (1-2 μm) containing nickel, chromium and cobalt in recycled Inconel 939 powder. Graff *et al.*^[17] showed that < 300 nm particles were present in the AM workplace environment air and that AM operators were exposed to nickel, chromium and cobalt while handling an Inconel 939 powder. For DED there is no published literature on emissions or exposure.

Throughout all three phases of AM occupational exposure to hazardous chemical substances (HCS) in the form of powders, liquids, vapours and solid based materials may take place when tasks such as the loading of feedstock, sieving of materials and cleaning of machinery are carried out.^[16,17,29] It should also be taken into account that once AM metal powders are sintered during the processing phase, metal dust may be formed and emitted. HCS are defined as any toxic, harmful, corrosive, irritant or mixture of such substances that may or may not have an occupational exposure limit but creates a hazard to health.^[30] In this thesis HCS include any particulate matter (particles and metals).

To date various respiratory symptoms such as nasal congestion, rhinorrhoea, coughing, and itchiness of the nose, throat or eyes as experienced by AM operators have been reported.^[31] Furthermore, Johannes *et al.*^[32] confirmed that an AM operator was diagnosed with chronic hypersensitivity pneumonitis, while a study by House *et al.*^[33] concluded that an AM operator developed asthma while working with desktop FDM™ printers. Despite the expansion of AM worldwide and numerous studies on particulate matter emissions from desktop FDM™ printers, the need for further investigation on emissions from, exposure to, and health effects associated especially with powder based AM processes has been expressed.^[10,16,18,22,24] There is therefore, an unbridged gap to identify the emissions from and the personal exposure of AM operators to HCS, during all three AM phases of industrial AM processes. Three industrial AM facilities using AM metal powders have been identified as primary role players in AM in South Africa and for the purpose of this study will be referred to as Facility A, B, and C. Emphasis will be placed on PBF and DED given that these AM process categories are applied in South Africa.

Findings of this thesis will provide the South African AM industry with much needed information on particle emissions from metal AM processes, exposure levels of AM operators to HCS (particles and metals), and anticipated potential health effects of exposure. Ultimately, this will provide the industry with information and guidance to control particle emissions and operator exposure during every phase of metal powder based AM processes.

1.2 Research aim and objectives

1.2.1 General research aim:

The general research aim of this thesis is:

1. To assess the emissions of and occupational exposure to hazardous chemical substances (particles and metals) associated with two metal powder based AM process categories (powder bed fusion and direct energy deposition) at three South African institutions utilising AM.

1.2.2 Specific research objectives:

The specific research objectives of this thesis are:

1. To establish the physico-chemical characteristics (particle size, shape and elemental composition) of virgin and used metal powders, used during powder bed fusion and direct energy deposition, and the relevance thereof to AM operators' health.
2. To assess particle emissions and respiratory metal exposure of AM operators when using three titanium and maraging steel powders during the pre-processing, processing and post-processing phases of AM at three AM facilities utilising powder bed fusion.
3. To assess particle emissions and respiratory metal exposure of AM operators when using two stainless steel powders during direct energy deposition at an AM facility.

1.3 Hypotheses

The following hypotheses for this thesis are postulated:

The particle size and chemical composition of AM powders are of importance when considering the respiratory health of AM operators.^[11] Limited information in SDSs and failure to specify important information of a substance may cause AM operators to be unaware of the possible respiratory risks and unintentionally lead to a false sense of protection of the AM operators health.^[16,17,34]

- 1) It is therefore, hypothesised that there is inadequate information regarding particle size and elemental composition of AM powders in the SDS documents as supplied by the manufacturers/suppliers which places AM operators' health at risk.

There are numerous studies that have investigated the emissions (UFPs and VOCs) from smaller desktop FDM™ printers using acrylonitrile butadiene styrene (ABS) and poly lactic acid (PLA) filaments.^[18,20,21,23] There is, however, limited emission and exposure information available for AM process categories other than material extrusion, and currently less attention has been given to emissions from larger industrial AM machines using metal powders and exposure of AM machine operators.^[17,18,35] AM machines are designed to operate unattended, however, all powder handling is performed manually by the AM operator especially during the pre-processing and post-processing phases. Even though the processing phase is enclosed the AM operator may intermittently inspect the progress of the build during which metal dust may be emitted. To date there has only been one study by Graff *et al.*^[17] that has investigated both emissions from and personal exposure monitoring to metals during PBF. The authors reported that peak number concentration of approximately 16 000 p/cm³ (1.60×10^{10} p/m³) during post-processing while cleaning the AM machine and that AM operators were exposed to detectable levels of metals during different AM tasks. Furthermore there is no literature available on emissions from or exposure to HCS during DED.

- 2) Thus it is hypothesised that the mean particle number concentrations are the highest during the post-processing phase followed the pre-processing phase, with the lowest particle number concentrations during the processing phase of PBF.
- 3) It is also, hypothesised that there is respiratory exposure of AM operators to metals during all three process phases of PBF using titanium and maraging steel powders with the highest exposure during the post-processing phase followed by the pre-processing phase and the lowest exposure during the processing phase.
- 4) Finally, it is hypothesised that particles are emitted from and AM operators are exposed to metals during DED when using stainless steel.

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Chapter 2: LITERATURE STUDY

This chapter contains a discussion on the available scientific literature related to additive manufacturing (AM) process categories, feedstock materials, occupational exposure during AM and exposure routes. Firstly the definition of and relevant terminology used regarding AM are discussed, followed by a brief history of AM both internationally and in South Africa. This is followed by a classification of the AM process categories, description of technology types and AM feedstock materials. Emphasis is placed on powder bed fusion, direct energy deposition and metal feedstock materials used in these AM process types. From an occupational hygiene point of view, attention is given to particle emissions from AM process types and respiratory exposure of AM operators to metals specifically. To conclude this chapter a concise summary is given of the potential health effects and toxicity respectively associated with AM and AM feedstock materials.

2.1 Additive Manufacturing

Additive Manufacturing (AM) is a process which enables the joining of materials layer by layer to fabricate a three-dimensional (3D) part generated from a computer aided design (CAD).^[1-4] AM has become a multi-disciplinary application combining all facets of science including engineering, the biomedical field, chemistry, environmental sciences and occupational health and related sciences.^[5,6] The AM process is also known as rapid prototyping, additive fabrication, additive processes, additive layer manufacturing, freeform manufacturing and 3D printing.^[7] Initially, the term rapid prototyping was used to describe the process of rapidly creating an automated part before it became commercially available.^[8] As this technology developed and expanded in different industries, the American Society of Testing and Materials' (ASTM) International Committee F42 defined and accepted AM as the standard terminology.^[2] The term 3D printing is also used interchangeably with AM although it is more applicable to usage by the general public and is associated with machines that are lower in price and inferior capability.^[9,10]

In general, but depending on the AM process or technology, three different process phases are included namely pre-processing, processing and post-processing, covered by eight distinguished steps indicated schematically in Figure 1. A more detailed description of each of the three AM process phases and the potential occupational exposure during each phase is discussed in Section 2.7 of this chapter. All AM processes commence with the design of a 3D

model incorporating CAD software; this software presents the part's geometry. The designed 3D model is saved in a stereolithography (STL) file format which includes the CAD file and serves as the basis for the calculation of the slices of the part. Each slice represents one of the multiple layers of the designed part to be manufactured. This STL file is transferred to the AM machine and the AM machine is set up (prepared) by the AM operator prior to the build. The desired part is then created (built) by adding layers of feedstock material on top of each other until the part is completed. Depending on the type of process or technology and feedstock, several post-processing techniques/tasks such as sanding, grinding or machining of the part may be required to ultimately yield the final/finished part.^[11]

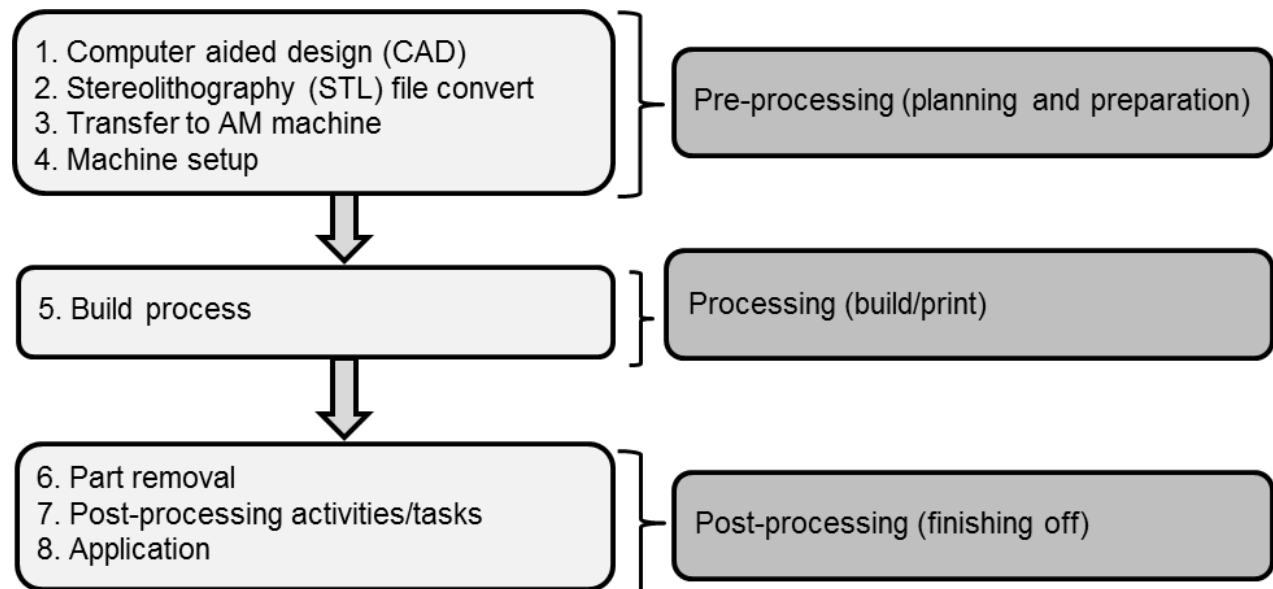


Figure 1: A schematic presentation of the eight generic AM steps. ^[11,12]

2.2 A brief history of AM

AM was launched in the 1980s with the first completed 3D part created by Charles Hull in 1983. In 1986 he co-founded a company called 3D Systems in South Carolina in the United States of America (USA). 3D Systems was the first company that commercialised AM and they sold their first machine in 1987. Ever since the establishment of AM, the technologies, AM feedstock materials and applications thereof have evolved rapidly every year.^[10,13] AM has found application in design and development in almost every consumer product sector imaginable,

presenting an advantage to create features that are not possible in conventional manufacturing methods.^[8,10] AM offers freeform of design where nearly any object (part) of any shape and complexity can be produced. Globally, the top three fastest growing applications of AM are aerospace manufacturing, automotive manufacturing and in the medical sciences.^[3] In the aerospace and automotive industry AM is highly valued for manufacturing complex geometric, weight reduced parts and to produce parts on demand, thus making AM an important role player in today's marketplace.^[14] In the medical sciences the manufacturing of customised medical products contributes to implants being fitted perfectly to a patient, thereby improving a patient's recovery rate.^[3] The general public is able to purchase smaller 3D printers also known as entry level machines, making AM more accessible not only to industry but also to consumers.^[3,4,8,10]

While AM is changing the traditional manufacturing approach and achieving new frontiers of production, this technological application unfortunately also comes with disadvantages.^[3] AM has not entered the large scale industrial production stage, which could be ascribed to manufacturing costs and higher specific energy requirements.^[4] Environmental concerns have been raised regarding waste material from AM processes and the potential toxicological hazards of materials used.^[15,16] For further information on AM related environmental issues, which is beyond the scope of this thesis, the reader is referred to Kellens *et al.* (2017)^[4] and Rejeski *et al.* (2018).^[6]

2.3 AM in South Africa

The first AM machine was introduced to South Africa in 1991 by 3D System (Pty) Ltd. followed by two machines introduced by the Council for Scientific and Industrial Research. The initial uptake of this technology was slow, possibly due to the strong traditional manufacturing industry in South Africa. However, from 2010 to 2017 exponential growth in both industrial AM machines and entry level 3D printers has been experienced.^[17,18] As the interest in the technology grew, the Rapid Prototyping Product Development Association of South Africa (RAPDASA) was established in 2000 to assist the South African AM industry in gaining international relevance. Currently, RAPDASA consists of academical, governmental and industrial role players to ensure the sustainable development of AM in South Africa. South Africa is the second largest producer of titanium mineral concentrate in the world. Currently, the titanium dioxide (TiO₂) or titanium slag is being exported and imported back to South Africa as titanium powder for AM.^[18,19] For this reason, an initiative named the Titanium Centre of Competence was introduced for the development of a titanium metal production plant. Once the process to develop titanium in

South Africa is completed the production of titanium powder will begin, enabling and implementing more titanium AM processes. This progress will increase the need for information and training needed by all role players including AM powder manufacturers/suppliers, employers and AM operators/employees to promote the health of the AM operator, and other interested parties.

Due to the growth of AM and the future potential thereof, an AM Roadmap was commissioned by the Department of Science and Technology of South Africa, for the purpose of establishing South Africa as a global leader in AM.^[10] The Roadmap, which started in 2014 and will run till 2023, consists of literature research, national and international market research, stakeholder workshops, surveys and meetings with local manufacturers for implementation of AM. The focus areas of the Roadmap are the aerospace and medical markets, material and technology development and the development of small, medium and micro-enterprises support programmes.^[17] All the above mentioned initiatives have enabled South Africa to align both existing and new AM research for future development.^[20] With increasing concerns raised on emissions from AM and the potential health effects presented to AM operators, the need for assessing particle emissions from AM and respiratory exposure of AM operators in South Africa was identified. Therefore, findings from this thesis serve as a starting point for assisting AM facilities, now and in future developments, in implementing effective control measures necessary to prevent and eliminate or reduce AM operator/employee exposure to emissions and respiratory hazards.

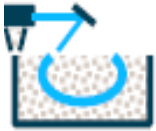
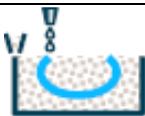
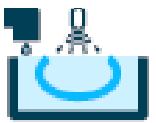
2.4 AM process categories

The following section describes the classification of AM according to the physical state of process materials, the process categories, the technologies and feedstock materials. This is followed by a detailed but concise description of each process category. Each AM process category is described and accompanied by the significant technologies and relevant feedstock materials, including the material extrusion process category since most of the published scientific literature on emissions and exposure focuses on this process category. However, for the purpose of this thesis, emphasis is placed on the powder bed fusion and direct energy deposition process categories. The different AM process categories depend on the type of production required and the physical state/form of different feedstock materials used. According to Monzón *et al.* ^[21] AM processes can be categorised either according to the feedstock used, the deposition technique or by the way the material is fused or solidified. For the purpose of this

thesis the AM (developmental) process is divided into three main techniques based on the physical state of the feedstock materials, namely: powder-based techniques, liquid-based techniques (polymer liquids and epoxy resins) and solid-based techniques (filaments, sheet or wire materials).^[2,22-24] AM is then sub-divided into seven process categories each with their technologies and applicable feedstock materials as classified by the ASTM standard 52900.^[2]

The seven standard process categories are the following: powder bed fusion (PBF), direct energy deposition (DED), binder jetting, material jetting, vat photopolymerisation, material extrusion and sheet lamination.^[2] A brief summary of the seven process categories, short descriptions of the technologies of each process category and the feedstock materials used is presented in Table 1. A more detailed description of all seven AM process categories, including the most significant feedstock materials used during operation, is given in the following section.

Table 1: The seven AM process categories and descriptions, technology types and feedstock materials^[2,7,10,11,23,25]

Illustration*	Physical state of feedstock	Process category	Description	Technology	Feedstock materials
	Powder	Powder bed fusion	Creates objects by using thermal energy to selectively fuse regions of a powder bed	Direct metal laser sintering (DMLS) Selective laser melting (SLM) Selective laser sintering (SLS) Selective heat sintering (SHS) Electron beam melting (EBM)	Metal powders Metal alloys Polymers
	Powder / Solid	Direct energy deposition	Builds parts by using focussed thermal energy to fuse materials by melting as they are deposited	Laser based technologies Electron beam technologies Electric/plasma arc technologies	Metal powders Metal alloys Metal wire
	Powder	Binder jetting	Creates objects by selectively depositing a liquid bonding agent to join powdered material	3D Printing Ink Jetting S-print	Metal alloys Polymers Ceramics
	Liquid	Material jetting	Builds parts by depositing droplets of build material, which are cured / hardened by UV light exposure	Ink-jetting Polyjet	Photopolymers Wax
	Liquid	Vat photopolymerisation	A liquid photopolymer in a vat is selectively cured by light activated polymerisation	Stereolithography Digital light processing	UV curable resins Polymers Ceramics
	Solid	Material extrusion	Creates objects by dispensing material through a nozzle to build layers	Fused deposition modelling (FDM™)	Polymers
	Solid	Sheet lamination	Sheet lamination bonds sheets of material to form a part	Ultrasonic additive manufacturing (UAM) Laminated object manufacturing (LOM)	Sheet metals Paper Plastic

*Pictograms provided for use with the written permission of Bernhard Langefeld.

2.4.1 Powder bed fusion

Powder bed fusion (PBF) is the AM process category in which a thermal energy source selectively fuses regions of a powder bed.^[2] The different PBF technologies consist of either a laser or an electron beam used to melt and fuse material powder together. Lasers as the thermal energy source are most widely used during PBF. PBF includes the following technologies: direct metal laser sintering (DMLS), selective laser melting (SLM), selective laser sintering (SLS), selective heat sintering (SHS) and electron beam melting (EBM).

The metal feedstock powders used during PBF can be fed through a hopper or from metal bins (feed region) next to the machine.^[2,26] Each process starts with depositing a thin metal powder layer on a substrate (build/base) plate. During all PBF technologies powder feedstock is spread over previous powder layers, using a roller or a blade. As each layer is deposited, a laser/electron beam is used to fuse the selected area as per instruction from the processed data. After each scan is completed the build/base plate is lowered and powder is deposited and the scan repeated.^[26] The excess powder remains loose around the part that is built and serves as a support. Unused powder can be recycled.^[8] Due to the high temperatures required during PBF technologies, parts are built in an enclosed chamber where an inert gas atmosphere is maintained with argon or nitrogen to prevent oxidation and to maintain the mechanical properties of the part.^[7,26,27]

DMLS sinters powdered layer by layer then melt the powder; this technology is only for use with metals and not polymers. SLM machines always consist of three components namely a heat source, a method to control the heat source, and a mechanism to add feedstock. The SLM and SLS technologies are very similar, except that SLM is used to create parts of uniform material by fully melting the powder particles. SHS uses a heated thermal print head instead of a laser for the fusion of powders. EBM uses an electron beam instead of a laser to melt metal powders.^[8,10]

A wide variety of feedstock material can be used during PBF including polymers, and various metals such as titanium and its alloys, stainless steel, maraging steel, tool steel and nickel based alloys.^[11]

2.4.2 Direct energy deposition

Direct energy deposition (DED) is an AM process category which utilises a concentrated heat source, which can be a laser, electron beam or plasma arc in a controlled chamber with reduced oxygen levels.^[2,28] A typical DED machine will consist of a nozzle that is mounted on a multi axis arm. Focussed thermal energy is used to fuse materials by melting as they are being deposited by a nozzle on a specific substrate to solidify.^[2] The cooling down period of the printed part is faster when compared to PBF. The difference between DED and PBF is that DED does not melt feedstock that is pre-laid in a powder bed, but rather melts feedstock as it is being deposited.^[8] DED also have the following general characteristics: the ability to process large build volumes, the ability to process at high deposition rates and the ability to deliver feedstock directly onto existing components.^[29]

This process can use polymers, ceramics, but titanium and various metal alloys in powder form are mostly used; it is therefore, sometimes referred to as metal deposition. Metal wire used as feedstock material is considered less accurate due to its preformed shape. DED is one of the more complex AM processes mostly used to repair or add additional material to existing components.^[8] The machine's nozzle can move in multiple directions, unlike material extrusion with a fixed nozzle.

The difference between the DED technologies is determined by the thermal energy source required: including laser based, electron beam or electric arc sources for melting feedstock material.^[11,28,29] Each technology also consists of sub categories. For a full list of sub categories of each technology the reader is referred to Table 2. It is important to note that the basic principle of DED is the same for all sub categories of which most "names" of DED machines are trademarks of different machine manufacturers. Direct metal deposition (DMD) uses a laser as a heat source for melting powder. When a laser is used as a thermal energy source the process categories can also be referred to as laser based additive manufacturing (LBAM). An example of DMD is called laser cladding, where metal powder feedstock is fed through a nozzle on to an existing substrate base, and a laser beam is focused on the substrate to create a melt pool on the surface.^[26,30] Laser cladding is similar to welding, and can be applied to repair, join or coat metal structures. Direct manufacturing (DM) makes use of an electron beam and metal wire for melting and depositing. Shaped metal deposition (SMD) is a DED technology that uses an electric arc and metal wire.

Table 2: DED technologies based on the thermal energy source used, technology descriptions and sub categories^[11,29]

DED technology	Thermal energy source	Description	Sub categories
Direct metal deposition (DMD)	Laser based technologies	A laser is and metal powder for melting and depositing is used with a patented close loop process	Laser cladding Laser direct casting Laser-aided direct rapid manufacturing (LADRM) Freeform laser consolidation Laser forming or 'Lasform' processing Laser-augmented manufacturing (LAM) Laser engineered net shaping (LENS)
Direct manufacturing (DM)	Electron beam technologies	An electron beam and metal wire is used for melting and depositing	Electron beam additive manufacturing
Shaped metal deposition (SMD)	Electric/plasma arc technologies	An electric arc and metal wire for melting and depositing is used	Shaped metal deposition (SMD) or wire and arc additive manufacturing (WAAM)

2.4.3 Binder jetting

Binder jetting is an AM process category where a print head selectively deposits a liquid bonding agent onto a powdered bed to join powder materials.^[2] Binder droplets form agglomerates of the binder liquid and the powder particles and ensures binding with the previous printed layer. As each layer is printed the printing bed is lowered and a roller spreads the newly deposited layer of powder over the printed layer. This process is repeated until the product is completed.^[31] Powder materials used in binder jetting include metals, polymers and ceramics.^[7]

2.4.4 Material jetting

Material jetting is the AM process category in which droplets of feedstock material are selectively deposited, and cured through light exposure.^[2] This AM process is similar to two dimensional ink jet printing where material is dispensed from a print head and jetted onto a build platform.^[7,8] The material droplets can either be deposited continuously or on a drop-on-demand approach, followed by the curing or hardening of the materials using ultraviolet (UV) light.^[7] Since this process requires deposition of feedstock material in droplets, not many forms of feedstock materials are available.^[32] Suitable feedstock material that can be used is limited to polymers such as acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), polycarbonates (PC), high-impact polystyrene (HIPS) and poly methyl methacrylate (PMMA).

2.4.5 Vat photopolymerisation

Vat photopolymerisation is an AM process category in which a liquid photopolymer resin in a vat (tank) is selectively cured by light-activated polymerisation.^[2] The build platform is lowered from the top of the resin vat and the part being built is moved downwards as each layer is cured. The resins are cured or hardened using UV light or photopolymerisation. Photopolymerisation is a complex chemical reaction that the material undergoes to become solid.^[8] The most used vat photopolymerisation technology is stereolithography.

2.4.6 Material extrusion

Material extrusion is an AM process category in which material is selectively dispensed through a nozzle or orifice.^[2] Material extrusion units are mostly found as desktop units due to the simplicity of their operation. A spool of thermoplastic filament is mostly used with units.^[33] Fused deposition modelling (FDMTM) is an example of the material extrusion process category where material feedstock is heated then extruded through a nozzle to solidify quickly. The nozzle of the FDMTM system increases the temperature of feedstock material to cause melting. It is also deposited in different layers which may be bonded at different temperatures or by using chemical thermoplastics such as ABS, PLA, nylon and PC.^[8]

2.4.7 Sheet lamination

Sheet lamination is the AM process category in which sheets of material such as metal or paper sheets are bonded to form a part.^[2] The two types of sheet lamination are ultrasonic AM (UAM) or ultrasonic consolidation (UC) and laminated object manufacturing (LOM). The UAM technology bonds sheets of metal together using ultrasonic welding.^[8] LOM is described as a combination of additive and subtractive techniques to build a part layer by layer from a rolling sheet of paper. A sheet of paper is deposited from a roller and a carbon dioxide laser cuts the shape of the layers (from the CAD file). Layers are bonded by the application of pressure and heat.^[34] Feedstock materials used in sheet lamination include any type of sheet material that can be rolled such as paper, plastic or sheet metals such as titanium, aluminium, copper and stainless steel.^[8]

2.5 AM operators' (set of) expertise

AM operators are required to operate some of the most advanced manufacturing equipment in the world. The AM process is not a single discipline and involves a range of technologies, materials and different types of AM machines, and therefore, requires highly skilled engineers. The operator actually has to complete the tasks acting as a designer, technician and as an engineer.^[11,35,36] Due to the AM process being a complex task, specific training as well as practical understanding of an AM system is necessary. Traditional manufacturing entails large production lines with several operators overseeing different processes, whereas AM reduces the number of operators. The operation of an AM machine mostly requires a single user; therefore, less labour input is needed for the AM process.

2.6 AM feedstock materials

AM feedstock materials are defined by the ASTM as the bulk raw material supplied to the AM building process.^[2] The first applied AM feedstock was limited to polymeric materials, waxes and paper laminates.^[8] As the technology developed a large range of feedstock material has become available, including powder based metals, metal alloys, polymers, ceramics and composites. Therefore, feedstock material is classified as either powder, solid or liquid based materials.^[23] AM operators are exposed to a variety of hazardous chemical substances in the form of powders, liquids, vapours and other solid based materials.^[23,37,38] It should also be taken into account that once AM metal powders are sintered during the processing phase, metal fumes are likely to be formed. HCS are defined as any toxic, harmful, corrosive, irritant or a mixture of such substances that may or may not have an occupational exposure limit but presents a health hazard to humans.^[39] In this thesis, HCS include any particulate matter (particles) and metal dust. Also, the focus is placed on titanium and steel alloy powders used in PBF and DED. Feedstock metal alloy powders, with emphasis on titanium and steel alloys and their properties, are briefly described in the following section. The potential health effects of each of the metal powder constituents are discussed in Section 2.9. Although polymers, ABS, and PLA, is not the focus of this thesis, they are briefly described in Section 2.6.2 as the use of these types of materials is increasing and health consequences following use have emerged in recent times.^[3,40]

2.6.1 Metal alloy powders

There is a wide range of metal powders that are commercially available for AM metal manufacturing. The most prominent of metal alloy powders are, but not limited to, stainless steel, tool steel, maraging steel, aluminium alloys, cobalt-chrome powders, nickel based

alloys, pure titanium and titanium alloys.^[8,10] Most of the metal powder feedstock can be recycled and reused. Therefore, metal powders can either be used as new (as provided by the manufacturer) or as reused (recycled) powder.

2.6.1.1 Titanium alloys

Titanium is described as a metallic transition element and is considered to be a light element. It is the ninth most commonly occurring element, the fourth most abundant structural metal found in the earth's crust, and is extracted from mineral ores such as rutile and ilmenite.^[41,42] Titanium is regarded as one of the most important of the advanced materials which are applied to improved performance in aerospace and terrestrial systems.^[29] The crystal structures of titanium are referred to as alpha (α) and beta (β) structures. The alpha structure refers to hexagonal titanium and the beta structure represents cubic titanium.^[7,43] When titanium is alloyed with different elements three main classes of alloys form, namely alpha alloys, alpha-beta alloys and beta alloys each with distinctive properties. Further class subdivisions include near-alpha and metastable-beta alloys.^[42,45] In the AM industry titanium is alloyed with other widely-used elements such as aluminium, chromium, copper, iron, manganese, tin, molybdenum and vanadium.^[44,45,46] Ti₆Al₄V is the most widely applied titanium alloy and consists of 6% aluminium, 4% vanadium, 0.3% (maximum) iron, 0.2% (maximum) oxygen, and titanium as the remainder.^[11,43] Titanium is highly valued for its high fatigue and corrosion resistance; in most instances titanium's resistance exceeds that of stainless steel. Titanium is also biocompatible and can be applied in a variety of biomedical applications.^[41-43]

2.6.1.2 Steel alloys

Steel is most commonly used as an engineering material making it also of high interest to the AM industry.^[26] There is a variety of different types of steel used in the AM industry, namely stainless steels, tool steels and maraging steels.

Stainless steels are iron-based alloys, rarely consisting of more than 30% chromium, with a minimum of 50% iron. Other elements such as nickel, molybdenum, copper, titanium and aluminium can be added for the improvement of specific characteristics.^[47,48] The word "steel" indicates that iron constitutes the bulk of the material, and the word "stainless" refers to the absence of staining/rusting of the material.^[48] Stainless steels are widely applied in a variety of AM products due to its desirable characteristics such as high strength, corrosion resistance and durability.^[49]

Tool steel is described as the alloys that are used to manufacture tools and moulds or applications where strength and toughness are essential for optimum performance.^[50] Tool steel is a combination of carbon and alloyed steel(s) that are able of being hardened and they are resistant to abrasion.^[47] According to the American Iron and Steel Institute's classification system, tool steel can be divided into groups based on their characteristics such as alloying, application and heat treatment. Tool steel may contain elements such as chromium, molybdenum and vanadium.^[50]

Maraging steel is a steel alloy composed of iron and 18-25% nickel, which is produced by heating steel in the austenite phase followed by cooling in the air to form a martensitic microstructure. The hardening of the martensite is done by precipitation of molybdenum titanium.^[51] Martensite is a form of steel crystalline structure, and aging refers to the type of heat treatment process.^[52] Maraging steel is applied in the aerospace industry, and is known for its strength, good corrosion resistance, processing ability and weldability.^[53,54]

2.6.1.3 Aluminium based alloys

Aluminium in its pure form is a light and ductile metal and is often alloyed with copper, manganese, magnesium and zinc. Aluminium is used during the SLS technology and has a widespread and important use in industrial applications and consumer products due to its beneficial characteristics such as being light in weight, castable and weldable.^[7,55]

2.6.1.4 Cobalt-chrome alloys

The main components of cobalt-chrome (CoCr) alloys are cobalt, chromium, molybdenum and in some instances nickel.^[56] CoCr alloys are used in the AM of gas turbines, biomedical implants and dental restorations and applications due to its corrosion and wear resistance.^[8,57] CoCr alloys were the first alloys to be applied in dentistry. Cobalt-chrome is alloyed with molybdenum to increase corrosion resistance and is especially used where extreme wear-resistance is required, such as in knee implants.^[58] CoCr alloys are used in SLM and EBM AM technologies.^[57]

2.6.1.5 Nickel based alloys

Nickel-based alloys are developed and used for the manufacturing of high performance parts, such as gas turbines and engines. These alloys contribute to the improvement of tensile properties and its resistance to oxidation.^[8] Certain nickel alloys may contain a small

amount of aluminium, titanium or chromium. Inconel is an example of a widely used nickel-based superalloy. The term superalloy is used when referring to a metallic alloy with special qualities such as high temperature corrosion strength and oxidation resistance.^[59]

2.6.2 Polymers

Polymers belong to the general class of plastic based materials, which can be moulded easily. Polymers are organic compounds and contain carbon as an essential element.^[22] In AM, polymers are referred to as thermoplastics, where a polymer can be mixed with a blend of materials known as additives. Thermoplastic materials are opposed to thermoset materials which refer to the manner in which a material will respond to heat treatment.^[60] A thermoplastic can be heated, become a liquid, cooled and reheated. In AM, thermoplastics are mostly solid filaments that are heated and subsequently undergo physical and chemical changes.^[61] The two most prominent thermoplastics used in AM are ABS and PLA.

2.6.2.1 Acrylonitrile Butadiene Styrene (ABS)

ABS is a petroleum-based, durable, production-grade thermoplastic and is commercially available in different colours and used across many industries.^[7] It can be used in high temperature applications and although ABS is not biodegradable, it is recyclable. Advantages of ABS include that it adheres well thereby enabling high printing speeds, it is easy to machine and fabricate and can be also be blended with PC.^[7,8,62] Disadvantages include that the material tends to warp off the build/base plate during the production of larger parts and causes a burning plastic odour during printing.^[5]

The difference between ABS and PLA based 3D printers are the feedstock origin, built plate temperatures and build (nozzle) temperatures.^[63]

2.6.2.2 Polylactic acid (PLA)

PLA is manufactured from plant based materials such a corn starch and sugar cane which makes it biodegradable and compostable. It is also referred to as a biopolymer.^[64-66] PLA is a thermoplastic that is a high-strength and high modulus (elasticity) polymer, although PLA is slightly more brittle than other plastics and can lose molecular weight during thermal treatment.^[62,67,68] Advantages of PLA include that no heated bed is required during printing, it adheres well, and is also able to print at high speeds. The disadvantages of PLA are that it can deform and is known to have a mild organic odour during printing.^[5,7]

2.7 Occupational exposure during AM

AM is described as a transforming manufacturing technology, that has become more accessible, extending to homes, schools, universities and various manufacturing industries. It is of utmost importance for the AM operator - whether the engineer or the general user - to be aware of the possible health hazards associated with this technology.^[69,70] In this thesis the focus is on the emissions from AM and the potential respiratory exposure that the industrial AM operator may experience when using metal feedstock powders. Although AM machines are designed to operate unattended, all material handling is performed manually. Depending on the AM technologies process, occupational exposure to different process materials may take place during the pre-processing, processing and post-processing phases.^[37,38] It is important to note that not all AM processes are performed according to these three distinct phases and that certain AM processes that may take place as a continuous process.

2.7.1 Pre-processing

The pre-processing phase of AM commences with the initial design of the part and the setting up of software needed for the AM machine to produce the part. The machine setup during pre-processing includes cleaning the machine from a previous build, sieving of, for example metal powders, and manual handling of feedstock material in order load feedstock hoppers/bins into the AM machine.^[8,12,38]

2.7.2 Processing

During the processing phase the door of the large AM machines is closed until the part production process has been completed. This is in contrast to smaller desktop FDM™ printers as not all of them can be closed. Some 3D printers are built on an open frame without any enclosure or extraction devices.^[71,72] In industrial work environments the AM operator stays in the room for approximately 15 to 20 minutes followed by regular entries to establish the progress of the build. In the case of FDM™ desktop printers the operator is mostly situated in close proximity to the 3D printer, as these machines are often placed in what is described as non-traditional locations such as libraries, offices, meeting rooms, and homes.^[41,70]

Published studies emphasise that ultrafine particles (UFPs) and volatile organic compounds (VOCs) are emitted during the processing phase when using FDM™ desktop printers.^[63,73,74] While AM operators manually handle AM metal powders which can generate airborne dust, it

should also be taken into account that once AM metal powders are sintered during the processing phase, metal fumes may be formed and inhaled by the AM operator when emitted.

When AM parts are printed (processing phase) the concept similar to welding is applied as AM metal powder layers are joined by melting AM powders together.^[75,76] The difference between the two processes is that metal AM is an enclosed process, while welding is an open process. The metal fumes generated during the processing phase might be compared to welding fumes for the reason that metal AM powders are also iron based and contain metal elements similar to welding such as aluminium, titanium, nickel and chromium.^[76] Not all large AM machines are equipped with extraction ventilation systems, and some AM machines require additional extraction systems.^[63]

2.7.3 Post-processing

All AM manufactured parts require some form of post-processing which is usually performed manually and can contribute to possible exposure of the AM operator to feedstock material.^[8,10,37,69] Depending on the type of technology used to manufacture the part, different post-processing activities may take place. Metal post-processing entails a number of manual tasks/activities performed by the AM operator before the manufactured part is ultimately finished. The following section provides a brief description of the post-processing steps and activities performed by the AM operator. Although polymers is not the focus of this thesis, the post-processing thereof is also briefly described.

2.7.3.1 Metal post-processing

Metal powder post-processing requires the removal of surplus powder and/or support structures.^[37,69] After a metal part has been printed the AM operator manually sweeps excess powder surrounding the part into overflow bins, which liberates metal powder dust into the workplace atmosphere.^[35,37] The build/base plate on which the part has been built is removed by the AM operator and trapped powder inside the part may be removed by vacuuming. When an AM part is built with support structures, the structures have to be removed from the printed part as well, after all loose powder has been removed from the part and built/base plate. Support removal can include wire cutting, or mechanical machining such as sanding, shot peening, electroplating, laser micro machining and hot cutter machining, milling, turning and grinding which are all manually performed by the AM operator. Afterwards, the AM operator may also clean the AM machine by vacuuming or dry sweeping inside the AM machine and the surrounding work area.^[35,77]

2.7.3.2 Polymer post-processing

Once a polymer (thermoplastic) part is build, it is removed from the build/base plate by using a scraper tool. Some thermoplastic parts may have a support structure that needs to be removed from the part itself. The material used to manufacture support structures is different from the material of the printed part: the support structure can in some instances be broken off the part or otherwise needs to be chemically removed. For thermoplastic parts the post-processing may include cleaning of the part with organic solvents, solvent in baths or by vapour polishing.^[7,69,72] Solvent baths are used to dissolve the support structure from the part and, depending on the type of feedstock material, the solvent bath can contain acetone or chloroform as solvents. If a part requires a smooth finish, vapour polishing is done. For ABS parts, acetone vapour polishing is used and for PLA parts, chloroform vapour polishing.^[72,78]

The appropriate solvent is usually placed in a container and the printed part is placed on a suspended platform above the solvent. The container is sealed off, and the solvent is heated until it produces a vapour.^[78] During the vapour polishing process the AM operator is usually present. The different post-processing tasks for thermoplastics are mostly conducted in the same room as where the processing phase takes place.

2.8 Exposure routes

When comparing traditional manufacturing methods to AM, the latter is regarded as a self-contained process that uses less material and produces less waste. In some instances, however, the immediate health concerns are often overlooked. Furthermore, even though AM is an enclosed process, AM operators may still be exposed to various HCS. Exposure to AM feedstock material may come from interaction with feedstock (pre-processing and post-processing) and release of emissions from the AM machine (processing). The main route of exposure associated with AM is respiratory exposure, but in some instances dermal exposure cannot be excluded. However, dermal exposure is not within the scope of this thesis and will not be discussed further. For further reading on dermal exposure, please refer to Creytens *et al.*^[79]

The presence of airborne particulates in indoor environments is a cause of concern due to its association with adverse health effects.^[80,81] Airborne particulate matter varies in size and composition and can be a heterogeneous mixture of solid and liquid particles.^[73] The composition of ambient particulate matter can be described as complex and includes coarse particles (2.5 to 10 µm), fine particles (< 2.5 µm) and UFPs (< 100 nm).^[82]

Particle size determines whether particles are inhalable, and if inhalable where it may be deposited in the respiratory tract.^[63,80] Aerodynamic diameter is the criteria used to describe particulate matters transport ability in the atmosphere and the inhalation ability through the respiratory system.^[73] Particles are classified into size fractions, namely inhalable, extrathoracic, thoracic or respirable particles depending on the regions of deposition. Inhalable are the mass fraction of airborne particles inhaled through the nose and mouth and are deposited in the nasopharyngeal region. Extrathoracic particles can be inhaled, but do not penetrate beyond the larynx. Thoracic sized particles is the mass fraction of inhaled particles where penetration of particles is expected beyond the larynx, while respirable particles can penetrate the unciliated airways and are deposited in the alveolar region of the lungs.^[83,84,85]

UFPs are defined as the fraction of fine particles with a diameter of less than 100 nm.^[82,86,87] Inhaled UFPs are efficiently deposited in the nasal, tracheobronchial, and alveolar regions of the lung and may lead to particles penetrating deeper in the lungs. The growing concern about exposure to UFPs is of interest due to the potential acute and chronic health effects linked to exposure.^[86,87] The health effects and the toxicity of UFPs will be discussed in Section 2.10.11.

There is a limited number of studies indicating what the levels of exposure to UFPs of the AM operators carrying out AM printing tasks are, with studies mostly estimating exposure levels based on emissions from AM.^[1,37,71,88]

2.8.1 Metal emissions and exposure

There are only two studies that have investigated particle sizes of AM metal powder feedstock used in industrial AM machines.^[37,88] Mellin *et al.*^[88] investigated nano-sized by-products from production (processing) during SLM processing using Inconel 939, an alloy powder containing nickel, chromium and cobalt. SLM is one of the five technologies of the PBF process category. Scanning electron microscopy (SEM) and particle shape distribution were performed with both virgin and recycled powder to compare powder particles' shape and size. From SEM images small spherical particles called satellites were observed in the recycled powder. Satellite particles (1.2 μm to 5.8 μm) became attached to larger particles (23.4 μm) during the processing phase, and could detach from larger particles during powder handling. Mellin *et al.*^[88] also states that there is a possibility of even smaller particles depending on the type of powder used. No particle emissions or static area monitoring was performed by Mellin *et al.*^[88] and, therefore, the authors could only speculate

during which phase possible emission of and exposure to powder could take place. The possible exposure was expected when powders are sieved (during pre-processing), when printed parts are removed and separated from powder, and when equipment is cleaned (post-processing). Although personal monitoring of AM operators was not performed, it was found that small respirable metal particles ($\sim 1\text{ }\mu\text{m}$ to $2\text{ }\mu\text{m}$) were generated during SLM processing.

Graff *et al.*^[37] also investigated the SLM technology with Inconel 939 powder feedstock. Their study included the analysis of virgin and recycled Inconel 939 powder, static area monitoring of the workplace environment (including emissions and metal concentrations in the workplace area), and personal exposure monitoring of AM operators. The metal powder feedstock used during the study was analysed through laser diffraction and volume and number percentages were determined as well. The powder supplier indicated that the powder particles are in a range of $15\text{ }\mu\text{m}$ to $45\text{ }\mu\text{m}$, however, Graff *et al.*^[37] found particles significantly smaller ($< 10\text{ }\mu\text{m}$) than the indicated size range. When particle emissions in the 10 to 300 nm size range was investigated, emission of aerosols, approximately 50 to 150 nm in size and peak numbers of approximately $16\text{ }000\text{ p/cm}^3$, was detected during the cleaning of the AM machine.

Different measuring points during various AM tasks were investigated to determine the airborne metal particle emissions in the particle range of 300 nm to $10.00\text{ }\mu\text{m}$ generated while the SLM machine was in operation (processing phase). The AM tasks included the opening of the AM machine door, vacuuming the build/base plate, removing of build/base plate, sieving of metal AM powder, cleaning the AM machine and filling up the AM machine with metal powder. These locations indicated peak number of particles at $1 \times 10^8\text{ p/m}^3$ in the $0.50\text{ }\mu\text{m}$ size fractions and $3 \times 10^7\text{ p/m}^3$ in the $10.00\text{ }\mu\text{m}$ size fractions. Other measurement points also included measurements while the AM machine was in operation and when processing stopped and was $< 1 \times 10^7\text{ p/m}^3$ in both the $0.50\text{ }\mu\text{m}$ and $10.00\text{ }\mu\text{m}$ size fractions. All these tasks were performed manually by the AM operator, and indicate that AM operators were exposed to emissions.^[37]

Stationary (area) exposure monitoring and personal exposure of the AM operator was performed with a 25 mm , $0.80\text{ }\mu\text{m}$ pore mixed cellulose ester filter inside a closed-face polystyrene cassette during the processing of the metal alloy powder. Stationary exposure monitoring was performed in close proximity to the sieve and to the SLM machine during operation (processing). A total of four metals were detected during the stationary (area) exposure monitoring. Measurements performed close to the SLM machine were higher in

comparison to those performed closer to where powder sieving took place. Overall results in the workplace area indicated the presence of chromium ($21 \mu\text{g}/\text{m}^3$ to $50 \mu\text{g}/\text{m}^3$), nickel ($48 \mu\text{g}/\text{m}^3$ to $110 \mu\text{g}/\text{m}^3$) and cobalt ($13 \mu\text{g}/\text{m}^3$ to $42 \mu\text{g}/\text{m}^3$).^[37]

Personal exposure monitoring was performed for 45 minutes during activities that included opening the AM machine, vacuuming the build/base plate, handling of the build/base plate, sieving metal powder, cleaning of the AM machine and filling up the AM machine with metal powder. Personal exposure of AM operators to inhalable metals was established. The results confirmed exposure to dust ($210 \mu\text{g}/\text{m}^3$), chromium ($< 44 \mu\text{g}/\text{m}^3$), nickel ($< 99 \mu\text{g}/\text{m}^3$), cobalt ($< 38 \mu\text{g}/\text{m}^3$) and iron ($< 100 \mu\text{g}/\text{m}^3$).^[37] Unfortunately Graff *et al.*^[37] only determined total dust ($\mu\text{g}/\text{m}^3$) and metal content in the air and did not perform time weighted average (TWA) calculations and therefore, could not compare exposure to legislative occupational exposure limits of the individual metals. To date the findings of these two studies serve as evidence that AM operators are exposed to emissions from metal alloy AM and are exposed to detectable levels of metals during AM.^[37,88]

2.8.2 Polymer emissions and exposure

Published literature provides ample evidence that the focus on emissions from the AM process categories such as material extrusion and binder jetting utilising polymers has been studied quite extensively. The reader is referred to Table 4 where all AM emissions and exposure studies to date are listed. Numerous studies have found that desktop FDMTM printers are high emitters of particulate matter.^[1,61,71,73,89] Different AM technologies and feedstock materials used can contribute to UFPs being emitted.^[63,71-74] Emission rates of UFPs up to 1×10^{10} p/min have been reported during the use of PLA, while a study by Azimi *et al.*^[74] reported UFP emission rates for a variety of feedstock including ABS, PLA, PC, HIPS and nylon ranging between approximately 10^8 p/min and 10^{11} p/min.^[81] Studies have found that ABS particle emission rates are higher (1-2 orders of magnitude) when compared to PLA emission rates. This can be ascribed to a difference in extruder temperatures, and differences in filament materials including the colour of the filaments used.^[40,66,73,81,89]

Total volatile organic compounds (TVOCs) emitted from ABS have been reported to be 155 ± 3.4 ppb.^[73] Individual VOCs emitted by ABS and PLA differ from one study to the next. The most prominent VOCs emitted from ABS include acetone, styrene, ethylbenzene and a variety of polyaromatic hydrocarbons.^[66] Two studies investigated the emissions of gaseous compounds from FDMTM printers during the thermal degradation of polymers and no emissions of ozone, oxygen, carbon monoxide, ammonia, nitrogen dioxide, nitrogen

monoxide, hydrogen cyanide were detected.^[64,66] While a study by Stefaniak *et al.*^[61] found low ozone concentrations and various carbonyl compounds during a chamber study with ABS and PLA. Emissions and exposure from binder jetting machines have indicated aerosol (UFPs) emissions 10^4 to 10^5 times by number lower than that of FDM™ printers using PLA, but by size emitted aerosols larger than 200 nm.^[1]

Current literature studies on polymer emissions have estimated the potential occupational exposure risks based on exposure scenarios. Exposure scenarios aim to mimic real life exposure of an AM operator working in close proximity to a FDM™ printer mostly by conducting chamber emission studies.^[71,96] Chambers can be constructed in accordance to the National Institute of Standards and Technology or to the researchers own discretion. These chambers can be made of stainless steel, acryl or glass. The desktop 3D printers are placed inside the chamber supplied with ventilation holes and inlets for probes of direct reading instruments.^[61,65,73,74,96] A drawback of chamber studies is that it is only suitable for small desktop FDM™ printers and almost impossible to use with large industrial AM machines. Chamber based studies are highly valued for their contribution in providing a better understanding of emissions generated by 3D printers, although there is a great need to conduct real life exposure studies in workplace settings, reflecting actual AM operator exposure.^[71,73]

Table 3: A summary of current AM studies reporting on emissions from and/or exposure associated with different AM process categories

Process category	Technology	Feedstock used	Emissions and/or exposure	Reference
Powder bed fusion	SLS	Inconel 939	UFPs, dust and metals	Graff <i>et al.</i> ^[37]
	SLS	Inconel 939	UFPs	Mellin <i>et al.</i> ^[88]
Binder jetting	3D printing	Zp®150 powder, Zp®60 binder, Zp®90 colour bond	UFPs, super-micron particles, TVOCs	Afshar-Mohajer <i>et al.</i> ^[1]
Material extrusion	FDM™	ABS, PLA	UFPs	Stephens <i>et al.</i> ^[63]
	FDM™	ABS, PLA	UFPs, larger particles, dust, TVOCs	Kim <i>et al.</i> ^[73]
	FDM™	ABS	UFPs	Zhou <i>et al.</i> ^[90]
	FDM™	ABS, PLA, PC, HIPS, Nylon bridge Laybrick, Laywood, PCTPE, T-Glase	UFPs, VOCs, TVOCs	Azimi <i>et al.</i> ^[74]
	FDM™	ABS, PLA	UFPs	Deng <i>et al.</i> ^[88]
	FDM™	ABS	UFPs	Geiss <i>et al.</i> ^[91]
	FDM™	ABS, PLA, Nylon, PC	UFPs, fine particles, VOCs	McDonnell <i>et al.</i> ^[92]
	FDM™	ABS, PLA	UFPs, VOCs, PAHs	Steinle ^[64]
	FDM™	ABS, PLA	UFPs, larger particles,	Yi <i>et al.</i> ^[65]
	FDM™	ABS, PLA, PC, HIPS, Nylon, Laybrick, Laywood, PCTPE, TGlase	UFPs, VOCs	Azimi <i>et al.</i> ^[93]
	FDM™	PLA	UFPs	Bharti and Singh ^[5]
	FDM™	ABS, PLA, PCABS, HIPS, Nylon, PVC, Bronze-PLA, PET	UFPs, larger particles, VOCs	Floyd <i>et al.</i> ^[71]
	FDM™	ABS, PLA, HIPS, Nylon, PVA, Laywood	UFPs	Kwon <i>et al.</i> ^[94]
	FDM™	ABS, PLA	UFPs	Simon <i>et al.</i> ^[95]
	FDM™	PLA, Wood 1 and 2, Copper, Bamboo, Flex PLA, CP, CP-Carbon, Nylon, Ninjaflex	UFPs, nanoparticles, larger particles	Stabile <i>et al.</i> ^[81]
	FDM™	ABS, PLA	VOCs, TVOC, ozone, carbonyls	Stefaniak <i>et al.</i> ^[61]
	FDM™	ABS, PLA	UFPs, VOCs, TVOCs,	Mendes <i>et al.</i> ^[66]
	FDM™	ABS, PLA, Wood infused PLA, Copper infused PLA	UFPs, TVOCs	Vance <i>et al.</i> ^[96]
	FDM™	ABS, PLA, Nylon, PET	VOCs	Wojtyla <i>et al.</i> ^[62]
	FDM™	ABS, PLA, Nylon	UFPs, larger particles	Zhang <i>et al.</i> ^[40]
	FDM™	ABS, PLA	UFPs	Zontek <i>et al.</i> ^[97]
	FDM™	ABS, PLA	UFPs, VOCs, TVOCs	du Preez <i>et al.</i> ^[72]

ABS (acrylonitrile butadiene styrene), PLA (polylactic acid), Zp®150 composite powder (80% plaster, 10% vinyl polymer, 10% carbohydrate), Zp®90 colour bond (cyanoacrylate, hydroquinone), PC (polycarbonate), HIPS (high-impact polystyrene), PCTPE (plasticized copolyamide thermoplastic elastomer), PVC (polyvinyl chloride), PET (polyethylene terephthalate), PVA (polyvinyl alcohol), CP (co-polyester), UFPs (ultra fine particles), TVOCs (total volatile organic compounds), VOCs (volatile organic compounds), PAHs (polyaromatic hydrocarbons), UFPs (< 0.1 µm), super-micron particles (0.45-20 µm), large particles (> 100 nm), fine particles (< 2.5 µm), nanoparticles (< 100 nm).

2.9 Health effects and toxicity associated with AM

With the exception of studies mentioned in the next section (Section 2.9.1) literature regarding the actual health effects associated with AM has been limited to studies mostly speculating or estimating possible health effects and actual AM operator exposure levels.^[1,37,71,88] Most AM research is primarily focussed on the improvement of feedstock, applications and design, and although the technology has evolved, the research on health risks associated with exposure has not progressed enough.^[3,4,71] Inhalation of materials used during AM may cause respiratory irritation, coughing, nose and throat irritation.^[23,98] With the application of a diversity of feedstock (raw materials) in AM, there is concern regarding the potential hazardous effects of such substances on human health.^[4,23,69] The use of a variety of feedstock materials including powder materials, chemical substances and consumables presents a challenge in determining the health hazards associated with AM.^[23,99] More importantly limited information provided in safety data sheets (SDSs) and no safe operating guidelines in user manuals, could wrongfully offer a false sense of protection of AM operator health,^[23] while in reality a risk to health may exist.

2.9.1 Reported health effects associated with AM

This section addresses the known health effects of AM to date.

There are only six studies that have evaluated and reported health effects associated with AM (summarised in Table 3). House *et al.*^[100] concluded that an AM operator developed asthma due to emissions while working with ABS and desktop FDMTM printers. Johannes *et al.*^[101] confirmed that an AM operator was diagnosed with chronic hypersensitivity pneumonitis due to the inhalation exposure to nylon powder. In a study by Chan *et al.*^[102] a questionnaire was completed by AM operators that worked with various types of 3D printers, in order to establish whether they experienced any respiratory symptoms. It was reported that 57% the participants that worked more than 40 hours a week experienced various respiratory symptoms that included nasal congestion, rhinorrhoea; coughing, and itchiness of the nose, throat or eyes experienced by AM operators. Stefaniak *et al.*^[103] was the first to study cardiovascular function in rats following inhalation of 3D printing emissions and observed acute hypertension and microvascular dysfunction.^[103]

Table 4: Reported health effects of different process categories, technologies and feedstock materials

Process category	Technology	Reported health effect	AM feedstock material	Reference
Powder bed fusion	SLS	Chronic Hypersensitivity Pneumonitis	Nylon	Johannes <i>et al.</i> ^[101]
Material extrusion	FDM™	Work-related asthma	ABS	House <i>et al.</i> ^[100]
*	3D printing	Allergic contact dermatitis	Epoxy resins	Creytens <i>et al.</i> ^[79]
Material extrusion	FDM™	#Acute hypertension and microvascular dysfunction	ABS	Stefaniak <i>et al.</i> ^[103]
Variety of processes	3D printing	Respiratory symptoms including asthma and allergic rhinitis	Variety of feedstock	Chan <i>et al.</i> ^[102]
Material extrusion	FDM™	Eosinophilic inflammation	ABS, PLA	Gümperlein <i>et al.</i> ^[104]

*There was no reference to a specific process category in the study, it was only classified as 3D printing, correspondence with the authors was unsuccessful in establishing the process category.

#in rats.

More recently, a controlled exposure experiment was performed on 26 volunteers printing with ABS and PLA. UFPs were monitored and assessments included spirometry and exhaled biomarkers testing, nasal secretions, urine samples and VOC emissions assessments before and after the exposure to ABS and PLA. These parameters did not show significant changes between exposures and no acute changes were observed in the volunteers, with the exception of PLA.^[104] There was however, a slight increase in exhaled nitric oxide after ABS printing when compared to PLA printing due to eosinophilic inflammation from inhaled UFP particles.^[104]

2.10 Toxicity and health effects of AM feedstock materials

Based on the various AM metal feedstock materials and their applications in AM, as described in Section 2.5, the following section addresses the anticipated toxicity and health effects of AM feedstock materials. To conclude the health effects section, the toxicity and health effects of UFPs will also be discussed.

2.10.1 Titanium and titanium alloys

Titanium in its pure form is poorly absorbed by ingestion, although it was found that patients who were exposed to titanium along with several other metals had an impaired immune response and cytokine release.^[105] There is, however, a lack of epidemiological studies on the health effects of titanium. Titanium is highly reactive, and in the presence of oxygen,

leads to the formation of TiO_2 . TiO_2 particles are classified as being poorly soluble and having low toxicity.^[106,107]

Concerns have been raised regarding nano-sized ($< 100 \text{ nm}$) TiO_2 due to their potential toxicity.^[108,109] Occupational exposure to TiO_2 nanoparticles (NP) can take place through inhalation or ingestion. The inhalation of TiO_2 can aggravate pre-existing respiratory diseases in certain individuals.^[110] Once TiO_2 NP are inhaled they can deposit in the respiratory tract in the nasopharyngeal, tracheobronchial and alveolar region and cause inflammation, and may translocate to the central nervous system through sensory nerves.^[107-109] *In vitro* studies have shown that the inhalation of TiO_2 NP has the ability to activate endothelial cells and induce pro-inflammatory reactions.^[111] Although only a few inhalation, intratracheal instillation and intranasal studies have been performed, they have demonstrated the translocation of TiO_2 NP from the nasal cavity into sensory nerves and that they can translocate from the lung into the circulatory system.^[107]

As a powder or in the form of metal shavings, titanium metal poses a significant fire hazard and, when heated in air, an explosion hazard may exist.^[98]

2.10.2 Steel alloys

Steel alloys contain various metal elements such as iron, nickel, chromium and aluminium, which will each be discussed briefly.

2.10.3 Iron based alloys

Steel materials contain iron that serves as a base alloying element. Iron dust is hazardous when inhaled and can cause fibrotic and non-fibrotic damage in the lungs.^[112] Iron oxide fumes and dust which are mostly found in occupational settings may cause pneumoconiosis.^[106]

2.10.4 Aluminium based alloys

Inhalation is the main route of exposure to aluminium. The bioavailability of aluminium is dependent on the particular aluminium species and particle size of the inhaled material. Aluminium is known to be a highly reactive metal with the potential to cause toxicity due to chronic exposure.^[112] Long-term inhalation exposure to aluminium can induce pulmonary fibrosis.^[113,114]

2.10.5 Vanadium

Vanadium is a trace element and it has been reported that adverse respiratory effects such as coughing, wheezing and sore throats could be observed in workers exposed to vanadium compounds.^[115,116]

2.10.6 Cobalt-chrome powders

Chromium exist as one of two valance states, namely trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)]. The inhalation of chromates in chromium sensitised workers can lead to coughing and wheezing. Hexavalent chromium is classified a Group 1 carcinogen by the International Agency for Research on Cancer (IARC), and may increase the risk of nasal and lung cancer.^[112,117]

Cobalt is neurotoxic and inhaling cobalt dust may lead to respiratory irritation, rhinitis and occupational asthma.^[113] Tungsten carbide cobalt is widely used for the production of hard metals but not yet commercially available to be used in AM due to microstructural and mechanical properties that are still being investigated.^[118,119] Studies have found that exposure to cobalt in the hard metal industry may induce pulmonary fibrosis and cause lung cancer.^[120]

Molybdenum is an essential element for humans, with low toxicity. If high concentrations of metallic molybdenum are inhaled it may cause inflammation in the lungs.^[121]

2.10.7 Nickel

Exposure to nickel has been known to cause respiratory irritation and occupational asthma.^[112] Nickel compounds are classified as Group 1 carcinogens by the IARC; while metallic and nickel alloys are considered to be a possible human carcinogens (Group 2B).^[122] Nickel compound and nickel metals may cause lung, nasal cavity and paranasal sinuses cancer.^[122]

2.10.8 Polymers

The two most prominent polymers are ABS and PLA and their potential health effects are briefly discussed.

2.10.8.1 Acrylonitrile Butadiene Styrene (ABS)

During FDM™ printing ABS material is heated up and undergoes thermal degradation, which generates acrylonitrile vapours, butadiene and styrene and produces volatile organic compounds (VOCs).^[61,123] Many VOCs are respiratory irritants and allergic asthmagens.^[61] Acrylonitrile is classified as carcinogenic (Group 2B) and damaging to the eyes while butadiene is carcinogenic and mutagenic.^[124,125] Styrene is an organic chemical that plays an important role in producing polymers for plastics. Occupational exposure to styrene occurs through the inhalation of vapours and skin contact.^[126] Styrene is classified as a Group 2B carcinogen.

2.10.8.2 Polylactic acid (PLA)

In a study by Kim *et al.*^[73] it was found that ABS resulted in higher particle concentrations during printing when compared to PLA. PLA is classified as being a low hazardous respiratory irritant, although it has been suggested that further information is still needed on the inhalation exposure of PLA.^[73,124]

2.10.9 Toxicity and health effects of UFPs

In workplace environments UFPs are generated in processes involving high temperatures, combustion and mechanical processes. UFPs emitted in AM work environments are due to different AM technologies and feedstock materials.^[63,71-73] Although the epidemiological evidence on the health effects of exposure to UFPs is still to be said unclear, epidemiological studies have associated UFPs with respiratory and cardiovascular causes of mortality. UFPs possess large surface areas enabling them to transport harmful chemicals.^[87] Inhaled UFPs cannot be filtered out by the nose or bronchioles due to their size which allows them to penetrate deep into the lungs and deposit in the alveolar epithelium. There is a concern especially regarding allergen sensitised individuals which may be more susceptible to the adverse health effects of UFPs.^[127]

Once inhaled, UFPs can lead to acute airway inflammation, impaired lung function, increased asthma symptoms and has also been linked to possible lung cancer.^[82,87,127] Chronic exposure to UFPs may also lead to chronic obstructive pulmonary disease. The inhalation of UFPs can lead to inflammation via oxidative stress. It is important to understand that the physiochemical properties differ among the different UFPs, and that they have a soluble component and release transition metals which act as primary pro-inflammatory mechanisms.^[127] These transition metals can interact with the lining fluids in the lung they

can undergo redox reactions that produce reactive oxygen species.^[82,127] These particles may also enter the circulatory system and have the potential to easily cross-over to the bloodstream and may be transported to the brain via the olfactory nerve.^[65,89,128] UFPs that enter the circulatory system may lead to deep vein thrombosis.^[87]

AM operators are exposed to UFPs in their work environments but in terms of occupational hygiene, their exposure is distinctly regulated as part of current occupational exposure limits. Further research as well as larger epidemiological studies is needed to provide a better understanding of different levels of occupational exposure to UFPs.^[87]

2.10 Concluding paragraph

This literature study elucidated on available scientific literature related to AM process categories, feedstock materials, occupational exposure during AM, exposure routes, potential health effects and toxicity respectively associated with AM and AM feedstock materials. The relevant terminology used regarding AM, a brief history of AM both internationally and in South Africa have been discussed, which was followed by the classification of the AM process categories, descriptions of the technology types and AM feedstock materials. Throughout this literature study emphasis was placed on PBF, DED, and metal feedstock materials as used by these process categories. In Chapter 3 of this thesis powder characterisation was performed for new and used titanium powders in order to investigate the relevance of these powders on the respiratory health of the AM operator. There is a body of literature that has provided a better understanding on particle emissions from FDM™ 3D printers, however, most conducted studies on particle emissions and exposure have been in controlled environments.^[71,96] Chapter 4 and Chapter 5 of this thesis are the first studies of its kind in South Africa to investigate and report on emissions from and AM respiratory exposure in industrial AM work environments.

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CHAPTER 3: ARTICLE I

du Preez S, de Beer DJ, du Plessis JL. (2018) Titanium powders used in Powder Bed Fusion: its relevance to respiratory health. Accepted (16 October 2018) for publication in *The South African Journal of Industrial Engineering*.

3.1 Instructions to authors

The South African Journal of Industrial Engineering (SAJIE) publishes articles with the emphasis on research, development and application within the fields of Industrial Engineering and Engineering and Technology Management. In this way, it aims to contribute to the further development of these fields of study and to serve as a vehicle for the effective interchange of knowledge, ideas and experience between the research and training oriented institutions and the application oriented industry. Articles on practical applications, original research and meaningful new developments as well as state of the art surveys are encouraged.

3.2 Author Guidelines

Manuscript format:

All submissions must be as per the guidelines. Authors are required to conform to the instructions and format of the Word template for use by authors. The Title Page should conform to the following centred format. The text of the article should only start on the next page. The Trebuchet font at 9 point size, single spacing and a page margin of 20 mm along the sides and 20 mm at the top and 25 along the bottom, gutter 10 mm, gutter position left, with full justification, should be used on B5 paper size. Header and footer layout 15 mm.

Figures and Tables:

Figures and tables should fit within the prescribed margins and should form an integral part of the article and be numbered consecutively in Arabic numerals. Labelling and lettering of figures and tables should be Trebuchet at 8 point size.

References:

References in the text should be by author with the reference number in square brackets e.g. Li[1]. References should be in order of appearance. The required reference format is illustrated below.

Reference examples:

Article, journal:

- [1] **Neale, J. and Kamp, P.** 2009. Compressed air system best practice programmes: What needs to change to secure long-term energy savings for New Zealand, *Energy Policy*, 37(9), pp. 3400-3408.
- [2] **Vosloo, J., Liebenberg, L. and Velleman, D.** 2012. Case study: Energy savings for a deep-mine water reticulation system, *Applied Energy*, 92, pp. 328-335.

Book:

- [3] **Li, J.C.R.** 1964. *Statistical Inference*, 3rd Edition, McGraw-Hill.
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TITANIUM POWDERS USED IN POWDER BED FUSION: ITS RELEVANCE TO RESPIRATORY HEALTH

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ABSTRACT

This study aimed to characterise three titanium powders used in Powder Bed Fusion in terms of particle size, shape and elemental composition for comparison with Safety Data Sheet (SDS) information, and the relevance thereof to additive manufacturing (AM) operator's respiratory health. Thoracic (< 10 µm) and respirable (< 4 µm) particles were present in the virgin and used powders. If inhaled, these particles have the potential to cause adverse health effects. Discrepancies in particle size and elemental composition to what was declared in the SDSs were found. SDSs provided insufficient information that places AM operators' health at risk. Recommendations promoting AM operator health are provided.

OPSOMMING

Hierdie studie se doel was om titaanpoeiers wat tydens poeierlaagsamesmelting gebruik word te karakteriseer volgens partikel grootte, vorm en materiaal element samestelling vir vergelyking met 'n veiligheidsdatavel (VDV) en die relevansie daarvan op die respiratoriese gesondheid van die additiewe vervaardigings operateur. Torakale (< 10 µm) en respireerbare (< 4 µm) partikels was in nuwe en herbruikte poeiers teenwoordig, en indien ingeasem word kan dit tot ongewenste gesondheidseffekte sal lei. Teenstrydighede is in die partikel groottes en element samestelling teenoor wat in die VDVe verklaar word, gevind. VDVe verskaf nie genoegsame inligting nie en hou dus 'n gesondheidsrisiko vir die operateur in. Aanbevelings vir die bevordering van die operateur se gesondheid word verskaf.

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INTRODUCTION

Powder Bed Fusion (PBF) is described as the leading additive manufacturing (AM) technology for the production of three-dimensional metal structures [1]. PBF technologies make use of either a laser or an electron beam to melt and fuse metal powder particles together. The metals powders used include titanium, titanium alloys and numerous stainless steel and other metal alloys. Titanium and its alloys is of importance and interest due to its broad application in the aerospace, the medical and the automotive industries [2]. When other elements are alloyed with titanium three classes of alloys form namely alpha alloys, alpha-beta alloys and beta alloys each with their distinctive properties [3]. Ti₆Al₄V is the most widely used titanium alloy and consists of 6% aluminium, 4% vanadium, 0.3% (maximum) iron, 0.2% (maximum) oxygen, and the remainder titanium [4-5].

Despite the fact that the build (processing) phase of AM is an enclosed process, AM (machine) operators may be exposed through inhalation to metal feedstock powders during the pre-processing and post-processing phases. Exposure can either be to virgin (new) powders (as provided by the powder manufacturer) or to used (recycled) powders. The pre-processing phase involves manual tasks such as vacuum cleaning of the AM machine build chamber to remove unmelted or unsintered powder, the handling of powder for size-selective powder sieving, and the loading of the powder into the AM machine feedstock bins. The post-processing phase involves manual removal of the printed part(s) from the build chamber and manual removal of unmelted/-sintered powder, but may also include sanding, drilling and sawing tasks to finish the product [6-7].

To date, several studies have investigated the particle emissions from smaller desktop fused deposition modelling (FDM™) 3D printers using acrylonitrile butadiene styrene (ABS) and poly lactic acid (PLA) filaments and found that these printers are high emitters of particulate matter [8-11]. Indoor air quality decline during long build periods due to particle emissions [8] is of concern due to its association with potential adverse health effects [12-13]. Recently, a case of work-related asthma was reported in an AM operator using FDM™ printers with ABS filaments [14]. However, emission information for other AM technologies are limited. Graff *et al.* [7] and Mellin *et al.* [15] reported the presence of submicron (< 1 µm) and ~1-2 µm particles that contained chromium, cobalt and nickel during the selective laser melting (SLM) from Inconel 939 alloy powder. Graff *et al.* [7] also reported the presence of smaller particle sizes in reused feedstock powders when compared to virgin powders.

The size and chemical composition of AM powders are of importance when considering the respiratory health of AM operators. Particle size determines whether particles are inhalable, and if inhalable where it may be deposited in the respiratory tract [12],[16]. Particles can be classified into size fractions, namely inhalable, extrathoracic, thoracic or respirable particles depending on the regions of penetration. Inhalable particles (< 100 µm) (50% cutpoint) are inhaled through the nose and mouth and is deposited in the nasopharyngeal region. Extrathoracic particles are inhaled, but do not penetrate beyond the larynx. Thoracic particles (50% penetration of particles with an aerodynamic diameter of 10 µm) can penetrate beyond the larynx, while respirable particles (50% penetration of particles with an aerodynamic diameter of 4 µm) can penetrate the unciliated airways and are deposited in the alveolar region of the lungs [17-19]. The chemical composition of inhaled particles is important when investigating possible health effects [20]. Each metal constituent of AM powders potentially poses a different respiratory health hazard. Titanium and iron inhalation may lead to respiratory irritation including coughing and sneezing while long-term inhalation of aluminium dust may lead to pulmonary fibrosis [21-23].

The purpose of a safety data sheet (SDS) is to provide information on chemical safety, potential hazards (health, fire, reactivity and environmental) and safe work practices for a specific chemical product. It serves as an essential starting point for the development of a complete health and safety programme in the workplace [24]. SDSs, provided with substances hazardous to health, are fundamental in evaluating the health and safety of a workplace [25]. Slotwinski and Garboczi [26] and Graff *et al.* [7] indicated that AM powder suppliers in most cases only declare a particle size range for virgin powders. Limited information provided in these SDSs and no safe operating guidelines in user manuals, could wrongfully provide for a false sense of protection of AM operator health [27], while in reality a risk to health may exist.

The aim of this study was to establish the particle size distribution (PSD), shape and elemental composition of titanium powders obtained from three AM facilities located in South-Africa in order to compare it with corresponding information declared in the SDSs of these powders. Furthermore, the relevance of any potential discrepancies or shortcomings in SDS information toward AM operator's respiratory health was explained and recommendations are provided to both AM powder manufacturers/suppliers and the end users thereof.

MATERIALS AND METHODS

Samples of virgin and used (recycled) titanium powders and their respective SDSs were collected from three AM facilities in South Africa utilising PBF. Samples were placed into separate storage vials for analysis. Particle size was evaluated by means of particle size distribution (PSD), and static image analysis [scanning electron microscopy (SEM)]. Particle shape was evaluated through static image analysis of dry dispersed powders. X-Ray diffraction (XRD) analysis was conducted to determine the elemental composition of powders.

Particle size and shape evaluation and analysis

PSD analysis by laser diffraction was conducted using a Malvern Mastersizer 2000 particle size analyser and its associated software (Malvern Instruments Ltd., United Kingdom). Virgin and used powder samples were analysed individually by mixing with a dispersing agent (1 ml of 99.9% purity ethanol). Prior to each measurement, a background measurement was performed. After completion of the background measurement a sufficient quantity of the raw powder was added to render an obscuration of 10 to 20%, where after, the particle size measurement was made. All samples were analysed in triplicate.

Particle shape evaluation was conducted using the Malvern Morphologi G3 with its associated software (Malvern Instruments Ltd., United Kingdom). Each powder sample (5 mm³) was placed in the instrument's sample dispersion unit. After powder dispersion, images of individual particles were captured and analysed by automatic microscopic scanning. All samples were analysed in triplicate.

SEM analysis was conducted by placing approximately 3 to 5 mm³ of powder on double-sided adhesive carbon strips and preparing the samples for observation of their surface topography by coating using an SPI Module sputter coater (SPI-Module™, Sputter Coater, SPI Supplies, USA) fitted with a gold palladium source. Samples were studied using a Phenom pro-desktop SEM (Phenom PRO Desktop SEM, Phenom-World B., the Netherlands) at a power of 5 kV at magnifications enabling visualisation of particles 100 µm and < 10 µm in size.

Elemental composition analysis

XRD analysis was conducted on powder samples using a powder diffractometer (X'Pert Pro XRD, PANalytical, Netherlands). The preparation method involved finely pulverising the powder and placing the undiluted powder samples, using a back-loading technique, onto a spinner stage inside the XRD. The samples were then scanned using X-rays generated by a Cu X-Ray tube (PW3376/00 Co LFF tube, PANalytical, Netherlands).

Statistical analysis of data

PSD and shape of virgin and used powders were compared with unpaired t-tests (Graphpad Prism, version 7, Graphpad Software Inc., USA). All p values ≤ 0.05 were considered as statistically significant.

RESULTS

The particle sizes of three titanium powders were compared to that declared in the representative powders SDS'. The PSD from Facility A's virgin Titanium 64 (Ti64) powder was in accordance to the SDS with no particle sizes measured larger than 50 µm (Table 1). Ten percent of virgin particles were < 11.11 ± 0.69 µm. Facility B's powder SDS indicated that the Ti₆AlV₄ virgin powder should contain particles in a size range of 25 to 45 µm, however 10% of particles were smaller than 25.78 ± 0.59 µm and particles larger than 45 µm [d(0.9) = 67.37 ± 2.70 µm] was also found. The SDS of Facility C's powder did not state any particle size for the CL41Ti EL (titanium alloy / Ti₆AlV₄) powder. The measured particle size results for the CL41Ti EL powder indicated that 10% of particles was smaller than 16.57 ± 0.44 µm for virgin powders and 10% was smaller than 20.96 ± 1.04 µm for used powders. In AM, powders are often recycled and reused. There were no significant differences found in the PSD of virgin and used powders, with the exception of CL41Ti EL powder, where the d(0.1), i.e. the mean size of 10% of particles, was significantly higher and the d(0.9) significantly lower for the used powder. From SEM images, thoracic (< 10 µm) and respirable (< 4 µm) particles were observed in powders from all three facilities (Figure 1). Static image shape analysis indicated that powder particles from all three facilities were spherical in shape with smooth surfaces. No significant changes in particle circularity and edge roughness (convexity) were evident between virgin and used powders.

The elemental composition analysis (XRD analysis) of all three powders differed from the composition stated in the respective SDSs. The titanium percentage in the Ti64 powder (Facility A) and CL41Ti EL powder (Facility C) were slightly higher, respectively 2.6% and 5.1%, than that stated in the SDSs. For Ti₆AlV₄ (Facility B) only the aluminium percentage was listed in the SDS. The aluminium and vanadium composition also differed from the reported SDS composition for all three powders. Rutile, is a common form of titanium dioxide (TiO₂) [4] and was identified in the CL41Ti EL powder (Facility C) although it was not listed as such in the SDS. XRD analysis also revealed differences in elemental composition between virgin and used Ti64 and CL 41 Ti EL powders.

RESULTS

Table 1 SDS information, PSD, particle shape and SEM analysis of virgin and used titanium powders. Data reported as mean $\pm$ standard deviation

	Powder	Type	SDS (μm)	PSD (μm)			Circularity number distribution	Convexity number distribution	SEM*
				d(0.1)	d(0.5)	d(0.9)			Respirable particles (< 4 μm)
Facility A	Ti64	Virgin	6 - 50	11.11 $\pm$ 0.69	20.84 $\pm$ 1.16	40.78 $\pm$ 6.08	0.95 $\pm$ 0.001	0.99 $\pm$ 0.001	Yes
		Used	-	11.33 $\pm$ 0.35	20.86 $\pm$ 0.68	44.17 $\pm$ 0.66	0.91 $\pm$ 0.004	0.99 $\pm$ 0.001	Yes
Facility B	Ti ₆ Al ₄ V	Virgin	25 - 45	25.78 $\pm$ 0.59	41.63 $\pm$ 0.47	67.37 $\pm$ 2.70	0.96 $\pm$ 0.003	1.00 $\pm$ 0.001	Yes
		Used	-	27.15 $\pm$ 0.52	42.26 $\pm$ 1.76	65.90 $\pm$ 4.74	0.95 $\pm$ 0.002	0.99 $\pm$ 0.001	Yes
Facility C	CL41Ti EL	Virgin	Not stated	16.57 $\pm$ 0.44 ^a	29.61 $\pm$ 0.45	55.63 $\pm$ 7.08 ^b	0.97 $\pm$ 0.003	1.00 $\pm$ 0.001	Yes
		Used	-	20.96 $\pm$ 1.04 ^a	30.43 $\pm$ 0.69	43.83 $\pm$ 0.82 ^b	0.96 $\pm$ 0.002	1.00 $\pm$ 0.001	Yes

Legend: d(0.1) 10% of the particles are smaller than the stated diameter; d(0.5) 50% of the particles are smaller than the stated diameter; d(0.9) 90% of the particles are smaller than the stated diameter. - Not indicated in SDS. ^{a-b} Statistically significant differences ($p \leq 0.05$). Circularity: The ratio of the perimeter of a circle with the same area as the particle divided by the perimeter of the actual particle image. Convexity: Measurement of the edge roughness of a particle. *Based on visual evaluation of SEM images.

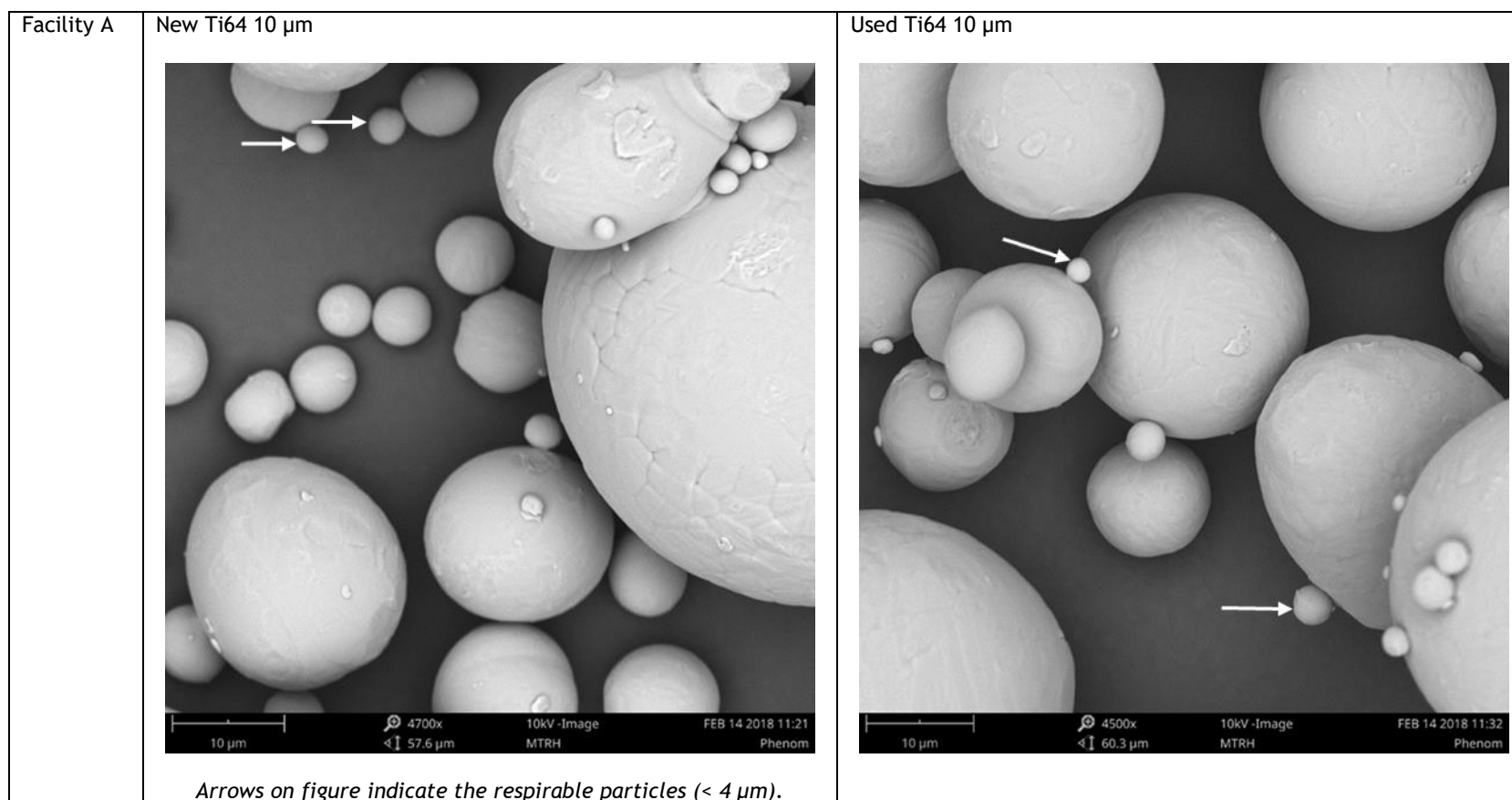
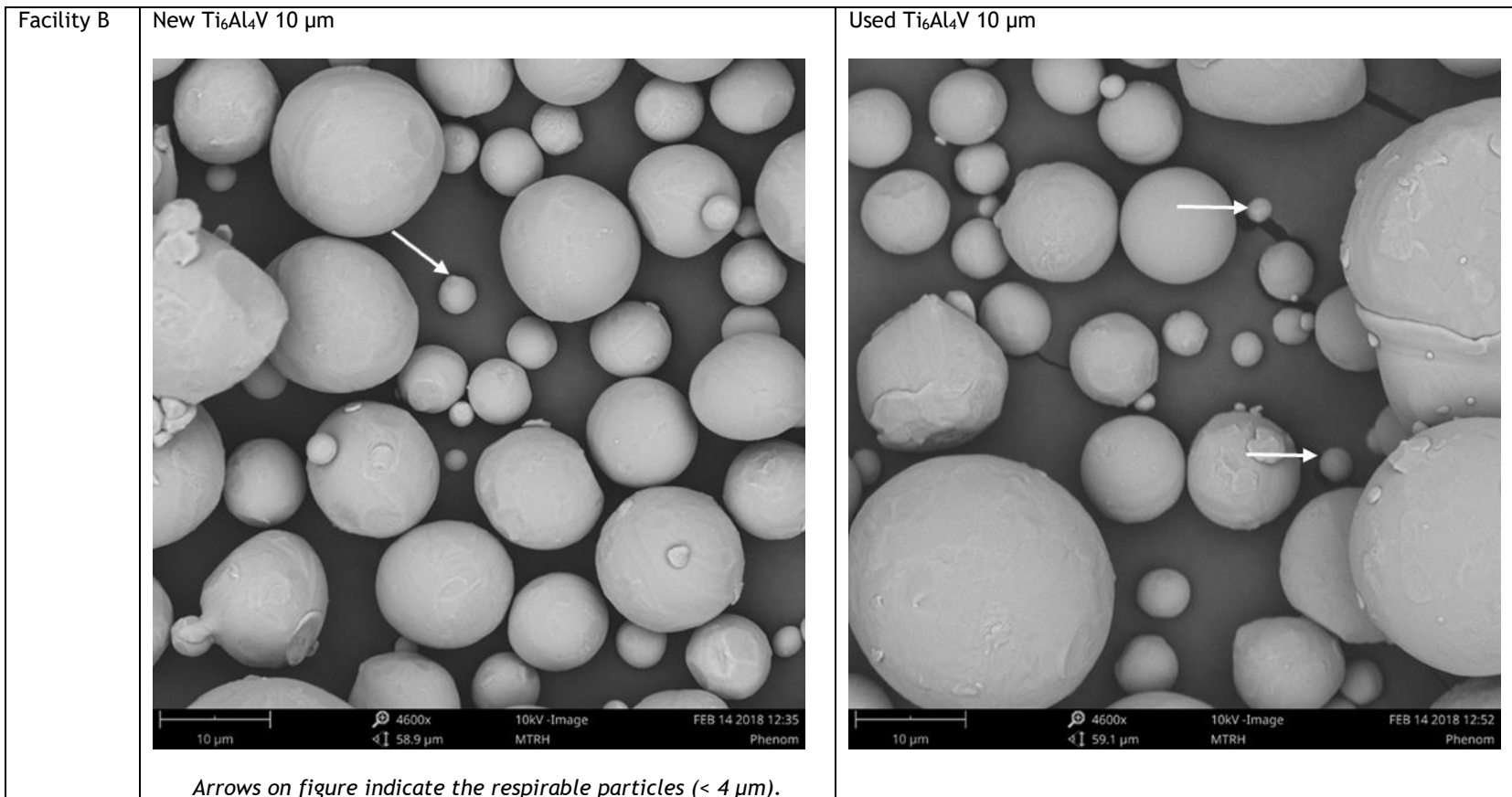


Figure 1 SEM images from virgin and used titanium powders from Facility A, B and C on a 10 μm scale showing the presence of respirable particles.



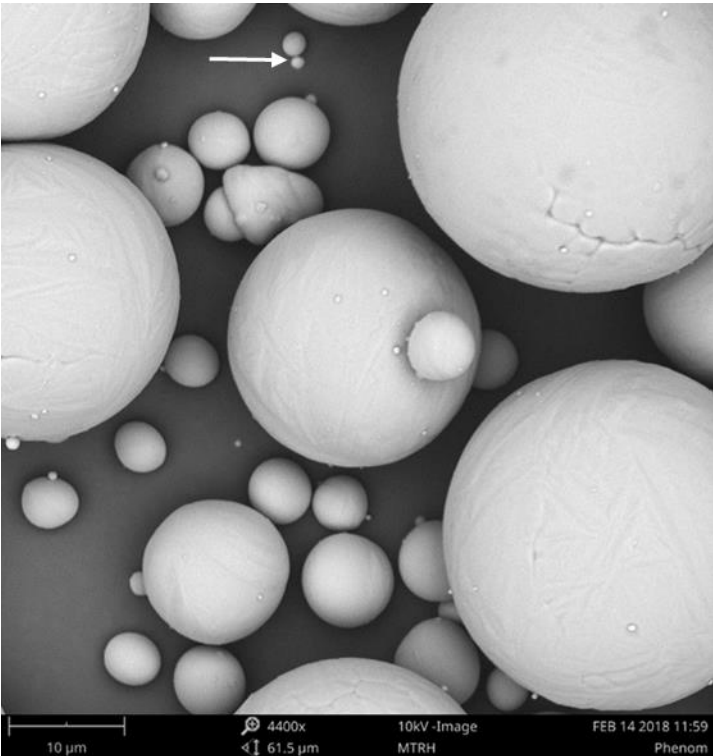
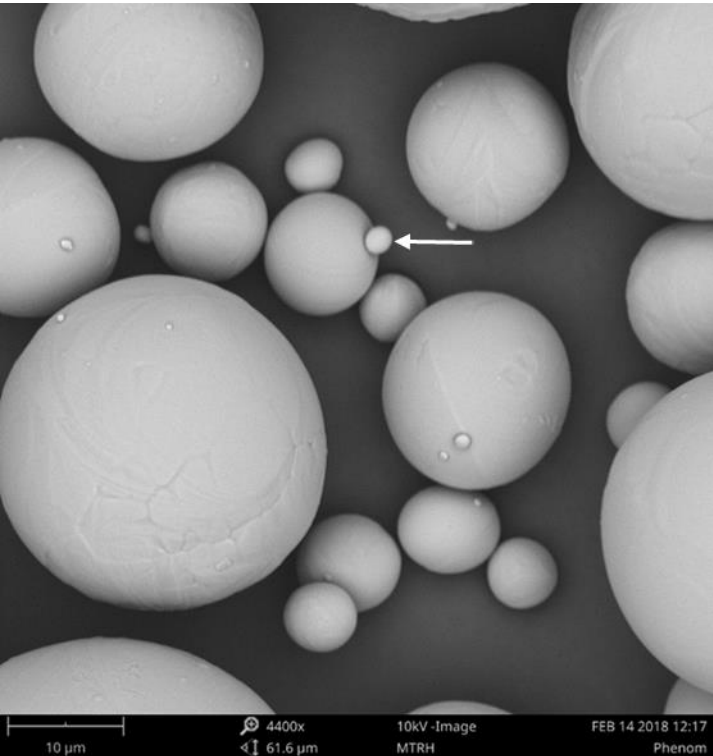
Facility C	New CL41Ti EL 10 μm  Arrows on figures indicate the respirable particles (< 4 μm).	Used CL41Ti EL 10 μm 
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Table 2 Elemental composition of virgin and used titanium powders

Facility	Powder	Sample	SDS/XRD	Elemental composition (%)				
				Titanium (Ti)	Aluminium (Al)	Vanadium (V)	Iron (Fe)	Rutile
A	Ti64	Virgin	SDS ^a	89.00-90.00	5.50-6.75	3.50-4.50	<3000 ppm	-
			XRD	92.60	7.40 ^b	-	-	-
		Used	XRD	86.00	14.00 ^b	-	-	-
B	Ti ₆ Al ₄ V	Virgin	SDS ^c	-	5.00-10.00	-	-	-
			XRD	93.9	4.5	1.6	-	-
		Used	XRD	94.2	4.3	1.5	-	-
C	CL41Ti EL	Virgin	SDS ^d	88.40-90.40	5.50-6.50	3.50-4.50	0-0.25	-
			XRD	95.50	4.30 ^b	-	-	0.20
		Used	XRD	95.10	4.90 ^b	-	-	-

- Not indicated in SDS ^aSDS also report O < 2000 ppm, N < 500 ppm, C < 800 ppm, H < 150 ppm; ^bXRD analysis reported AlV; ^cOnly Al is listed in the SDS; ^dSDS also report C 0 - 0.08%, O 0 - 0.13%, N 0 - 0.05%, H 0 - 0.012%. Rutile is the most common form of titanium dioxide (TiO₂) [4].

DISCUSSION

There is limited knowledge of emissions and exposure for AM process categories other than material extrusion (FDM™). To date, only two studies have indicated that particles containing metals are emitted from PBF (Selective Laser Melting) when using a nickel based Inconel 939 powder [7],[15]. Mellin *et al.* [15] also emphasised that the SDSs of the above-mentioned powder, as provided by the manufacturer/supplier, disclosed minimal information on the size of powder particles. To address this knowledge gap we compared the particle size and chemical composition of PBF titanium powders as declared in the SDSs to that obtained from our own particle size, shape and elemental composition evaluation.

PSD analysis of virgin powders indicated particle size conformance to that stated in the SDS for only one of the three powders included in this study (Facility A, Ti64). For the virgin Ti₆Al₄V powder, 10% of the powder particles were equal to or smaller [$d(0.1) = 25.78 \pm 0.59 \mu\text{m}$] than the minimum particle size (25 μm) stated in the SDS, while the SDS stated no particles size for the CL41Ti EL powder (Facility C). The SDS conformance of the one powder used in this study (Ti64) is in agreement with the finding of Graff *et al.* [7] who stated that the virgin powder particle size of an Inconel 939 powder corresponded to the size disclosed by the manufacturer. However, the presence of smaller sized particles in the Ti₆Al₄V powder and the non-disclosure of particle size of the CL41Ti EL powder confirms shortcomings in the respective SDSs. Recycled/reused powder particle sizes [$d(0.1)$, $d(0.5)$, $d(0.9)$] were similar than virgin powder particle sizes, except for the CL41Ti EL powder, where the virgin powder particles was statistical ($p \leq 0.05$) significantly smaller than that of the recycled/reused powder [$d(0.1)$]. Our findings are supported by Graff *et al.* [7] who reported that used Inconel 939 powder particle sizes corresponded to that of the virgin powder (15 to 45 μm), and Mellin *et al.* [15] finding spherical, smaller particles 1 to 5 μm in size in the recycled Inconel 939 powder. Mellin *et al.* [15] argued that these smaller particles are satellites, formed during powder manufacturing, that detaches from larger particles during the handling, shearing or heating of the powder.

Particles of all three powders, virgin and reused, are considered to be inhalable (Ti64 > Ti₆Al₄V > CL41Ti EL), with an estimated 9.1% of inhaled Ti64 particles [$d(0.5) = 20.84 \pm 1.16 \mu\text{m}$] being able to penetrate beyond the larynx and almost 0.9% thereof [$d(0.1) = 11.11 \pm 0.69 \mu\text{m}$] being able to reach the unciliated airways [17]. Static image shape analysis and SEM images showed the presence of spherical, smooth surfaced respirable powder particles < 4 μm in all three powders (virgin and reused) that supports the finding and explanation for their presence as provided by Mellin *et al.* [15]. From a health perspective, it is estimated that 99.6% of all inspired 4 μm sized particles will penetrate beyond the larynx, with 55.9% of these particles reaching the unciliated airways [17]. These respirable particles, therefore, penetrate deep into the lungs and may not be easily removed/cleared from the respiratory system and may be absorbed or elicit toxic effects [12],[18],[28]. Regardless of composition, repeated inhalation thereof over a long period of time, are in all likelihood hazardous [15].

Elemental composition analysis of virgin powders differed from the composition disclosed in the SDSs. For all three powders our analysis found slightly more titanium and consequentially less aluminium and vanadium (Table 2) when compared to the provided SDSs. Rutile, the most common form of titanium dioxide (TiO₂) in titanium ore [4],[29], was present in the CL41Ti EL powder, while we did not detect any iron. Our findings again confirm that there are shortcomings in the information provided by powder manufacturers in SDSs. Used powder's properties may change in the AM build chamber environment due to the repeated (recycled) use [30], and our analysis found less titanium present in the used Ti64 powder when compared to the virgin powder.

Titanium alloy AM powders contain several metals such as titanium, iron, aluminium and vanadium, that present a potential risk to health when inhaled. There is a lack on epidemiological studies on the health effects of titanium. However, titanium exposure along with co-exposure to other metals may cause an impaired immune response and cytokine release [31]. Titanium is highly reactive, and in the presence of oxygen, leads to the formation of TiO₂. Although TiO₂ is toxicologically inert, with the exception of nano-sized (<100 nm) TiO₂, it is considered to be a nuisance particulate [32]. Nuisance particulates are defined as airborne materials which have little harmful effect on the lungs, it may reduce visibility and deposits in eyes, ears, and nasal passages [24],[33].

Iron serves as a beta alloying element in titanium metal powders adding to the strength and fabricability of these alloys [3]. Inhalation of iron dust may lead to respiratory irritation and aluminium dust can possibly cause pulmonary fibrosis of the lungs [21-23]. Vanadium is a trace element and adverse respiratory effects such as coughing, wheezing and sore throats could be observed in workers exposed to vanadium compounds [35-36]. In a study by Li *et al.* [36] it was also reported that exposure to vanadium compounds can cause renal and neurotoxicity, and demonstrated an association between vanadium exposure and altered neurobehavioral function [36].

To summarise AM PBF powders investigated in this study are inhalable, containing thoracic and respirable sized particles with the potential to deposit beyond the larynx and alveoli if inhaled. The elemental composition

suggest the potential risk of respiratory health effects, therefore, AM operators handling powders should be informed about the health risks of the powders that they work with and proper control measures should be in place to reduce and/or eliminate respiratory exposure. Further studies assessing emissions during PBF and personal exposure of AM operators during titanium metal powder handling and processing tasks are required.

Our finding is that the majority of SDSs of metal AM powders have shortcomings when disclosing particle size and elemental composition. A SDS is an essential, legally required document provided by a manufacturer/supplier of in this case, the AM metal powder, for usage in an occupational setting [24],[37]. SDSs are intended to be a primary health and safety resource for employers and employees and should provide information about chemical safety, potential hazards (health, fire, reactivity and environmental), and safe work procedures (handling, and storage), for a specific substance [24]. A correct and comprehensive SDS should contribute toward effective decision making regarding employee health and wellbeing starting with the execution of initial health risk assessments and consequently the implementation of appropriate control measures, by the employer, aimed at reducing and/or eliminating exposure to the specified substance. Furthermore, occupational health and safety legislation, in this case the South African Occupational Health and Safety Act (Act 85 of 1993), require of manufacturers to ensure that the supplied substance, if properly used, is safe and contains no risk to the health of the person using it (Section 10) [38]. If, however a safety or health risk exists, the manufacturer/supplier should ensure that information is available regarding the risk to health and safety associated with the substance [38]. This will enable the employer to assess the risk, but also to reduce or eliminate the risk (Section 8). Our particle size and elemental composition findings, which differed in most instances from the SDSs, are of concern as it provides insufficient information to the employer and the AM operator about the powder composition and each element's potential health risks. Findings from this study suggest circumstances in which the inaccurate/incomplete SDS could create a false sense of protection of AM operators' health. It is therefore recommended that manufacturers should provide accurate and comprehensive information in SDSs on, in particular, the particle size and elemental composition of the AM powders. The AM operator should be able to refer to the SDS as a guidance for safe powder handling, and should be informed of the potential health risks involved. Of equal importance is that if an employer or an AM operator identifies an incomplete SDS, characterisation of the powder, in terms of particle size and elemental composition, be done before usage thereof.

Furthermore, Regulation 3 of the South African Hazardous Chemical Substances (HCS) Regulations (1995) states that an employer should ensure where a worker, in this case the AM operator, may be exposed to hazardous chemical substances (i.e. AM powders), he/she receives adequate training. The worker (AM operator) also has a responsibility, and according to Regulation 4 of the above mentioned regulations, the worker should obey instructions from the employer in preventing release and consequentially exposure to substances, the wearing of the correct personal protective equipment, the maintenance of proper housekeeping procedures in the workplace, and following the information and training provided by the employer.

CONCLUSION

This study investigated three different AM titanium alloy powders (virgin and used) along with their relevant SDSs and analysed the powders in terms of particle size, shape and elemental composition. Thoracic ($< 10 \mu\text{m}$) and respirable ($< 4 \mu\text{m}$) metal containing particles were present in the virgin and used powders, if inhaled these metal containing particles have the potential to cause adverse health effects. From the results only a small percentage of particles are able to penetrate beyond the larynx, although short term health effects may not immediately be experienced by AM operators, repeated inhalation thereof over a long period of time, may be hazardous. Discrepancies in particle size and elemental composition to what was declared in the SDSs were found. This study creates a better understanding of virgin and used titanium powders that AM operators in PBF are exposed to and highlights the shortcomings in SDS information. Recommendations, in line with occupational health and safety legislation, are provided to assist and guide manufacturers, employers and AM operators on promoting AM operator health.

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CHAPTER 4: ARTICLE II

du Preez S, de Beer DJ, du Plessis JL. (2018) Particle emissions and metal exposure during Powder Bed Fusion Additive Manufacturing using titanium powders. Submitted to *The Journal of Occupational and Environmental Hygiene* to be considered for publication.

4.1 Instructions to authors

The Journal of Occupational and Environmental Hygiene (JOEH) is a joint publication of the American Industrial Hygiene Association (AIHA®) and ACGIH®. The *JOEH* is a peer-reviewed journal devoted to enhancing the knowledge and practice of occupational and environmental hygiene and safety by widely disseminating research articles and applied studies of the highest quality. The *JOEH* provides a written medium for the communication of ideas, methods, processes, and research in core and emerging areas of occupational and environmental hygiene. Core domains include, but are not limited to: exposure assessment, control strategies, ergonomics, and risk analysis. Emerging domains include, but are not limited to: sensor technology, emergency preparedness and response, changing workforce, and management and analysis of "big" data.

4.2 Author Guidelines

Formatting requirements:

Manuscripts should be doubled spaced, except for the title page and figure/table legends which should be single spaced. Times New Roman 12 point font should be used except for section heading which should be ALL-CAP Bold text 16 point font. Sections include Title page, Abstract, Introduction, Methods, Results, Discussion and Conclusions, Acknowledgements, References, Figure and Tables. The abstract should state briefly the purpose of the research, the principal results and major conclusions. A minimum of three and a maximum of six keywords should be included in the manuscript.

Figures and Tables:

Figures should be added after the Reference section, and tables should follow after figures. The figure number and caption should be added below each figure using Arabic numerals to identify figures (e.g., Figure 1), figures should be single spaced. Table legend should be

singles spaced and titles of tables should be placed above each table using Arabic numerals to identify tables (e.g., Table 1). Page orientation can be portrait or landscape.

References:

References should be numbered sequentially in the order cited in the text and appear in text as superscript Arabic numerals enclosed in brackets and placed immediately to the right of any punctuation. Multiple, sequential references should be cited using the first and last number, e.g., ^[4-8]. For multi-authored articles up to six names should be listed, for more than six authors the first three should be listed followed by “et al.”. For example: “Smith et al. ^[4] found...” Publication titles and dates should not be listed in the body of the text. References should be cited only by superscript number or by author’s name and superscript number.

Reference examples:

Article, journal:

Miller, A.B., T. To, D. Agnew, C. Wall, and L. Green: Leukemia following occupational exposure to 60-Hz electric and magnetic fields among Ontario electric utility workers. *Am. J. Epidemiol.* 144:150–160 (1996).

Book:

Frymoyer, J.W.: *The Adult Spine: Principles and Practice*. New York: Raven Press, 1991. pp. 40–50.

Chapter in a Book:

Andersson, G.B.J.: Evaluation of Muscle Function. In *The Adult Spine: Principles and Practice*, J.W. Frymoyer (ed.). New York, NY: Raven Press, 1991. pp. 241–274.

Conference Presentation – Unpublished:

Wollen, G.H., G.T. Steel, and M.G. Hall: “Dinitrotoluene: Assessment of Absorption During Explosives Manufacture.” Poster presented at the International Seminar on Method of Monitoring Human Exposure to Carcinogenic and mutagenic Agents, Helsinki, Finland, December 11–15, 1983.

Conference Presentation – Published (Proceedings):

Published papers should follow the format for “Chapter in a Book” reference.

Internet Sources:

Author (if known): "Hazardous Substance Data Bank. Isopropylbiphenyl." Available at <http://toxnet.nlm.nih.gov/servlets/simple-search> (accessed May 11, 1999).

Standards:

American Industrial Hygiene Association (AIHA): Hearing Protection Standard (ISO 2300).
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Particle emissions and metal exposure during Powder Bed Fusion Additive Manufacturing using titanium powders

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Keywords: titanium, aluminium, vanadium, respiratory exposure, submicron particles, nanoparticle respiratory deposition sampler

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ABSTRACT

Purpose of work:

Powder Bed Fusion (PBF) is a prominent additive manufacturing (AM) process category for the production of 3D metal structures; however, research on emissions from and personal exposure of AM operators to hazardous chemical substances (HCS) (particles and metals) are limited. The purpose of this study was to assess particle emissions (0.01 to 10 μm) from and additive manufacturing (AM) operators' respiratory exposure to metals during the pre-processing, processing and post-processing phases of Powder Bed Fusion (PBF) at three industrial additive manufacturing (AM) facilities using titanium powders.

Methods:

Particle emissions were measured with a Condensation Particle Counter in a size range of 0.01 to $>1\ \mu\text{m}$ and an Airborne Particle Counter for particles sized 0.30 to 10.00 μm . Static area monitoring of metals took place at close proximity to AM workstations. Personal exposure monitoring of metals was performed according to the National Institute for Occupational Safety and Health method 7300 using closed-faced cassette samplers worn by the AM operators. Personal exposure to metals $< 300\ \text{nm}$, was assessed by using a nanoparticle respiratory deposition sampler.

Summary of results:

Particles $\leq 1\ \mu\text{m}$ were present in the workplace air. Increases in particle number concentrations were observed during specific pre- and post-processing tasks. Low concentrations of various metals were detected in the workplace areas of which titanium ($278.62\ \mu\text{g}/\text{m}^3$) and iron ($196.62\ \mu\text{g}/\text{m}^3$) was most prominent. AM operators were exposed to detectable concentrations of metals including aluminium, chromium, copper, iron, nickel,

titanium and vanadium during the three process phases, including metals < 300 nm in size. Full shift metal exposure was calculated for comparisons with Occupational Exposure Limits (OELs) and found personal exposure < 1.04% of the TWA-OELs.

Conclusion:

Particles $\leq 1 \mu\text{m}$ were emitted during pre-and post-processing phases indicating that PBF using titanium are high emitters of particles. Low concentrations of metals were present in the workplace atmosphere and AM operators were exposed to very low concentrations of metals (< 1.04% of the TWA-OELs), including < 300 nm metals. The findings of this study serve as a starting point to create awareness of AM operator exposure associated with metal AM, and to assist industrial AM facilities in identifying hazards and implementing phase and task specific control measures during PBF using titanium powders.

INTRODUCTION

Additive Manufacturing (AM) is the process of joining feedstock materials layer-by-layer at a time to produce objects from a three dimensional (3D) computer aided design (CAD).^[1,2] There are seven AM process categories used, one of which is powder bed fusion (PBF) which is described as being the dominant technology for the production of 3D metal structures. Also, PBF is one of the preferred process categories for utilising titanium and titanium alloys.^[2-4] Titanium and its alloys are of high value to AM due to their broad industrial application, especially in aerospace systems and their use in medical implants.^[4-6] Titanium (Ti) is often alloyed with other elements such as aluminium (Al), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), tin (Sn), molybdenum (Mo) and vanadium (V).^[7-9] Most of these metals are known to be hazardous to health. Long term inhalation of Al may

induce pulmonary fibrosis.^[10,11] Cu is a respiratory irritant, while Fe is associated with fibrotic and non-fibrotic damage in the lungs.^[10-12] Ti is highly reactive in the presence of oxygen, which leads to the formation of titanium dioxide (TiO₂), and although TiO₂ is toxicologically inert, it is still classified as a nuisance particulate.^[13]

PBF technologies are based on the principle of laying down a feedstock powder layer onto the build plate/platform and scanning the bed of powder with a heat source.^[14] Powder feedstock is repeatedly spread over existing powder layers, using a roller or a blade.^[2,3] The heat source, either a laser or an electron beam, then fuses the selected area of each powder layer that is laid down. After each scan is completed the build plate/platform is lowered, to repeat the scan.^[4] Two widely used PBF technologies are direct metal laser sintering (DMLS) and selective laser melting (SLM).^[2,4] DMLS uses a laser for sintering, melting and bonding of powder, whereas SLM is a PBF technology which uses a laser to fully melt and bond each layer of metal powder rather than sintering the powder.^[14]

Although PBF machines are designed to operate unattended, powder handling is performed manually and potential occupational exposure can occur during the three phases of AM, namely the pre-processing, processing and post-processing phases.^[15,16] During pre-processing AM operators are exposed to feedstock powders when powder is manually sieved and potentially when powder bins/hoppers are unloaded and reloaded into the AM machine.^[15] The build process of a metal part takes place in an enclosed build compartment. Throughout the processing phase metal powder is melted which generates metal fumes that, if not properly removed by exhaust ventilation, may be released and inhaled by the AM operator. For PBF all printed parts require some form of post-processing which is usually performed manually and may contribute to exposure of AM operators.^[2,15,17,18] Once

manufactured, the build chamber is opened and the excess powder is removed from the metal part and build plate with a brush, where after the build plate with the part is removed. Powder trapped within the part can be removed by vacuuming before removal of support structures. Support structures are removed by grinding or machining. Lastly the inside of the AM machine is vacuumed and dry swept using a brush.^[19,20]

As AM has significantly advanced as a technology, efforts are needed to ensure the safety and health of the AM operator.^[15,21,22] To date, a number of studies have investigated the particulate emissions from smaller desktop material extrusion fused deposition modelling (FDMTM) 3D printers using acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA) filaments.^[22-26] These FDMTM printers are high emitters of potentially hazardous ultrafine particles (UFP) (i.e. particles < 100 nm) and emit low concentrations of numerous VOCs.^[27,28] There is, however, limited emission and exposure information available for AM process categories other than material extrusion, and less attention has been given to emissions from larger industrial AM machines using metal powders and exposure of AM machine operators during the different phases of AM.^[15,22,29]

Of the seven AM process categories, PBF is the most researched technology in terms of the feedstock materials used and technology development. However, research on emissions from PBF exposure of AM operators and potential health risks remains limited.^[15,22,30] This could be attributed to the small number of PBF machines in operation as well as the industrial size of the machines, limiting access to study emissions but also preventing studies in a controlled environment (chamber studies). AM feedstock powder is nominally 20 µm to 150 µm in this size, and is determined by the technology utilised.^[31] A study by Mellin et al.^[32] found small respirable metal particles in a size range of 1-2 µm

containing Ni, Cr and Co in recycled Inconel 939 powder, while Graff et al.^[15] showed that particles < 300 nm were present in the AM workplace air and that AM operators were exposed to Cr, Co, and Ni while handling Inconel 939 powder. The authors acknowledged that the PBF SLM process is an enclosed process under atmospheric control to avoid oxidation, but that emission of and exposure to powder particles is possible when powders are sieved (during pre-processing), when printed parts are removed and separated from excess powder, and when equipment is cleaned (post-processing).^[32] In a study by du Preez et al.^[33] the particle size distribution (PSD), shape and elemental composition of three AM (virgin and used) Ti powders were investigated and compared to their Safety Data Sheet (SDS) information. Discrepancies were found in what was declared in terms of particle size and elemental composition. The concern raised was that thoracic (< 10 µm) and respirable (< 4 µm) metal containing particles were present in both the virgin and used powders. If these metal containing particles are inhaled, they have the potential to cause adverse health effects.

Metal AM is described as a complex task carried out by highly skilled engineers requiring specific training as well as practical understanding of an AM system.^[19,31] The operation of an AM machine typically requires a single AM operator, and thus, less labour input is required. The production of metal AM parts is mostly customised or consumer specific and does not always entail mass production runs.^[31]

The investigation of personal exposure of AM operators to hazardous chemical substances (i.e. particles and metals) has not progressed significantly and it would therefore, be of value to conduct real life exposure studies in industrial workplace settings that reflect AM operator exposure.^[15,22,24] This is especially relevant to the South African AM industry, where AM operators mostly use titanium or titanium alloys as feedstock powder.

The aim of this study was to assess particle emissions (0.01 to > 10 µm) from, and AM operators' respiratory exposure to metals and metal particles < 300 nm in the workplace air during the pre-processing, processing and post-processing phases of PBF at three industrial AM facilities using titanium powders.

METHODOLOGY

This study was carried out at three large industrial AM facilities (Facility A to C) in South Africa utilising PBF.

Facility descriptions and phase descriptions

The three process steps, namely pre-processing (machine cleaning, sieving, hopper loading), processing and post-processing (grinding, manual cleaning, vacuuming), were monitored at two of the facilities (Facility A and B). The exception was Facility C where no data could be collected for the pre-processing phase. At Facility A, a DMLS machine (EOS M280, Germany) with Ti64 as the feedstock material was used. According to the SDS of the Ti64 powder, the powder contained Ti (89-90%), Al (5.50-6.75%), V (3.50-4.50%) and Fe (< 0.3%). The machine is equipped with an internal recirculating filter system. Fresh air was supplied to the room via one supply vent, and the room was intermittently staffed by one AM operator. At Facility A, post-processing took place in two stages, over a two day period. Facility B used a SLM machine (Aeroswift, South Africa) and Ti₆Al₄V as feedstock. The SDS of Ti₆Al₄V only listed Al (5.00-10.00%) in the elemental composition of the powder. During pre-processing two AM operators were involved, one operator being the primary AM operator and the other the assistant operator. Fresh air was supplied by windows open to outside air. At Facility C a SLM machine (M2 LaserCusing, Concept Laser, Germany) that

used CL41TiEL feedstock powder. CL41TiEL contained Ti (88.40-90.40%), Al (5.50-6.50%), V (3.50-4.50%), and Fe (< 0.25%). Although the room had windows to supply fresh air, the windows were not used, and always kept closed. The machine is equipped with an internal recirculating filter system. The room was intermittently staffed by one AM operator. It should be noted that all three AM facilities regularly use a variety of metal powders and the production is not limited to printing with Ti alloy powders only.

Static area monitoring (emissions)

Particle number concentrations (p/m^3) were measured by using a TSI™ Condensation Particle Counter (CPC) model 3007 (TSI Inc., USA), and a TSI AeroTrak™ Airborne Particle Counter (APC) model 9310 (TSI Inc., USA). The CPC detected the total number concentration in real-time of fine and ultrafine particles in a size range of 0.01 to $> 1 \mu\text{m}$. It should be noted that the CPC is designed to effectively count the smallest of nanoparticles. The maximum detectable size of a CPC is generally anywhere from $1 \mu\text{m}$ to $3 \mu\text{m}$. However, particles larger than approximately $1 \mu\text{m}$ are very easily lost due to inertial impaction, (nanoparticles are essentially unaffected by this loss mechanism) and these supermicron sized particles cannot penetrate through the CPC flow path to the detection region.^[34] The APC was used to determine the number concentration of particles sized 0.3 to $10 \mu\text{m}$. For the purpose of this study only the $0.30 \mu\text{m}$, $0.50 \mu\text{m}$ and $1.00 \mu\text{m}$ size fractions are presented in the Results section, since no particles $> 1 \mu\text{m}$ was detected. At all three facilities background concentrations were measured prior to the start of each process phase (pre-processing, processing or post-processing). Data was recorded at one second intervals, and presented at intervals in minutes on the figures as average particle concentrations per minute. The time duration of monitoring varied and were dependent on the tasks to be performed. All static area monitoring was performed at workstations, where the highest potential emission of

metals for all three process phases was anticipated, at a distance (less than 1 meter and 1.5 m above floor level) from the AM machine.

The concentration of metals in the workplace air was measured according to National Institute for Occupational Safety and Health (NIOSH) method 7300.^[35] Gilair (Sensidyne, Florida, USA) constant flow sampling pumps with mixed cellulose ester (MCE) filters (SKC Pennsylvania, USA) (37 mm diameter, 0.8 µm pore size) in a closed-faced cassette (CFC) were used. Sampling pumps were calibrated at 2 l/min before and after use. Static area monitoring was performed for the duration of each AM processing phase. Sample analysis, in accordance to NIOSH method 7300, was conducted by a South African National Accreditation System (SANAS) analytical laboratory by means of inductively coupled plasma-mass spectrometry (ICP-MS). One field blank was included for each of the three samples for each process phase. Field blanks were handled, stored and transported in the same manner as the collected samples.

Personal respiratory exposure monitoring

Personal respiratory exposure monitoring corresponded to that used for static area monitoring with the exception of placement of the CFC which was worn by the AM operator and placed in the breathing zone (defined as the air around the worker's head). A sample was collected for each phase of AM. After analysis with ICP-MS to determine the mass of metals, the volume of air sampled and duration of the sample was used to calculate the time weighted average (TWA) exposure concentration for each metal. For metal mass below the analytical detection limit (DL), metal mass was calculated using the DL mass divided by the square root of two method to calculate TWA exposure.^[36] TWA was calculated to establish whether exposure complied with the specified legislative occupational exposure limit (OEL) set for

each metal. For this South African OELs as contained in the Hazardous Chemical Substances Regulations (HCSR) (1995)^[37] as well as the Threshold Limit Value (TLV[®]) of the *American Conference of Governmental Industrial Hygienists*^[38] was used. All AM machine operators involved in PBF at each facility participated in personal exposure monitoring. A total of four AM operators participated.

Graff et al.^[15] demonstrated that Co, Cr, and Ni-containing particles < 300 nm were present in AM workplace air. Therefore, personal exposures to particles < 300 nm, was assessed by using a nanoparticle respiratory deposition (NRD) (Zefon International, USA) sampler. This method has been used successfully to assess exposure to welding fume nanoparticles.^[39,40] The NRD sampler consists of a respirable cyclone (for the removal of particles > 4 µm) (50% cutpoint) an inertial impactor (for the removal of particles > 300 nm), and a diffusion stage (nylon mesh) where particles (< 300 nm) were collected, similar to their deposition in the respiratory tract.^[39,40] Sample analysis was also conducted with ICP-MS. Mines et al.^[41] reported that background metals were present in the nylon mesh of the sampler. In this study, the background metal mass (Cr and Ti) present in the nylon mesh of the NRD sampler reported by Mines et al.^[41] was subtracted from the measured metal mass.

Data analyses

The maximum, mean and standard deviation particle number concentrations for both the CPC and APC were calculated in Microsoft Office Professional Plus 2010 (Excel 2010, version 14.20) for static area monitoring (emissions) and background particle number concentrations. Within each particle size range, the significance ($p \leq 0.05$) between the means of background concentrations and phase particle number concentrations was investigated using the Unpaired t-test with Welch's correction and Mann-Whitney test for parametric and

non-parametric data, respectively. Furthermore, significant ($p \leq 0.05$) differences in particle number concentration means between the phases (pre-processing, processing and post-processing) were determined using the analysis of variance (ANOVA) (parametric data) and Kruskal-Wallis test (non-parametric data), followed by Tukey's and Dunn's multiple comparisons tests, respectively. The data distribution was determined using the D'Agostino and Pearson omnibus test. These statistical analyses were executed using GraphPad Prism 7 (GraphPad Software, La Jolla, USA).

Ethics approval

The scope of this study was described in detail in the informed consent form. All AM operators was invited to take part in this study, therefore, participants used for this research was voluntary as stated in the informed consent. This study was approved by the Health Research Ethics Committee of the North-West University (NWU-00004-16-A1).

RESULTS

Particle and metal emissions in the work areas are reported per facility and per process phase in order to describe activities/tasks that contributed to emissions. This is followed by personal exposure of AM operators to metals.

Particle and metal emissions

Throughout, at all three facilities, particle number concentrations in the 0.01 to $> 1 \mu\text{m}$ (Figure 1) size range measured by the CPC was higher when compared to that of the APC (0.30 μm , 0.50 μm and 1.00 μm size ranges) (Figure 2).

Background particle number concentrations ranged between $4.86 \times 10^7 \text{ p/m}^3$ ($0.3 \mu\text{m}$) to $0.41 \times 10^{10} \text{ p/m}^3$ (0.01 to $> 1 \mu\text{m}$) at Facility A (Figure 1, Supplementary Table S1). The 0.01 to $> 1 \mu\text{m}$ particle number concentration was significantly higher ($p \leq 0.0001$) during post-processing when compared to the background ($0.56 \pm 0.03 \times 10^{10} \text{ p/m}^3$ vs $0.72 \pm 0.08 \times 10^{10} \text{ p/m}^3$), reaching a maximum of $0.91 \times 10^{10} \text{ p/m}^3$ whilst grinding of the part took place (Figure 1, A3). The higher background concentration at the start of the processing phase could be ascribed to pre-processing that took place in the same room beforehand, followed immediately by processing (Figure 1, A2). The mean number concentration for 0.01 to $> 1 \mu\text{m}$ particles during the three process phases differed significantly from each other, with post-processing $>$ processing $>$ pre-processing (Table S1). For $0.30 \mu\text{m}$ and $0.50 \mu\text{m}$ sized particles a maximum of $6.68 \times 10^7 \text{ p/m}^3$ and $1.54 \times 10^7 \text{ p/m}^3$ was respectively measured during pre-processing (Figure 2, A1; Table S1). Machine cleaning and powder sieving lead to an increase in $0.30 \mu\text{m}$ sized particles emitted during pre-processing which was significantly higher ($p \leq 0.05$) than that emitted during processing and post-processing. A maximum of $0.38 \times 10^7 \text{ p/m}^3$ was emitted in the $1.00 \mu\text{m}$ size fraction during pre-processing.

At Facility B, pre-processing and post-processing particle number concentrations were higher than the background number concentrations in the 0.01 to $> 1 \mu\text{m}$ and $0.30 \mu\text{m}$ size ranges (Figure 1, B1; Figure 2, B1; Table S1). The higher particle number concentrations can be attributed to the tasks performed such as powder sieving and hopper loading (Figure 1 B1, pre-processing) and machine pre-build inspection. The transient increase in particle number concentration (both 0.01 to $> 1 \mu\text{m}$ and 0.30 - $1.00 \mu\text{m}$, Figure 1, B1; Figure 2, B1) during pre-build inspection could be ascribed to the machine doors being opened that in all likelihood released particles inside the build chamber into workplace area. In the 0.01 to $> 1 \mu\text{m}$ size range the maximum number concentration was $4.08 \times 10^{10} \text{ p/m}^3$. When

processing (printing) started, particle number concentrations fluctuated (Figure 1, B2; Figure 2, B2) with a maximum of $7.27 \times 10^7 \text{ p/m}^3$ emitted in the $0.30 \mu\text{m}$ size fraction. An increase in particle number concentration was observed during post-processing when manual cleaning of the printed part took place (0.01 to $> 1 \mu\text{m}$) (Figure 1, B3), while emissions from vacuuming of the printed part caused an initial decrease in particle number concentrations in the $0.30 \mu\text{m}$ size fraction and an overall increase in the 0.50 and $1.00 \mu\text{m}$ size fractions (Figure 2, B3). In the 0.01 to $> 1 \mu\text{m}$ and $0.30 \mu\text{m}$ particle size range there were significant differences ($p \leq 0.01$) in the particle number concentration between the three phases.

No data could be collected for pre-processing at Facility C. Number concentrations during the processing and post-processing phases in all size fractions (0.01 to $> 1 \mu\text{m}$ and 0.30 to $1.00 \mu\text{m}$) were significantly higher than the background (Table S1). The particle number concentration during the processing phase was significantly lower than that of the post-processing phase (Figure 1 C1; Figure 2, C1). In the $0.30 \mu\text{m}$ size fraction a gradual increase was observed during processing (Figure 2, C1), and a maximum concentration of $3.27 \times 10^7 \text{ p/m}^3$ was reached. A maximum of $6.12 \times 10^{10} \text{ p/m}^3$ was emitted in the 0.01 to $> 1 \mu\text{m}$ size fraction during the post-processing phase, when manual cleaning of the part took place (Figure 1, C2; Figure 2, C2). This was also evident in the $0.30 \mu\text{m}$, $0.50 \mu\text{m}$ and $1.00 \mu\text{m}$ size fractions with the highest number of particles emitted being $8.93 \times 10^7 \text{ p/m}^3$ ($0.30 \mu\text{m}$).

Table 1 summarises the airborne concentrations of metals within the workplace at all three facilities. Quantifiable concentrations of Al, Cr, Cu, Fe, Ni, Ti and V were detected in at least one sample, with Ti and Fe the most prominent in collected samples (Table 1). Airborne Ti concentrations ranged between BDL (Facility B and C) and $278.62 \mu\text{g/m}^3$ (Facility A,

Ti64, post-processing), where grinding took place. Cr and Cu were detected only at Facility B during pre-processing while Ti₆Al₄V was used. Al (58.92 µg/m³), Ti (278.62 µg/m³), and Fe (196.62 µg/m³) were detected during the second post-processing phase at Facility A. At Facility B the detected metals with the highest concentrations were Fe (18.75 µg/m³) and Ti (85.51 µg/m³). At Facility C the highest metal concentration was Fe (28.59 µg/m³) and Ni (61.17 µg/m³) during the processing phase. Even though all three the processing phases was enclosed, low concentrations of metals were detected in the workplace areas.

Personal respiratory exposure monitoring

The AM operator's personal exposure to metals during each process phase is presented in Table 2 and Table S2. AM operators were exposed to Al, Cu, Fe, Ni, Ti, and V. Due to real life working conditions monitoring was reliant on what tasks the AM operator carried out and what part was being printed at the time of exposure assessment. Metal constituents of all field blanks collected were below the detection limits for each metal. Metal concentrations in Table S2 were calculated as the total TWA for a full shift, representing exposure of an AM operator when completing a full process (pre-processing, processing and post-processing).

AM operators' TWA personal exposure to Ti ranged from 107.46 µg/m³ (Facility A, Ti64) to 830.18 µg/m³ (Facility B, Ti₆Al₄V), while printing with the CL41TiEL powder (Facility C) led to the highest TWA exposure to Al at 2.37 µg/m³. Ti exposure was the lowest during pre-processing (10.63 µg/m³) and increased (1352.16 µg/m³) during post-processing when machine cleaning and vacuuming took place at Facility, B. With the use of Ti64 in DMLS at Facility A the highest TWA exposure was to Cu (85.19 µg/m³) and Ni

(9.46 $\mu\text{g}/\text{m}^3$). At Facility B with the use of $\text{Ti}_6\text{Al}_4\text{V}$ in SLM (Table S2), the highest TWA exposure was to Fe (41.25 $\mu\text{g}/\text{m}^3$), Al (41.25 $\mu\text{g}/\text{m}^3$) and Ti (830.18 $\mu\text{g}/\text{m}^3$).

Table 3 contains the AM operators' exposure to metals < 300 nm during the different processing phases while, full shift exposure of AM operators is summarised in Table S3. AM operators were exposed to a maximum of five metals. In contrast to exposure measured using CFC samplers, Cu and V were below the detection limit for all AM operators, while Co (0.53 $\mu\text{g}/\text{m}^3$) was detected during the processing phase of Facility B and Cr (1.08-6.40 $\mu\text{g}/\text{m}^3$) at all three facilities (except for the processing phase at Facility C). Due to the background metal mass of the Ti present in the nylon mesh, the measured metal mass was found to be below the detection limit. Noteworthy at Facility B is exposure to Co, Cr, and Ni. No < 300 nm metal exposure occurred during processing when using CL41TiEL powder in SLM (Table, 3), with very low exposure also evident during post-processing.

DISCUSSION

While AM machines are designed to operate independently, all feedstock and product handling is performed manually and occupational exposure to different process materials may take place while tasks are being performed during pre-processing, processing and post processing phases.^[15] The aims of this study was to assess particle emissions as well as metal concentrations in the workplace air during the pre-processing, processing and post-processing phases of PBF and to assess AM operators' respiratory exposure to metals and to metal particles < 300 nm.

This study found that particles $\leq 1 \mu\text{m}$ were present in the workplace air before (background) and during AM phases. Pre-processing indicated the high maximum particle concentrations in the 0.01 to $> 1 \mu\text{m}$ size range (Facility B, Table S1), and in the 0.30 μm and 0.50 μm particles size fractions due to specific manual tasks conducted such as machine cleaning powder sieving and hopper loading (Figure 2, A1; Figure 2, B1).

In contrast, fewer manual tasks were performed by the AM operator during the processing phase. A study by Bours et al.^[18] pointed out that the operator is still exposed to hazardous material during the processing phase. When compared to background concentrations, it was evident that there were emissions during the processing phase at Facility C (Figure 2, C1). A prominent increase at Facility C can be observed close to the end of the processing phase when background number concentrations increased from 1.5×10^7 to $3.0 \times 10^7 \text{ p/m}^3$ (Figure 2, C1). This increase was due to the increased operator activity in close proximity to the AM machine, in preparation for the end of the processing phase.

All AM parts require post-processing and the various tasks such as part cleaning and grinding may contribute to additional operator exposure.^[2,18] Particle number concentrations during post-processing increased when grinding, machine cleaning, wire cutting and cleaning of the part took place especially in the 0.01 to $> 1 \mu\text{m}$ particle size range. Vacuuming was the only post-processing task that led to a decrease in particle concentration in the 0.01 to $> 1 \mu\text{m}$ size range and 0.30 μm size fraction, while 0.50 μm and 1.00 μm size fractions increased. No particle emissions larger than $> 1 \mu\text{m}$ was detected during this study. These size fractions may easily penetrate to the unciliated airways of the lungs.^[42] Occupational exposure to fine particles ($< 2.5 \mu\text{m}$) has been associated with the development of cardiovascular diseases and cancer.^[43]

In a study by Graff et al.^[15] different measuring points during various AM tasks were investigated to determine the airborne metal particles emissions in the particle range of 300 nm to 10 μm while using an AM SLM machine. They reported emissions in the size range of 0.01 to 0.30 μm and found a peak number concentration of approximately 16 000 p/cm^3 ($1.60 \times 10^{10} \text{ p}/\text{m}^3$) while cleaning the AM machine. In our study the highest particle number concentration was measured in 0.01 to $> 1 \mu\text{m}$ size range also during cleaning of the SLM machine (Facility C, $6.12 \times 10^{10} \text{ p}/\text{m}^3$). Although Graff et al.^[15] did not allocate a concentration to each task performed, they reported the peak number concentrations at the locations where tasks were performed. These tasks included machine opening, sieving, vacuuming and cleaning and indicated peak number of particles $< 5.0 \times 10^7 \text{ p}/\text{m}^3$ to $> 1 \times 10^8 \text{ p}/\text{m}^3$ in the 0.30 μm size fraction. This can be compared to tasks performed at Facility A (Figure 2, A1) which also included machine opening, cleaning and sieving, with a peak number concentration of $6.68 \times 10^7 \text{ p}/\text{m}^3$. In agreement with Graff et al.^[15] we found that the 0.30 μm size fraction was the most prominent particles emitted. Similar to Graff et al.^[15] the particle number concentrations (Facility B, 0.50 μm particle size range) increased when vacuuming took place, peaking at $2 \times 10^7 \text{ p}/\text{m}^3$.

To date existing literature has provided a better understanding on particulate emissions from FDMTM 3D printers using polymers and most of these studies were conducted in controlled environments, using chamber-studies to quantify emissions.^[24,26,28,44] A study by Zontek et al.^[45] reported $1.90 \times 10^4 \text{ p}/\text{cm}^3$ ($1.90 \times 10^{10} \text{ p}/\text{m}^3$) while Azimi et al.^[44] reported particle concentrations of $9.00 \times 10^5 \text{ p}/\text{cm}^3$ ($9.00 \times 10^{11} \text{ p}/\text{m}^3$). However, when particle emissions were conducted outside test chambers (enclosures) in room tests particle concentrations ranged between $5.60 \times 10^9 \text{ p}/\text{m}^3$ and $2.20 \times 10^{11} \text{ p}/\text{m}^3$.^[25] When comparing the

highest particle concentration from this study, which was 3.64×10^{10} p/m³ measured during PBF (processing phase), it was 16% lower than the highest particle concentrations found during room tests. When comparing particle emissions from PBF to emissions from FDMTM printers, it is clear that although FDMTM printers are higher emitters of particulate matter than PBF, emissions from PBF should not be disregarded.

Static area monitoring indicated that metals were present in the workplace atmosphere during each AM process phase. In the workplace areas, tasks ranged from manual machine cleaning, sieving of powders and hopper loading to grinding of parts from built/base plates. It was observed that even though the processing phases were enclosed, detectable concentrations of airborne metals were found. Overall the highest concentrations of Al (58.92 µg/m³), Ti (278.62 µg/m³), and Fe (196.62 µg/m³) were detected during the post-processing phase at Facility A. Graff et al.^[15] also detected Co, Cr and Ni during static area monitoring in a manufacturing plant that used a Ni based Inconel powder during SLM. From the static area results of this study metals such as Ti, Al, V and Fe in the workplace air is expected when considering the powder composition; however, our results also indicated the presence of Ni, Cr and Cu, possibly as a result of cross contamination from using other metal alloy powders in AM.

This study was carried out at “real life” manufacturing industrial scale AM facilities and the authors were dependent on manufacturing schedules to conduct personal monitoring. Irrespective of the three feedstock powders, AM operators were exposed to a maximum of six metals, namely Al, Cu, Fe, Ni, Ti and V. AM Ti or Ti alloy powder relevant to this study mostly consisted of Al, Ti, and V as well as Fe found in Ti64; however, we also found exposure to Cu and Ni. The PBF processes at all three Facilities in this study are not limited

to use of Ti metal powders only. Various powdered metals are utilised including stainless steels and other metal alloy powders. This in all likelihood explains metals found in area and personal exposure samples. A limitation in the study of Graff et al.^[15] was that they did not convert personal metal exposure concentrations to TWA exposure concentrations, therefore, their results could not be compared to legislative occupational exposure limits of the individual metals. The TWA concentration of a substance is used as the average exposure to a hazardous chemical substance which a worker may be exposed to without adverse effect over a time period of an 8-hour work day, taking into account the average concentrations of the substance and the time exposed to the substance.^[46] AM operator exposure to the individual metals was compared to their respective South African TWA-OELs and TLVs[®] of the ACGIH, and it was found that exposure were all < 1.04% of the respective OELs.

The NRD sampler used during personal exposure monitoring provides an estimation of concentration of < 300 nm particles that deposit in the respiratory system.^[40] Although Cu and V were BDL at all three facilities, low concentrations of Al were detected at Facility A and C, while Co, Cr and Ni was detected at Facility B. The NRD sampler was developed to selectively collect particles < 300 nm including UFPs that deposits in the respiratory system. The extent of the AM operators' health effects when exposed to ultrafine particulate matter is still unknown. Exposure to UFPs is of interest due to the potential acute and chronic health effects linked to exposure since these smaller particles can potentially elicit greater toxic effects than larger particles.^[43,47,48] The short term health effects may not immediately be experienced by AM operators although there is still unfamiliarity about the consequences regarding long term health effects, along with the concern about the lack of epidemiological evidence regarding the health effects of exposure to ultrafine particulate matter which remains unclear.

PBF takes place in three distinct phases and the tasks/activities during these phases may vary. From findings in this study AM operators were exposed to metal particle emissions during the pre-processing and post-processing phases while performing tasks specifically associated with these phases. AM operators are exposed to particle emissions and metals < 300 nm periodically during these three phases. The tasks performed during pre-processing, processing and post-processing lead to AM operators being exposed to low concentrations of metals, for short periods of time as opposed to a full eight hour shift. Therefore, control measures if implemented, should be phase and task specific. Although full shift personal exposure was far below the OELs of the respective metals, AM operators handling metal powders should be informed about the low concentrations of exposure, the potential health risk associated with exposure, the measures in place to control exposure and safe work practices to be followed.

The South African Occupational Health and Safety Act (Act 85 of 1993)^[49] require employers to implement control measures to firstly remove and secondly mitigate occupational health risks in the workplace. According to the hierarchy of control, engineering controls are regarded as the primary strategy.^[46] Since the AM industry is growing in South-Africa the production of AM parts and expansion of facilities are also increasing therefore, it is recommended that if a facility acquires a new AM machine installation, proper planning is needed to separate the process phases. By separating the process phases, spreading of airborne particles to adjacent processes can effectively be prevented. Powder characterisation, which includes particle size and composition of feedstock, can be performed before first use at each facility to identify potential respiratory hazards. Flushing the build chamber twice with non-flammable or reaction gases such as nitrogen or argon can be implemented to assist

in more effective depowdering of built metal parts before they are removed from the chamber.

Due to particle emissions from titanium powders used in PBF, that in all probability contain metals, it is still reasonably practicable to recommend PPE for task and phase specific activities carried out by AM operators. As filtering face piece class one (FFP1) respirators only provide protection against low toxicity substances and dust they cannot be recommended for AM operators. Elastomeric half-mask respirators class N95 or P100 with a combined filter have been found to provide protection for particles < 300 nm and can also remove fumes.^[50] These use of respirators will only be efficient if proper fit testing is performed, training on its use is provided and it is correctly used. Separate, clean containers or storage facilities should be provided for personal protective equipment when not in use, as required in terms of Regulation 11(3) (b) of the Regulations for Hazardous Chemical Substances 1995.^[37] This should be done to avoid contamination of the inside of respirators.

Future studies should include several PBF machines conducting identical pre-processing, processing and post-processing tasks when producing the exact same part, using the same feedstock material or different feedstock materials as this will enable quantitative comparison of findings.

CONCLUSION

There is a lack of studies regarding the emissions from, and exposure to AM metal powders especially when specific tasks are performed during the different processing phases. From this study PBF using titanium powders proved to emit particles especially in the 0.01 to 1 μm size range which in all likelihood consist of metals and may be harmful to AM

operators' respiratory health. Low concentrations of airborne metals were also present in the workplace atmosphere during the process phases. AM operators were exposed to detectable, but low concentrations ($< 1.04\%$ of the OELs) of various metals (Al, Cu, Fe, Ni, Ti and V). It was also found that AM operators were exposed to detectable concentrations of metals < 300 nm in size at Facility A and C (Al, Cr, Fe and Ni) and at Facility B (Co, Cr and Ni). This study contributes to the field of knowledge into the particle emissions from AM machines and respiratory exposure of AM operators to metals during the pre-processing, processing and post-processing phases of PBF. The findings of this study serve as a starting point to create awareness of AM operator exposure associated with metal AM, and to assist industrial AM facilities in identifying hazards and implementing phase and task specific control measures during PBF using titanium powders.

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FIGURES AND TABLES

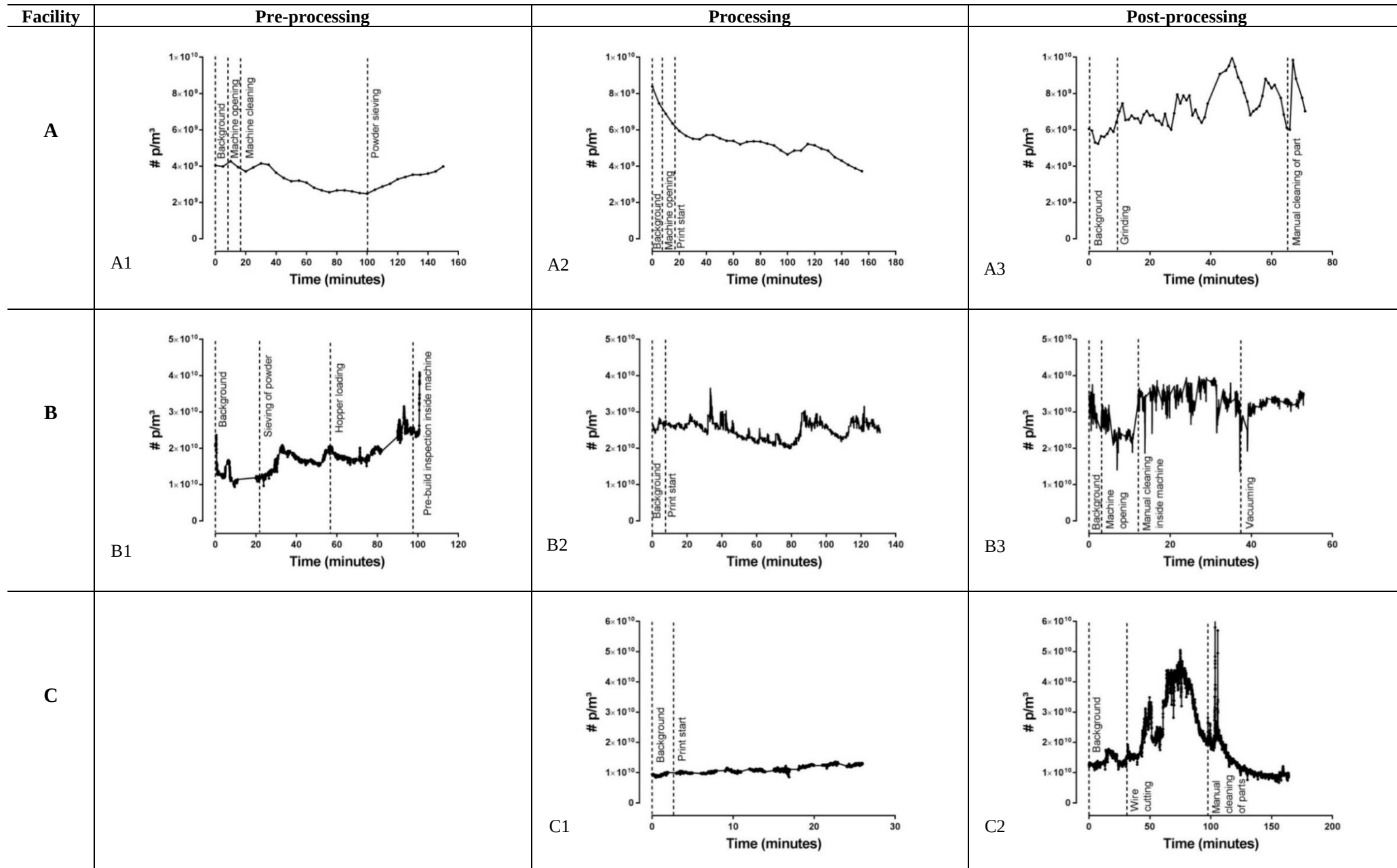


Figure 1: Particle number concentrations (0.01 to > 1 μm) at Facility A-C during Pre-processing (A1-B1), Processing (A2-C2), and Post-processing (A3-C3) phases.

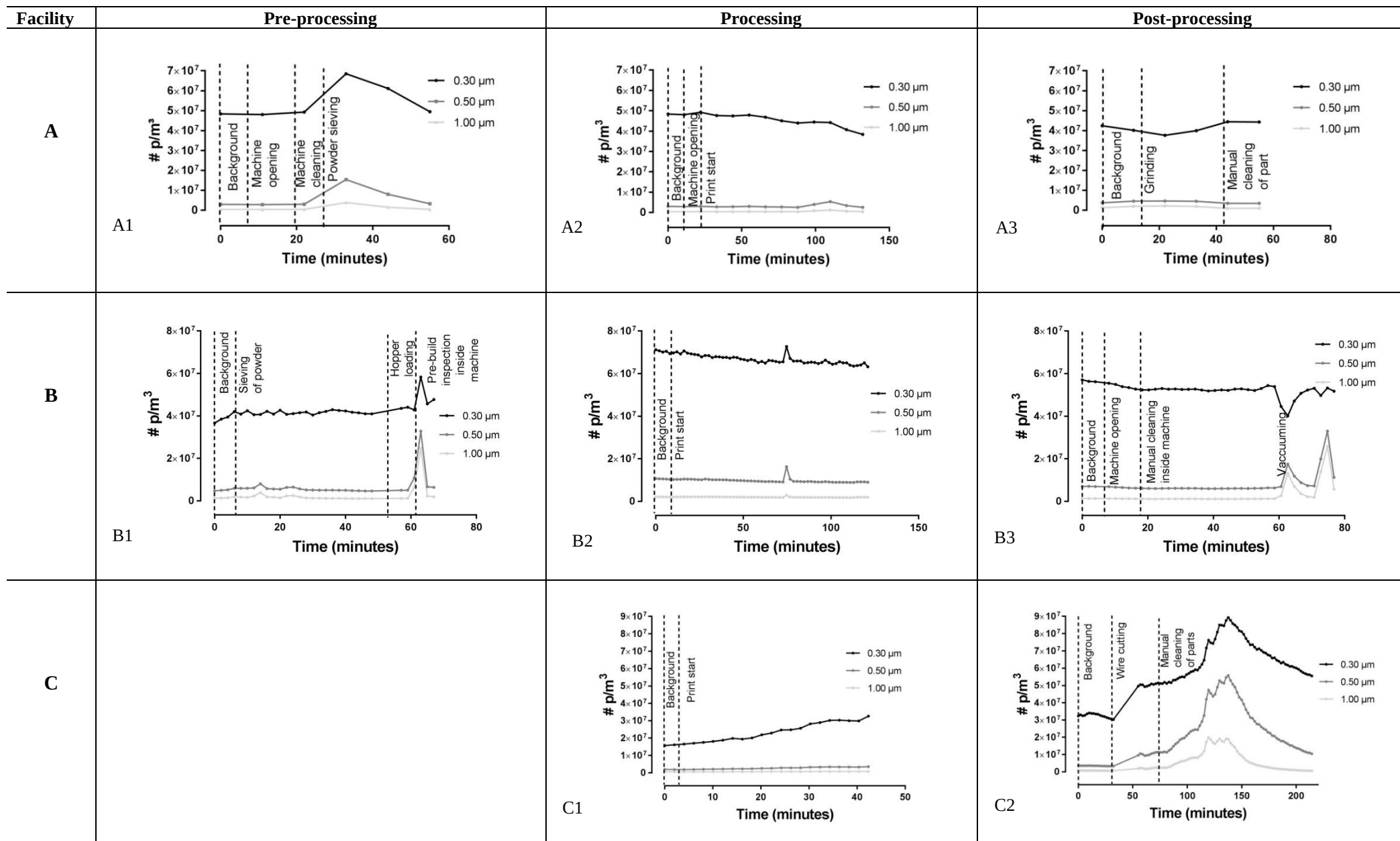


Figure 2: Particle number concentrations (0.30, 0.50 and 1.00 μm) at Facility A-C during Pre-processing (A1-B1) Processing (A2-C2) and Post-processing (A3-C3) phases.

Table 1: Metal concentrations in AM areas during each phase of AM at Facility A to C

Facility	Powder	n	Phase	Time (min)	Metals (µg/m³)						
					Al	Cr	Cu	Fe	Ni	Ti	V
A	Ti64	1	Pre processing	95	4.05	BDL	BDL	3.47	BDL	27.53	1.47
		1	Processing	275	BDL	BDL	BDL	0.71	0.22	4.53	BDL
		1	*Post-processing	35	BDL	BDL	BDL	BDL	BDL	115.71	5.00
		1		65	58.92	BDL	BDL	196.62	5.62	278.62	15.31
B	Ti ₆ Al ₄ V	1	Pre-processing	180	BDL	2.00	BDL	13.42	BDL	7.44	BDL
		1	Processing	240	BDL	BDL	14.58	18.75	BDL	BDL	BDL
		1	Post-processing	127	13.89	BDL	BDL	5.20	BDL	85.51	1.45
C	CL41TiEL	-	Pre-processing	-	-	-	-	-	-	-	-
		1	Processing	40	BDL	BDL	BDL	28.59	61.17	BDL	BDL
		1	Post-processing	310	BDL	BDL	BDL	0.24	5.31	BDL	BDL

n: number of samples, $\mu\text{g}/\text{m}^3$: micrograms per cubic meter, BDL: below detection limit.*At Facility A the post-processing was divided into two stages, which took place on two different days. - No data could be collected for pre-processing at Facility C.

Table 2: AM operator's personal respiratory exposure to metals during each phase of PBF at Facility A to C

Facility	Powder	n	Phase	Time (min)	Metals $\mu\text{g}/\text{m}^3$					
					Al	Cu	Fe	Ni	Ti	V
A	Ti64	1	Pre-processing	65	BDL	BDL	9.76	BDL	10.91	BDL
		1	Processing	40	BDL	170.91	4.86	1.35	16.22	BDL
		2	Post-processing	35	BDL	BDL	BDL	BDL	117.17	5.19
				95	3.05	BDL	18.00	1.21	89.47	5.31
B	Ti ₆ Al ₄ V	2	Pre-processing	40	BDL	6.12	7.62	0.13	10.63	BDL
				30	BDL	18.50	47.66	9.66	483.66	21.50
		1	Processing	150	BDL	1.65	5.86	0.13	BDL	BDL
		1	Post-processing	37	84.73	BDL	37.70	BDL	1352.16	57.02
C	CL41Ti EL	-	Pre-processing	-	-	-	-	-	-	-
		1	Processing	65	BDL	BDL	0.23	0.12	BDL	BDL
		1	Post-processing	310	BDL	BDL	0.16	0.13	BDL	BDL

n: number of samples, $\mu\text{g}/\text{m}^3$: micrograms per cubic meter, BDL: below detection limit, -:No data could be collected for pre-processing at Facility C.

Table 3: AM operator's personal respiratory exposure to < 300 nm metals during each phase of PBF at Facility A to C

Facility	Powder	n	Phase	Time (min)	Metals ($\mu\text{g}/\text{m}^3$)				
					Al	Co	Cr	Fe	Ni
A	Ti64	1	Pre-processing	160	BDL	BDL	1.36	BDL	BDL
		1	Processing	240	BDL	BDL	1.24	BDL	0.83
		1	Post-processing	130	4.30	BDL	2.29	3.99	0.92
B	Ti ₆ Al ₄ V	2	Pre-processing	90	BDL	BDL	1.51	BDL	2.23
				30	BDL	BDL	5.94	BDL	1.33
		1	Processing	150	BDL	0.53	6.40	BDL	0.80
		1	Post-processing	40	BDL	BDL	1.70	BDL	2.00
C	CL41Ti EL	-	Pre-processing	-	-	-	-	-	-
		1	Processing	65	BDL	BDL	BDL	BDL	BDL
		1	Post-processing	310	1.29	BDL	1.08	3.22	BDL

n: number of samples, $\mu\text{g}/\text{m}^3$: micrograms per cubic meter, BDL: below detection limit, -:No data could be collected for pre-processing at Facility C

SUPPLEMENTAL TABLES

Table S1: Particle number concentrations during all phases of PBF at Facility A to C

			Particle number concentrations (x 10 ¹⁰ p/m ³)				Particle number concentrations (x 10 ⁷ p/m ³)											
			0.01 - > 1 µm				0.30 µm				0.50 µm				1.00 µm			
Facility	Powder	Phase	Background concentration		Phase concentration		Background concentration		Phase concentration		Background concentration		Phase concentration		Background concentration		Phase concentration	
			Mean SD	Max	Mean SD	Max	Mean SD	Max	Mean SD	Max	Mean SD	Max	Mean SD	Max	Mean SD	Max	Mean SD	Max
A	Ti64	Pre-processing	0.41±0.01 ^a	0.42	0.32±0.05 ^{a,AB}	0.41	4.82±0.02	5.00	5.71±0.94 ^{DE}	6.68	0.29±0.01	0.30	0.74±0.58	1.54	0.03±0.01	0.04	0.15±0.16	0.38
		Processing	0.75±0.07 ^b	0.83	0.51±0.06 ^{b,AC}	0.63	4.86±0.06 ^d	5.00	4.47±0.31 ^{d,D}	4.79	0.29±0.01	0.30	0.31±0.08	0.53	0.03±0.00	0.04	0.05±0.02 ^F	0.12
		Post-processing	0.56±0.03 ^c	0.60	0.72±0.08 ^{c,BC}	0.90	4.13±0.16	4.25	4.16±0.33 ^E	4.44	0.41±0.05	0.45	0.40±0.06	0.46	0.16±0.04	0.20	0.15±0.06 ^F	0.22
B	Ti ₆ Al ₄ V	Pre-processing	1.37±0.29 ^e	2.36	1.81±0.39 ^{e,GH}	4.08	4.00±0.22 ^h	4.24	4.28±0.36 ^{h,JK}	5.8	0.54±0.50	0.62	0.68±0.55 ^M	3.30	0.15±0.24	0.16	0.72±0.47 ^O	2.48
		Processing	2.64±0.08 ^f	2.83	2.51±0.24 ^{f,GI}	3.65	7.03±0.65 ^j	7.10	6.65±0.19 ^{j,IL}	7.27	1.05±0.01 ^k	1.63	0.97±0.1 ^{k,MN}	1.63	0.21±0.001 ^l	0.20	0.19±0.01 ^{l,OP}	0.28
		Post-processing	2.68±0.39 ^g	3.75	3.31±0.35 ^{g,HI}	3.97	5.60±0.08 ^j	5.71	5.18±0.02 ^{j,KL}	5.55	0.69±0.01	0.70	0.82±0.55 ^N	3.30	0.13±0.001	0.13	0.31±0.51 ^p	2.58
C	CL41TiEL	Pre-processing	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		Processing	1.00±0.06 ^m	1.16	1.17±0.09 ^{m,Q}	1.36	1.68±0.08 ^o	1.81	2.55±0.46 ^{o,R}	3.27	0.19±0.01 ^q	0.21	0.29±0.04 ^{q,S}	0.35	0.05±0.004 ^s	0.06	0.07±0.001 ^{s,T}	0.07
		Post-processing	1.28±0.04 ⁿ	1.38	2.00±1.06 ^{n,Q}	6.12	3.30±0.06 ^p	3.41	6.05±1.53 ^{p,R}	8.93	0.36±0.001 ^r	0.63	2.24±1.50 ^{r,S}	5.58	0.07±0.001 ^t	0.07	0.56±0.58 ^{t,T}	2.00

- No data could be collected for pre-processing at Facility C.

^{a-t} indicate significant ($p \leq 0.05$) differences between the means of background and phase concentration within each size range.

^{A-T} indicate significant ($p \leq 0.05$) differences between the means of the phases (pre-processing, processing and post-processing).

Table S2: AM operator's TWA personal exposure to metals during all phases of PBF at Facility A to C

Facility	Powder	n	Time (min)	Metals (TWA $\mu\text{g}/\text{m}^3$)					
				Al	Cu	Fe	Ni	Ti	V
A	Ti64	1	235	7.00	85.19	16.72	9.46	107.46	6.05
B	Ti ₆ Al ₄ V	1	217	41.25	9.79	41.25	5.02	830.18	35.64
C	CL41TiEL	1	375	2.37	0.82	1.46	0.62	1.13	0.67
TWA OEL				10000	1000	1000	500	10000	-
ACGIH TLV [®]				1000	1000	1000	200	10000	-

n: number of samples, $\mu\text{g}/\text{m}^3$: micrograms per cubic meter, TWA OEL: South African Eight-hour Time Weighted Average Occupational Exposure Limit, ACGIH: American Conference of Governmental Industrial Hygienists. No OEL for Vanadium. *Note: The South-African TWA OELs are in accordance to the Hazardous Chemical Substances Regulations (HCSR, 1995).

Table S3: AM operator's TWA personal exposure to < 300 nm metals during all phases of PBF at Facility A to C

Facility	Powder	n	Time (min)	Metals (TWA $\mu\text{g}/\text{m}^3$)				
				Al	Co	Cr	Fe	Ni
A	Ti64	1	386	0.47	BDL	3.93	3.54	1.55
B	Ti ₆ Al ₄ V	1	280	BDL	1.16	0.95	BDL	2.92
C	CL41TiEL	1	310	0.83	BDL	0.69	2.08	0.08

n: number of samples, $\mu\text{g}/\text{m}^3$: micrograms per cubic meter, BDL: below detection limit, TWA: Time Weighted Average.

CHAPTER 5: ARTICLE III

du Preez S, de Beer DJ, du Plessis JL. (2018) Particle emissions from and exposure to metals during Powder Bed Fusion and Direct Energy Deposition additive manufacturing using maraging and stainless steel powders. Prepared for submission to *The Journal of Occupational and Environmental Hygiene* to be considered for publication.

5.1 Instructions to authors

The Journal of Occupational and Environmental Hygiene (JOEH) is a joint publication of the American Industrial Hygiene Association (AIHA®) and ACGIH®. The *JOEH* is a peer-reviewed journal devoted to enhancing the knowledge and practice of occupational and environmental hygiene and safety by widely disseminating research articles and applied studies of the highest quality. The *JOEH* provides a written medium for the communication of ideas, methods, processes, and research in core and emerging areas of occupational and environmental hygiene. Core domains include, but are not limited to: exposure assessment, control strategies, ergonomics, and risk analysis. Emerging domains include, but are not limited to: sensor technology, emergency preparedness and response, changing workforce, and management and analysis of "big" data.

5.2 Author Guidelines

Formatting requirements:

Manuscripts should be doubled spaced, except for the title page and figure/table legends which should be single spaced. Times New Roman 12 point font should be used except for section heading which should be ALL-CAP Bold text 16 point font. Sections include Title page, Abstract, Introduction, Methods, Results, Discussion and Conclusions, Acknowledgements, References, Figure and Tables. The abstract should state briefly the purpose of the research, the principal results and major conclusions. A minimum of three and a maximum of six keywords should be included in the manuscript.

Figures and Tables:

Figures should be added after the Reference section, and tables should follow after figures. The figure number and caption should be added below each figure using Arabic numerals to identify figures (e.g., Figure 1), figures should be single spaced. Table legend should be

singles spaced and titles of tables should be placed above each table using Arabic numerals to identify tables (e.g., Table 1). Page orientation can be portrait or landscape.

References:

References should be numbered sequentially in the order cited in the text and appear in text as superscript Arabic numerals enclosed in brackets and placed immediately to the right of any punctuation. Multiple, sequential references should be cited using the first and last number, e.g., ^[4-8]. For multi-authored articles up to six names should be listed, for more than six authors the first three should be listed followed by “et al.”. For example: “Smith et al. ^[4] found...” Publication titles and dates should not be listed in the body of the text. References should be cited only by superscript number or by author’s name and superscript number.

Reference examples:

Article, journal:

Miller, A.B., T. To, D. Agnew, C. Wall, and L. Green: Leukemia following occupational exposure to 60-Hz electric and magnetic fields among Ontario electric utility workers. *Am. J. Epidemiol.* 144:150–160 (1996).

Book:

Frymoyer, J.W.: *The Adult Spine: Principles and Practice*. New York: Raven Press, 1991. pp. 40–50.

Chapter in a Book:

Andersson, G.B.J.: Evaluation of Muscle Function. In *The Adult Spine: Principles and Practice*, J.W. Frymoyer (ed.). New York, NY: Raven Press, 1991. pp. 241–274.

Conference Presentation – Unpublished:

Wollen, G.H., G.T. Steel, and M.G. Hall: “Dinitrotoluene: Assessment of Absorption During Explosives Manufacture.” Poster presented at the International Seminar on Method of Monitoring Human Exposure to Carcinogenic and mutagenic Agents, Helsinki, Finland, December 11–15, 1983.

Conference Presentation – Published (Proceedings):

Published papers should follow the format for “Chapter in a Book” reference.

Internet Sources:

Author (if known): "Hazardous Substance Data Bank. Isopropylbiphenyl." Available at <http://toxnet.nlm.nih.gov/servlets/simple-search> (accessed May 11, 1999).

Standards:

American Industrial Hygiene Association (AIHA): Hearing Protection Standard (ISO 2300).
[Standard] Fairfax, VA: AIHA, 1994

Particle emissions from and exposure to metals during Powder Bed Fusion and Direct Energy Deposition additive manufacturing using maraging and stainless steel powders

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ABSTRACT

Purpose of work:

Powder bed fusion (PBF) and direct energy deposition (DED) are two powder based metal additive manufacturing (AM) processes used commercially. Studies on emissions from and exposure of AM operators to particulates and metals during PBF are limited, while at present there is no published literature on DED. This study firstly aimed to characterise maraging steel and stainless steel powders from two AM facilities in South Africa in terms of the particle size, shape and elemental composition for comparison with Safety Data Sheet (SDS) information. This study's second aim was to investigate particle emissions from and AM operators' personal respiratory exposure to metals resulting from the use of these powders.

Methods:

Samples of virgin and used (recycled) powders were collected from the two AM facilities in South Africa to characterise the powders in terms of particle size, shape and elemental composition. Real time monitoring devices namely a Condensation Particle Counter (0.01 to $> 1 \mu\text{m}$) and an Airborne Particle Counter (0.30 to $10.00 \mu\text{m}$) were used to investigate particle number concentration emissions associated with PBF and DED processes. Static area monitoring was carried out according to the National Institute for Occupational Safety and Health 7300 method with a closed-faced cassette (CFC) to determine the airborne concentration of metals in specific work areas. AM operators wore CFC samplers to determine their respiratory exposure to metals as well as nanoparticle respiratory deposition samplers to assess exposure to $< 300 \text{ nm}$ sized metals.

Summary of results:

SDSs of maraging steel powder were inadequate in terms of particle size and elemental composition information provided. Thoracic sized ($< 10 \mu\text{m}$) particles were present in maraging steel powder. Particles were emitted during both PBF and DED while tasks such as unloading of the AM machines led to particle concentrations (0.01 to $> 1 \mu\text{m}$) as high as $5.98 \times 10^{10} \text{ p/m}^3$ during PBF and $5.75 \times 10^{10} \text{ p/m}^3$ during DED. Static area monitoring indicated low concentrations of metals in the work place atmosphere during PBF and DED. AM operators were exposed to six metals (Al, Cr, Cu, Fe, Ni, and Ti) during PBF of maraging steel and to seven metals (Al, Cr, Cu, Fe, Ni, Ti and V) when using stainless steel during DED, however all personal exposures were $< 3.60\%$ of the respective time weighted average - occupational exposure limit (TWA-OELs) and $< 9.01\%$ of the respective threshold limit value (TLV[®]) of metals. Exposure to Ni a human carcinogen and sensitiser was the highest ($16.77 \mu\text{g/m}^3$). AM operators were also exposed to Al, Cr and Ni $< 300 \text{ nm}$ in size.

Conclusion:

There is a shortage of studies reporting particle emissions from and AM operators' respiratory exposure to metals resulting from use of metal powders used in PBF and DED. The lack of detailed information with regard to powder particle size in the SDSs may mislead employers and AM operators regarding the protection of AM operator health, as thoracic sized particles were found in the maraging steel powders. Powder characterisation should form an essential part of the initial risk assessment at each facility and for every powder used during AM. The maximum particle number concentrations emitted from DED were comparable to that of PBF indicating that both are high emitters of particles. Low concentrations of metals were present in the workplace atmosphere and AM operators' personal respiratory exposure was well below the OELs. This study will assist industrial AM

facilities in proactively identifying potential exposure hazards and setting up exposure control measures not only specific to the AM powders but also specific to AM tasks/activities at each facility.

INTRODUCTION

Additive Manufacturing (AM) is based on the principle that a three-dimensional (3D) model from a computer aided design (CAD) file can be produced by joining material layer-upon-layer to manufacture a part.^[1] All metal AM processes share the same approach in building the part by repetitive deposition of feedstock material layers and application of a heat source to solidify or fuse material.^[2] AM processes can either be categorised according to the material used, the deposition technique or to the manner in which the material is fused or solidified.^[3] Two of the AM processes that are powder-based and used commercially for the production of metal parts are powder bed fusion (PBF) and direct energy deposition (DED).^[4]

Direct metal laser sintering (DMLS) is a PBF AM technology where metal powder feedstock is fed through a hopper; spread in thin layers over previous powder layers using a roller or a blade and sintered when a thermal print head fuses the powder layer-by-layer while the build platform lowers the part after each layer has been deposited.^[2,5,6] Laser cladding is a DED AM technology, where metal powder feedstock is fed layer-by-layer through a nozzle onto an existing substrate base, and a laser beam is focused on the substrate to create a melt pool on the surface.^[2,7] The powder is bonded with the base material to form a new layer once the melt pool solidifies.^[2]

Earlier studies have indicated that smaller desktop polymer material extrusion fused deposition modelling (FDMTM) 3D printers are high emitters of particulate matter and volatile organic compounds (VOCs).^[8-10] However, emission information for AM technologies other than FDMTM is limited. Characterisation of particle emissions from AM machines has gained wide interest although the focus has mostly been on 3D desktop printers using polymers, and not as much on and larger industrial AM machines using AM metal powders and AM machine operators exposure.^[10,12-17] It is therefore, of interest to establish particle emissions and assess AM operators' respiratory exposure during AM when using metal powders.

In a study by Graff et al.^[13] on a selective laser melting (SLM) PBF machine using Inconel 939 powder it was found that nano-sized particles (< 300 nm) were emitted in the workplace environment and that AM operators were exposed to carcinogenic chrome (Cr), cobalt (Co) and nickel (Ni) while handling the powder. Particle emissions in the size range of 0.01 to 1 μm was also found, peaking at a number concentration of approximately 16 000 p/cm³, during the cleaning of the AM machine.^[13] Mellin et al.^[18] found small round respirable metal particles (1 to 2 μm) containing Co, Cr, and Ni in used Inconel 939 powder following selective laser melting PBF.

Stainless steel has desirable characteristics such as high strength, corrosion resistance and durability.^[19] Stainless steels are iron-based alloys, rarely consisting of more than 30% Cr or less than 50% iron (Fe). Other elements such as Ni, molybdenum (Mo), copper (Cu), titanium (Ti) and aluminium (Al) can be added for the improvement of specific characteristics.^[20,21] Maraging steel is a steel alloy composed of Fe and Ni (18-25%), which is produced by heating the steel in the austenite phase followed by cooling in air to form a martensitic microstructure. The hardening of the martensite is done by precipitation of Mo

and Ti.^[22,23] Maraging steel is used widely in the aerospace industry, and is known for its strength, processing ability and its weldability and toughness.^[24,25]

AM metal powder feedstock particles should be spherical and have a specific size distribution. However, DED is known to be less sensitive to dimensional qualities of the feedstock material.^[4] Most metal powder feedstock can be recycled and reused. Therefore, metal powders can either be used as virgin (new, as provided by the manufacturer) or used (recycled) powder. In a study by du Preez et al.^[26] virgin Ti powders were compared to their safety data sheets (SDS). Discrepancies as to what was declared in terms of particle size and elemental composition were found in SDSs. The limited information given in these SDSs and no safe operating guidelines provided in user manuals, could wrongfully provide a false sense of protection of AM operator health,^[26,27] while in reality a risk to health may exist. It is therefore, necessary to establish the particle size distribution (PSD), shape and elemental composition of maraging and stainless steel powders in order to compare it to corresponding information declared in the SDSs of these powders.

All powder handling actions required for AM processes are performed manually by AM operators. The operation of an AM machine mostly requires single user operation, implying less labour input for the AM process. Metal AM is a complex task carried out by highly skilled engineers. Specific training as well as practical understanding of an AM system are necessary for AM engineers.^[1,28] AM processes such as PBF require long periods for building or cooling down of the produced parts, and may therefore, be categorised into pre-processing, processing and post-processing phases.^[28,29] On the other hand DED and especially laser cladding is operated more continuously and is not categorised into phases. Concerns have been raised regarding AM operators respiratory exposure to AM powders,

since powder handling actions include manual loading of powders, manual removal of finished parts and manual machine and part cleaning afterwards.^[13,29]

The aim of this study was firstly to establish the PSD, shape and elemental composition of a maraging steel and two stainless steel powders obtained from two AM facilities in South Africa. Secondly this study's aim was to assess particle emissions from and AM operators' respiratory exposure to metals resulting from use of these powders in PBF and DED.

METHODOLOGY

This study was carried out at two different AM facilities in South Africa, utilising maraging and stainless steel powders. Samples of powders were collected from the two AM facilities to characterise particle size, shape and elemental composition of the powders. Real time monitoring devices were used to investigate particle number concentrations emitted along with area (static) sampling to establish the concentration of airborne metals in specific work areas. AM machine operators' respiratory exposure to metals was assessed by conducting personal exposure monitoring.

Facility descriptions

Facility A is a manufacturing facility that utilises direct metal laser sintering (DMLS) with an Electro Optical Systems machine (EOS M280, Germany), which is a PBF technology, and used maraging steel as the feedstock material. Fresh air was supplied to the room via one supply vent, and the room was intermittently staffed by one AM operator. The machine was equipped with an internal recirculating filter system. The three process phases

namely pre-processing, processing and post-processing were monitored. At Facility B, a laser cladding (DED technology) is utilised, using a Rofin Sinar machine (Rofin-Sinar Technologies Inc., USA) and two stainless steel powders, referred hereafter to as stainless steel I and stainless steel II as the feedstock material. Laser cladding was not performed in three separate process phases, such as in PBF, due to the process being continuously operated once initiated. The room did not have any extraction ventilation, and the machine was not fitted with an extraction system. The room was intermittently staffed by one AM operator. It should be noted that the two AM facilities use a variety of metal powders and are not only limited to printing using maraging steel and stainless steel. Therefore, the AM operators involved do not exclusively work with these alloys but also with other metal alloys.

Particle size and shape evaluation and analysis

Virgin and used (recycled) maraging steel feedstock powder was collected from Facility A. Used (recycled) stainless steel I and stainless steel II powders were collected from Facility B as this was the preferred feedstock used. All samples were placed into separate storage vials for analysis. Particle size was evaluated by means of particle size distribution (PSD) and static image analysis [scanning electron microscopy (SEM)]. Particle shape was evaluated through static image analysis of dry dispersed powders. Particle size and shape evaluation were conducted using the Malvern Morphologi G3 with its associated software (Malvern Instruments Ltd., United Kingdom). Approximately 5 mm³ of each powder sample was placed in the instrument's sample dispersion unit. After powder dispersion, images of individual particles were captured and analysed by automated scanning. All samples were analysed in triplicate.

For the preparation of SEM analysis 3 to 5 mm³ of each powder was placed on double-sided adhesive carbon strips and the samples for observation were prepared. The surface topography of each sample was coated with a gold palladium source by means of a SPI Module sputter coater (SPI-ModuleTM. Sputter Coater, SPI Supplies, USA). Samples were studied using a Phenom pro-desktop SEM (Phenom PRO Desktop SEM, Phenom-World B., Netherland) at a power level of 5 kV for magnifications enabling visualisation of particles of < 10 µm in size.

Elemental composition analysis

For elemental composition analysis of each powder, the feedstock was prepared beforehand by pulverising the feedstock to a fine powder and placing the undiluted powder samples onto a spinner stage, using a back-loading technique, inside the XRD. XRD analysis was conducted on powder samples using a powder diffractometer (X'Pert Pro XRD, PANalytical, Netherland). The samples were then scanned using X-rays generated by a Cu X-Ray tube (PW3376/00 Co LFF tube, PANalytical, Netherland).

Static area monitoring (emissions)

Particle number concentrations (p/m³) were determined by using a TSITM Condensation Particle Counter (CPC) model 3007 (TSI Inc., USA), and a TSI AeroTrakTM Airborne Particle Counter (APC) model 9310 (TSI Inc., USA). The CPC detected the total number concentration in real time of fine and ultrafine particles in a size range of 0.01 to > 1 µm. It should be noted that the CPC is designed to be effective for the detection of small nanoparticles. The maximum detectable size of a CPC ranges from 1 to 3 µm. However, particles larger than approximately 1 µm are easily lost due to inertial impaction.^[30] The APC was used to determine the number concentration of particles sized

0.30 to 10.00 μm . For the purpose of this study only the 0.30 μm , 0.50 μm and 1.00 μm size fractions are presented in the Results Section since no particles $> 1 \mu\text{m}$ were detected.

At Facility A only the CPC could be used and background concentrations were measured prior to the start of each process phase (pre-processing, processing or post-processing). Data was recorded at one second intervals. For Facility B the CPC and APC continuously monitored particle number concentrations emitted for the duration of the laser cladding technology. This procedure was not performed for three process phases, but rather as one continuous process. Data was recorded at one second intervals. In all instances, the time duration of monitoring varied and were dependent on the tasks to be performed in producing the part. All static area monitoring was performed at workstations, where the highest potential emission of metals during all three process phases was anticipated, at a distance less than 1.00 m from the AM machine and 1.5 m above floor level.

The concentration of metals in the workplace air was measured according to the National Institute for Occupational Safety and Health (NIOSH) 7300 method.^[31] Gilair (Sensidyne, USA) constant flow sampling pumps with mixed cellulose ester (MCE) filters (SKC, USA) (37 mm diameter, 0.8 μm pore size) in a closed faced cassette (CFC) were used. Sampling pumps were calibrated at 2 ℓ/min before and after use. Sample analysis, in accordance to NIOSH method 7300, was conducted by a South African National Accreditation System (SANAS) analytical laboratory by means of inductively coupled plasma-mass spectrometry (ICP-MS).^[31] One field blank was included for every three samples of each process phase. The field blanks were handled, stored and transported in the same manner as the collected samples.

Personal respiratory exposure monitoring

Personal respiratory exposure monitoring corresponded to that used for static area monitoring with the exception of placement of the CFC, which was worn by the AM operator and placed in the operators breathing zone. A sample was collected for each phase of AM. After metal mass analysis with ICP-MS, the volume of air sampled and duration of the sample was used to calculate the time weighted average (TWA) exposure concentration for each metal. For metal mass below the analytic detection limit (DL) metal mass was calculated using the DL mass divided by the square root of two method in order to calculate TWA exposure.^[32] The TWA was calculated to establish whether exposure complied with the specified legislative occupational exposure limit (OEL) set for each metal. For this comparison, South African OELs as included in the Hazardous Chemical Substances Regulations (HCSR) (1995)^[33] as well as the threshold limit value (TLV[®]) of the American Conference of Governmental Industrial Hygienists were used.^[34] All AM machine operators involved in PBF at each facility participated in personal exposure monitoring. A total of four AM operators participated.

Both Graff et al.^[13] and du Preez et al.^[35] reported the presence of metal particles < 300 nm present in AM workplace air. Therefore, personal exposures to metals < 300 nm, were assessed by using a nanoparticle respiratory deposition (NRD) (Zefon International, USA) sampler. NRD samplers consist of three parts, namely a respirable cyclone, an inertial impactor and a diffusion stage (nylon mesh) where < 300 nm particles are collected, similar to their deposition in the respiratory tract.^[35-37] Sample analysis was also conducted with ICP-MS. Mines et al.^[38] reported that background metals were present in the nylon mesh of the sampler. For the purpose of this study, the background metal mass (Cr and Ti) present in the

nylon mesh of the NRD sampler reported by Mines et al.^[37] was subtracted from the measured metal mass.

Data analysis

The maximum, mean and standard deviation particle number concentrations for both the CPC and APC were calculated in Microsoft Office Professional Plus 2010 (Excel 2010, version 14.20) for static area monitoring (emissions) and background particle number concentrations. As a prerequisite for the statistical analyses to follow, the data distribution was determined using the D'Agostino and Pearson omnibus test. Within each particle size range, the significance ($p \leq 0.05$) between the means of background concentrations and phase particle number concentrations was investigated using the Unpaired t-test with Welch's correction and Mann-Whitney test for parametric and non-parametric data, respectively. Furthermore, significant ($p \leq 0.05$) differences in particle number concentration means between the phases (pre-processing, processing and post-processing) were determined using the analysis of variance (ANOVA) (parametric data) and Kruskal-Wallis test (non-parametric data), followed by Tukey's and Dunn's multiple comparisons tests, respectively. These statistical analyses were executed using GraphPad Prism 7 (GraphPad Software, La Jolla, USA).

Ethics approval

The scope of this study was described in detail in the informed consent form. All AM operators was invited to take part in this study, therefore, participants used for this research was voluntary as stated in the informed consent. This study was approved by the Health Research Ethics Committee of the North-West University (NWU-00004-16-A1).

RESULTS

Powder characterisation (particle size, shape and elemental composition) is presented first and is followed by particle and metal emissions in the workplace atmosphere and personal exposure of AM operators to metals

Particle size and shape evaluation and analysis

The particle sizes of three metal alloy powders were compared to that declared in the SDS of representative powders. The SDS of virgin maraging steel powders at Facility A listed powder size as $< 1000 \mu\text{m}$, while 90% of particles measured were $< 31.68 \pm 1.77 \mu\text{m}$ and 34.37 ± 0.89 for virgin and used powders respectively (Table 1).

The SDS of the virgin stainless steel I powder used at Facility B did not state a minimum or maximum particle size. However, used stainless steel I and II powders were used at Facility B. Ten percent of used stainless steel I particles were $< 15.09 \pm 0.38 \mu\text{m}$, and 90% percent of particles were $< 35.46 \pm 3.03 \mu\text{m}$. The SDS of virgin stainless steel II powder (Facility B) indicated a particle size range of 11-45 μm . Our analysis of used powder found that 90% of particles were $< 43.44 \pm 0.38 \mu\text{m}$ and 10% of particles $< 22.33 \pm 0.64 \mu\text{m}$.

The PSD indicated that 10% of virgin maraging steel powder particles ($< 7.8 \pm 0.30 \mu\text{m}$) were thoracic sized particles ($< 10 \mu\text{m}$), which is supported by the SEM image (Figure 1, A1). Some particles $< 10 \mu\text{m}$ were also observed in SEM image of used maraging steel. No thoracic sized particles were observed in any of the images of the stainless steel powders. There were significant differences in the PSD of virgin and used maraging steel powders, where the $d(0.1)$, i.e. the mean size of 10%, and $d(0.5)$, i.e. the median particle size were significantly smaller than that of the used powder. The particles of virgin and used

maraging steel powders were smooth and spherically shaped (Table 1, Figure 1). Stainless steel powder particles were slightly less spherical and smaller particles being attached to larger particles were observed.

Elemental composition

The elemental composition analysis of the virgin maraging steel powder differed from the composition stated in the respective SDSs. The percentage of Al (0.05 to 0.10%) and Cu (< 0.03%) as listed in the SDS of the virgin maraging steel powder was found to be respectively 10.00 times and 76.67 times lower to what was found with XRD analysis (Table 2). The percentage Cr in the same powder was 58.8 times higher than was stated in the SDS, while the percentage Fe (70.50 to 73.90%) listed in the SDS was higher than that found by XRD. No virgin stainless steel I and stainless steel II powders were collected from Facility B as only used powders were used. The SDS for the virgin stainless steel powders indicated that powders should contain Tungsten Carbide (WC), although it was not detected by XRD in used powders analysed. The SDS of stainless steel II indicated that virgin powder contains 1.00 to 2.50% silicon metal, 1.00 to 2.50% carbon and 0.10 to 1.00% manganese, which was also not detected by XRD analysis. Tetrataenite, a metal composed of Fe and Ni was not listed in the SDS, but was detected by XRD.^[39]

Static area monitoring (emissions)

Due to availability only the CPC was used at Facility A during PBF to measure 0.01 to > 1 µm particles in the workplace air prior to process phases (background) and during each process phase (pre-processing, processing or post-processing). Background particle number concentrations ranged between $0.27 \pm 0.01 \times 10^{10}$ p/m³ and $2.53 \pm 0.01 \times 10^{10}$ p/m³ (Figure 2, A1-A3; Table S1). The background concentration observed in Figure 2, A1, could be

ascribed to overnight printing that took place prior to the time that our data collection started. Particle number concentration decreased throughout pre-processing, with the exception of powder sieving, which led to a slight increase, (maximum of $0.21 \times 10^{10} \text{ p/m}^3$), however, this was still lower than the mean background particle number concentration (Figure 2, A1). The particle number concentration remained stable, and averaged $0.13 \times 10^{10} \text{ p/m}^3$ during the processing phase. Grinding of the manufactured part during the post-processing phase led to a drastic increase in particle number concentration (Figure 2, A3) ($5.98 \times 10^{10} \text{ p/m}^3$) followed by a decrease in particle concentration once grinding ended. The mean particle number concentration during post-processing was significantly higher ($p \leq 0.01$) than that of pre-processing.

At Facility B the CPC was used for two printing cycles of stainless steel I, and the APC was used for the first printing cycle with stainless steel I and for the second printing cycle with stainless steel II. When the machine was loaded with stainless steel I (print cycle 1) a observable increase in particle number concentrations was observed (Figure 3, B1 and Figure 4, B1). Once printing of stainless steel I commenced, the particle number concentration decreased but increased at the end of processing (Figure 3, B1 and Figure 4, B1). With unloading, particle number concentrations increased reaching a maximum of $5.85 \times 10^7 \text{ p/m}^3$ ($0.30 \mu\text{m}$) (Table S2; Figure 4, B1). In the 0.01 to $> 1 \mu\text{m}$ size range the maximum particle concentration reached $5.75 \times 10^{10} \text{ p/m}^3$ (Table S1) for stainless steel I (print cycle 2). Unloading of the machine also led to an increase in particle number concentrations (Figure 2, B2).

With stainless steel II (Figure 4, B2, Table S2) there were significant differences in the background particle concentrations and process concentrations in the 0.30 to $1.00 \mu\text{m}$ size

range (Table S2). An increase in particle number concentrations in the 0.30 to 1.00 μm size range was observed during machine loading (Figure 4, B2) and reached a maximum of $7.19 \times 10^7 \text{ p/m}^3$ during printing (Table S2; Figure 4, B2). When comparing stainless steel I with stainless steel II, the latter emitted higher maximum particle number concentrations in the 0.30 μm to 1.00 μm size fractions (Table S2).

Table 3 summarises the airborne concentrations of metals within the workplace atmospheres measured at both facilities. Tasks performed included manual machine cleaning, sieving of powders, machine loading, grinding of parts from build plates and cleaning of the manufactured part. Quantifiable concentrations of Al, Cu, Fe, Ni, Ti and V were detected at Facility A when using maraging steel, while Al, Cr, Cu, Fe and Ni were detected at Facility B when using stainless steel. Fe was detected in all samples.

At Facility A, pre-processing and processing were carried out on the same day in the same workplace area, followed by post-processing of the manufactured part the following day. For the second print cycle with the maraging steel only a pre-processing and processing phase could be monitored. The six metals mentioned were detected in workplace air during pre-processing and processing with maraging steel, with no metal concentrations exceeding $26.69 \mu\text{g/m}^3$ (Fe). The higher concentrations of Fe could be ascribed to pre-processing immediately following processing in the same work area and the high Fe content of maraging steel powders (Table 2). Only Fe ($14.81 \mu\text{g/m}^3$), was detected during post-processing of maraging steel. The Fe concentration in the workplace air ranged between $14.92 \mu\text{g/m}^3$ and $1915.91 \mu\text{g/m}^3$ at Facility B. Stainless steel II printing led to the highest concentrations of Cr ($29.94 \mu\text{g/m}^3$) and Fe ($1915.91 \mu\text{g/m}^3$) in the workplace area. Use of the same feedstock material led to different metals being detected. This is evident for both maraging steel and

stainless steel I where metal elements detected differed from what was listed in the respective SDSs.

Personal respiratory exposure monitoring

The AM operators' respiratory exposure to maraging steel was calculated as the TWA for a full shift when completing a full process (pre-processing, processing and post-processing phases). Due to real life working conditions, monitoring was reliant on the tasks as performed by the AM operator and the part being printed at the time of exposure monitoring. In Table S3 (supplemental table) the TWA of each AM operator's personal exposure to maraging steel during each AM process phase is presented. AM operators were exposed to six metals namely Al, Cr, Cu, Ni, Fe and Ti (Table 4). The highest exposure was to Fe ($72.87 \mu\text{g}/\text{m}^3$) using maraging steel at Facility A. Noteworthy concentrations of Cu ($19.83 \mu\text{g}/\text{m}^3$) and Ti ($15.83 \mu\text{g}/\text{m}^3$) were present during post-processing of maraging steel (Table S3), while Ni concentrations during pre-processing ranged between $50.13 \mu\text{g}/\text{m}^3$ and $96.11 \mu\text{g}/\text{m}^3$, and Fe concentrations ranged between $27.33 \mu\text{g}/\text{m}^3$ and $204.00 \mu\text{g}/\text{m}^3$ (Table S3).

At Facility B, AM operators were exposed to seven metals namely Al, Cr, Cu, Fe, Ni, Ti and V when using stainless steel during DED. The highest exposure was to Fe at $10.35 \mu\text{g}/\text{m}^3$ during the use of stainless steel I. Fe concentrations ranged between $4.02 \mu\text{g}/\text{m}^3$ and $10.35 \mu\text{g}/\text{m}^3$.

Full shift exposure of the AM operator to $< 300 \text{ nm}$ sized metals during printing with maraging steel is summarised in Table 5, while Table S4 represents the AM operators exposure during the individual phases. Exposure to Cu, Fe, Ti and V were below the

detection limit while Al, Cr and Ni were detected (Table 5). During DED (Facility B), AM operators were only exposed to < 300 nm Cr and Ni.

DISCUSSION

There are many factors to be taken into consideration when determining an AM operator's respiratory exposure. This study aimed to provide a better understanding of the PSD, shape and elemental composition of metal alloy powders and to assess particle emissions from and AM operator's personal respiratory exposure to maraging and stainless steel AM metal powders.

There are seven AM process categories, but not all can produce metal parts and fulfil the requirements of industrial applications. Therefore, extensive research is being performed to develop a wider variety of AM metal powders.^[2] A limited number of studies are available on emissions and exposure of AM process categories other than material extrusion (FDMTM). There are two studies to date, that have indicated that particles containing metals are emitted from PBF when using AM metal alloy powders, while there are currently no information available regarding emissions from DED.^[13,35] A study by du Preez et al.^[26] found that SDSs provided by the manufacturer/supplier, disclosed only minimal information and revealed discrepancies to what is declared by the manufacturer/supplier, which could unintentionally be misleading to the AM operator regarding the protection of their respiratory health.^[27]

According to the International Organization for Standardisation (ISO 7708)^[40] inhalable particles are defined as the mass fraction of airborne particles inhaled through the nose and mouth. Thoracic sized particles is the mass fraction of inhaled particles which is expected to deposit beyond the larynx.^[41,42] In this study, 90% of virgin maraging steel

particles ($< 31.68 \pm 1.77 \mu\text{m}$) can be considered as inhalable particles and 10% ($< 7.8 \pm 0.30 \mu\text{m}$) as thoracic sized particles. The PSD differed between virgin maraging steel and used powder due to the recycling of powder during AM processes, which may influence the particle size.^[26] SEM images indicated that powder particles were spherical as required for PBF and DED processes. A few smaller particles being attached to larger particles were observed in used stainless steel I and stainless steel II powder. These smaller particles may detach from larger particles, upon handling or heating of the powder.^[18] These smaller particles have the potential to become airborne in the workplace and easily be inhaled by AM operators.

Elemental composition analysis of virgin and used powders differed from the composition disclosed in the SDS. For maraging steel, the Cr and Cu were higher than what was listed in the SDS. The changes in elemental percentages (composition) between virgin and used maraging steel could be ascribed to the properties of used powder that may have changed due to the repeated (recycled) use and possible cross contamination from working with a variety of other metal powders.^[43] At Facility B no virgin powders was collected for the stainless steel I and stainless steel II powders. Interpretations of the elemental composition of used stainless steel powders should be done with caution, since powders were already used (recycled).

PBF at Facility A was carried out in three phases, namely pre-processing, processing and post-processing. It was evident that the post-processing phase had the highest particles number concentration followed by the pre-processing and the processing phases. During post-processing the particles number concentration increased during grinding of the AM printed part which generated metal dust into the workplace atmosphere. DED was continuous and did

not take place in different phases. Initially when printing started particle number concentrations were high and declined after a while, with a slight increase once unloading of the machine took place.

Studies carried out with FDMTM 3D printers printing ABS feedstock found particle concentrations between 3.30×10^9 p/m³ and 2.20×10^{11} p/m³, proving that FDMTM printers are high emitters of particulate matter.^[44,45] In a study by Zontek et al.^[45] particle concentrations recorded during processing in room tests with ABS indicated peak concentrations of 1.90×10^{10} p/m³ which is approximately nine times higher than during our study (0.21×10^{10} p/m³, processing phase from maraging steel). When comparing the highest process concentration of 5.75×10^{10} p/m³ during processing of stainless steel I with that of the room tests with ABS we found that DED particle number concentrations was three times higher.^[45] Particle number concentrations PBF with maraging steel was 2.29% lower than that of PBF with titanium from du Preez et al.^[35] particle number concentrations of DED with stainless steel was 3.00% lower than that of PBF with maraging steel. Specific pre-processing and post-processing tasks lead to an increase in particle emissions.

The findings of the area monitoring at Facility A and B indicated that metals were detected in the work place atmosphere during PBF and DED. Our findings support findings of Graff et al.^[13] and du Preez et al.^[35] who also detected metals during area monitoring while using AM metal based powders. The highest concentrations in the workplace area was Fe ($1915.91 \mu\text{g}/\text{m}^3$) when printing of stainless steel II took place. Both maraging steel and stainless steel powders are high in Fe content, explaining the Fe measured in the workplace area.

Various tasks during AM can contribute to AM operator exposure in the form of particles or metal dust.^[5,46] Personal exposure monitoring depended on the AM facility's schedule as well as the part that was manufactured at the time the monitoring took place, therefore, the duration of the monitoring varied. AM operators were exposed to a total of six metals during PBF and seven metals during DED. During PBF it was found that AM operators were also exposed to Ti and V, which were not listed in the SDS of maraging steel. Detectable Al and Cu were also found during DED with stainless steel I and stainless steel II and were not listed in the respective SDSs. These deviations may be due to cross contamination as AM operators work with a variety of metal powders at each facility. AM operator exposure to the individual metals was compared to their respective South African TWA-OELs, and it was found that all exposure were < 3.60% of the respective OELs. When compared to the TLVs[®] it was found that exposure was < 9.01% of the respective TLVs[®]. The individual metal with the highest exposure was Ni.

The NRD sampler used during personal exposure monitoring provided an estimation of exposure to < 300 nm sized metals that may deposit in the respiratory system.^[37] Low concentrations of < 300 nm Al, Cr and Ni were detected from AM operators at Facility A and AM operators at Facility B were only exposed to Cr and Ni.^[47] When compared to du Preez et al.^[35] low concentrations of Cr and Ni were also detected, however, the exposure concentrations from this study was lower.

When AM parts are printed especially with DED a concept similar to welding is applied as AM metal powder layers are joined by melting AM powders together.^[48,49] Metal fumes generated during processing can be compared to welding fumes for the reason that metal AM powders are also Fe based and contain metal elements similar to welding such as

Al, Ti, Ni, and Cr.^[49] Although AM operators' personal exposure levels were below the OELs for both AM processes, the concern is that AM operators are exposed to carcinogenic metals such as Cr and Ni. Particles < 300 nm that are emitted into the workplace air, have raised concerns as these particles are small enough, that when inhaled they can be deposited throughout the lungs. Metallic particles can lead to impairment of lung function or chronic respiratory disease.^[50] The < 300 nm particles may include ultrafine particles (UFPs i.e. particles < 100 nm), exposure to UFPs are linked to acute and chronic health effects.^[51-53]

According to the South African Occupational Health and Safety Act (Act 85 of 1993)^[54] employers are required to implement control measures to remove, and if not possible, reduce health risks in the workplace. Before control measures can be implemented, risk assessments need to be carried out in order to improve identification of possible hazards, therefore, powder characterisation of feedstock is recommended for each facility. An inventory of all feedstock can be kept at facilities containing the powder characterisation results, which includes particle size and feedstock composition, to compare with the manufacturer provided SDS. This measure will assist facilities to identify possible shortcomings in an SDS. AM control measures should be based upon the AM process type and on the specific tasks/activities that takes place during the respective AM processes. For PBF, an engineering control such as flushing the build chamber twice with non-flammable or reaction gases such as nitrogen or argon before the final AM part is removed from the build chamber was previously recommended by du Preez et al.^[35] For DED an administrative control measure such as frequently scheduled housekeeping should be implemented and maintained and cleaning schedules such as cleaning the areas thoroughly before and after processing should be added to operating schedules.

In combination with engineering controls, it is important that the AM operators handling metal powders, should be informed that in case a risk of exposure to carcinogens arises, it is sensible for the AM operator to wear suitable PPE. According to the HCSR the control of exposure to substances with an occupational exposure-control limit (OEL-CL), such as Ni, should as far as inhalation of the substance is concerned, be regarded as adequate only in case the level of exposure is reduced as far as it is reasonably feasible.^[33] Therefore, the current filtering face piece class one (FFP1) respirators that are being used at both facilities cannot be recommended for AM operators as they are only effective for protection against low toxicity substances and dust. Due to the metal exposures all being < 3.60% of the TWA-OELs and < 9.01% of TLVs[®] and the detection of metal particles < 300 nm, it is recommended that AM operators should be issued with the correct PPE at the AM facilities using metals during PBF and DED. As previously reported it is recommended that elastomeric half-mask respirators with class N95 or P100 filters should be used for protection against metal particle exposure. These respirators have been found to be effective for the removal of particles in the < 300 nm size range.^[35,55] Effective performance of respirators is dependent on filter performance, prior to fit testing for each AM operator and appropriate storage facilities when personal protective equipment is not in use. AM operators who are required to wear respirators should be informed, instructed and trained in the use of respiratory protective equipment in accordance with Regulation 11 of the HCSR.^[33]

Due to the variety of powder feedstock at AM facilities which can cause cross contamination, future studies should aim to conduct powder characterisation for all feedstock powders available at facilities. Future studies may also include further investigation of different PBF and DED technologies with regard to particle emissions from and exposure to other available feedstock materials.

CONCLUSION

It was found that the provided SDSs of maraging steel powder contained inadequate information regarding the PSD and elemental composition indicating a lack of emphasis on required information in the provided SDS. The maraging steel powders contained thoracic sized ($< 10\ \mu\text{m}$) particles and if inhaled these metal containing particles have the potential to cause adverse health effects. Task specific activities led to an increase of particles emitted while the maximum particle number concentrations emitted from DED were comparable to that of PBF indicating that both are high emitters of particles. Metals were present in the workplace atmosphere when tasks were performed during PBF and DED at both facilities. During PBF AM operators were exposed to low concentrations of six metals (Al, Cr, Cu, Fe, Ni, and Ti) and to seven detectable metals (Al, Cr, Cu, Fe, Ni, Ti and V) during DED. AM operator exposure to the individual metals was $< 3.60\%$ of the respective TWA-OELs and $< 9.01\%$ of TLVs[®]. The individual metal with the highest exposure was Ni, which is a human carcinogen. It was also found that AM operators were exposed to detectable concentrations of Al, Cr and Ni during PBF and only to Cr and Ni during DED, all $< 300\ \text{nm}$ in size. This study not only provides additional information of particle emissions from and exposure to metals during PBF, but is also the first to investigate particle emissions from and exposure to metals during DED. Facility specific control measures and the implementation of appropriate PPE to provide adequate protection against carcinogens and $< 300\ \text{nm}$ sized metal particles are necessary. The findings of this study create awareness and serve as guidance for AM industrial facilities on particle emissions from and metal exposure to maraging steel and stainless steel powders, during the use of these powders.

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TABLES AND FIGURES

Table 1: SDS information, PSD, particle shape and SEM analysis of virgin and used metal alloy powders. Data reported as mean $\pm$ standard deviation

	Powder	Type	SDS (μm)	PSD (μm)			Particle shape		SEM*
				d(0.1)	d(0.5)	d(0.9)	Circularity number distribution	Convexity number distribution	Thoracic particles ($< 10 \mu\text{m}$)
Facility A	Maraging steel	Virgin	< 1000	7.80 ± 0.30^a	14.26 ± 0.36^b	31.68 ± 1.77	0.93 ± 0.003	0.99 ± 0.001	Yes
		Used	-	10.94 ± 0.19^a	19.13 ± 0.20^b	34.37 ± 0.89	0.94 ± 0.001	0.99 ± 0.001	Yes
Facility B	Stainless steel I	Used	-•	15.09 ± 0.38	22.84 ± 1.38	35.46 ± 3.03	0.92 ± 0.003	0.99 ± 0.009	No
	Stainless steel II	Used	*	22.33 ± 0.64	32.40 ± 0.67	43.44 ± 0.38	0.90 ± 0.003	0.99 ± 0.001	No

Legend: d(0.1) 10% of the particles are smaller than the stated diameter; d(0.5) 50% of the particles are smaller than the stated diameter; d(0.9) 90% of the particles are smaller than the stated diameter. ^{a,b} Statistically significant differences ($p \leq 0.05$). Circularity: The ratio of the perimeter of a circle with the same area as the particle divided by the perimeter of the actual particle image. Circularity values range from 0-1, a perfect circle will have a circularity of 1. Convexity: Measurement of the edge roughness of a particle. A smooth shape will have a convexity of 1, and an irregular object a convexity of 0 *Based on visual evaluation of SEM images. •The SDS of virgin Stainless steel I at Facility B did not provide a minimum or maximum powder size. *According to the SDS the minimum or maximum powder size range for virgin Stainless steel II was in the range of 11 - 45 μm powder.

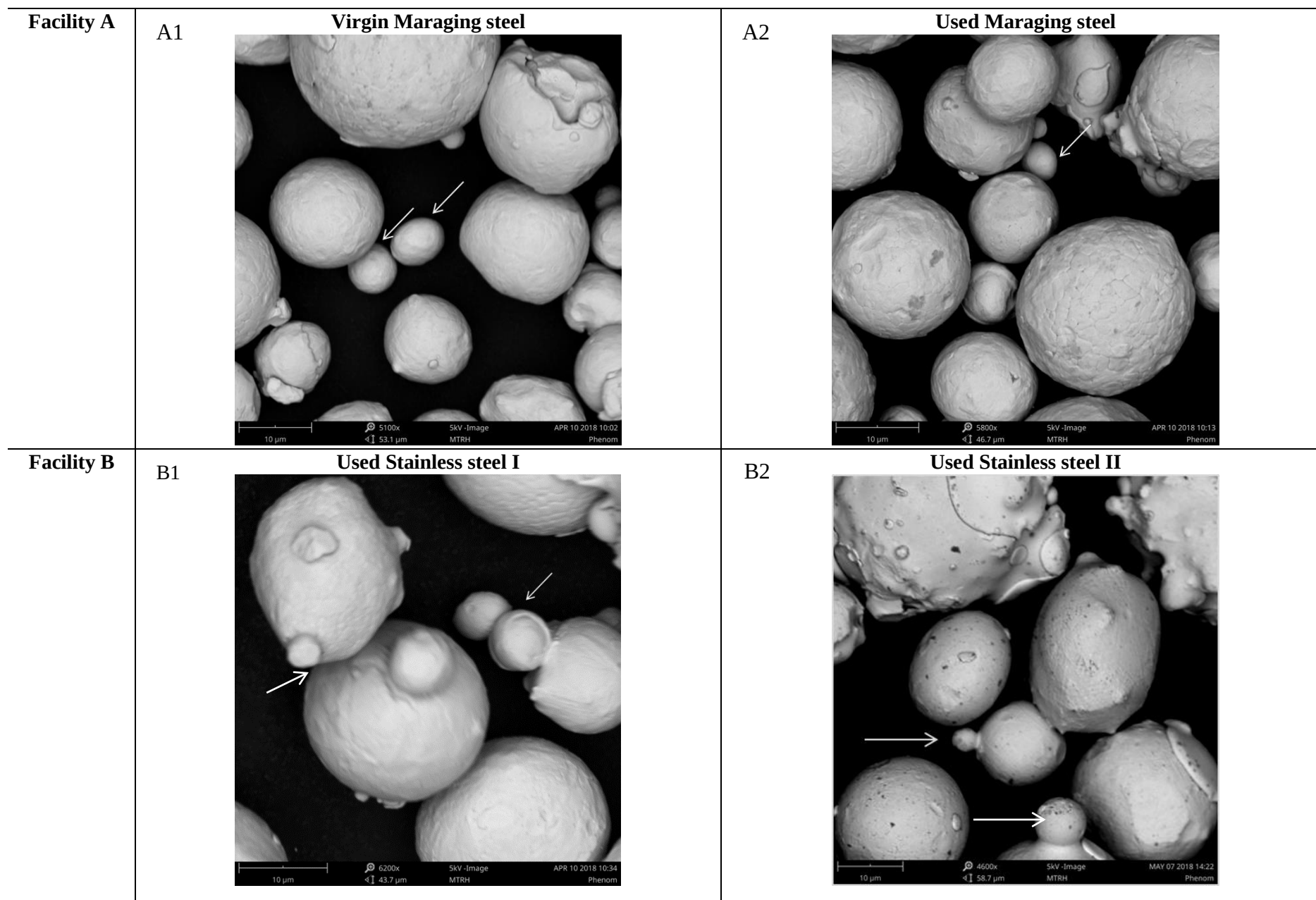


Figure: 1 SEM images from virgin and used (A1 and A2) metal alloy powders from Facility A and B on a 10 µm scale, indicating thoracic sized particles at Facility A and the presence of small particles (B1 and B2) attached to larger particles at Facility B.

Table 2: Elemental composition of virgin and used metal alloy powders at Facility A and B

			Elemental composition (%)							
	Powder	Sample	SDS/XRD	Al	Co	Cr	Cu	Fe	Ni	WC
Facility A	Maraging steel	Virgin	SDS	0.05-0.10	8.50-9.50	<0.50	<0.03	70.50-73.90	17.00-19.0	-
			XRD	1.00	2.90	29.40	2.30	67.00	1.30	-
		Used	XRD	1.20	2.90	31.80	2.90	63.60	1.70	-
Facility B	Stainless steel I	Virgin	SDS	-	10.00	3.50	-	1.00	14.0	70.00
		Used	XRD	0.2	7.90-11.10	15.00-39.60	1.00	46.50-48.70	1.80-7.90	-
	Stainless steel II	Virgin	SDS ^a	-	>50	25-55	-	1.00-2.50	1-2.50	3.00-5.00
		Used	XRD ^b	0.7	13.9-19.5	0.70-12.8	0.80-41.5	3.50 ^b	15.00-45.70	-

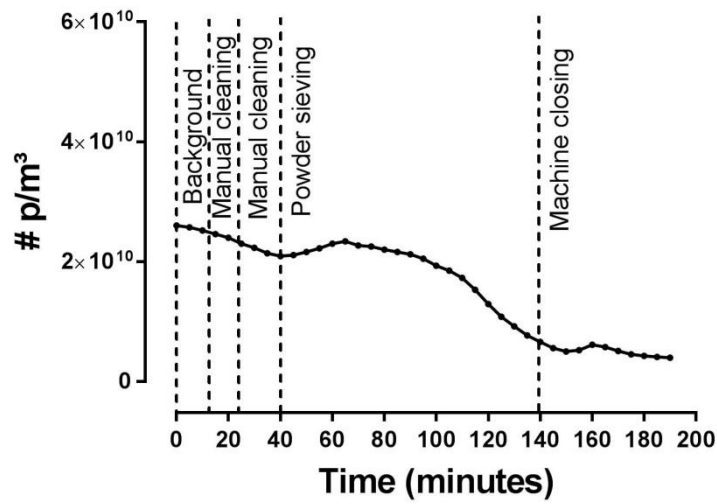
Aluminium (Al), Cobalt (Co), Chromium (Cr), Copper (Cu), Iron (Fe), Nickel (Ni), Tungsten Carbide (WC).

^aSDS also reported that the Stainless steel II powder contained 1.00-2.50% silicon metal, 1.00-2.50% carbon and 0.10-1.00% manganese.

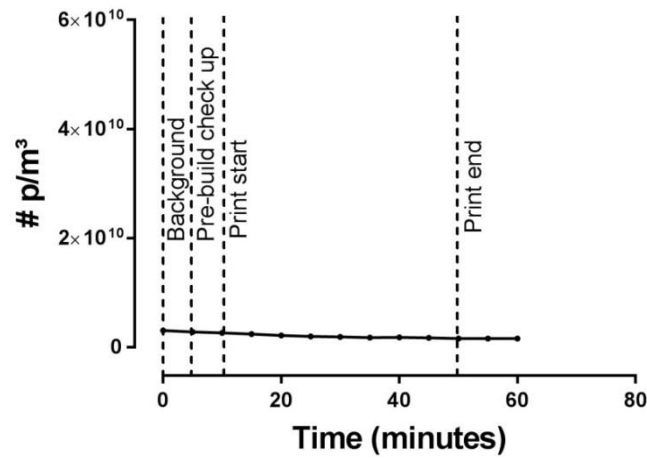
^bXRD results also detected Tetrataenite which is a metal composed of Fe and Ni.^[39]

It should be noted that the SDS of Stainless steel II stated that the exact percentage (concentration) of composition was withheld as it is a trade secret and these percentages are provided as estimates.

A1



A2



A3

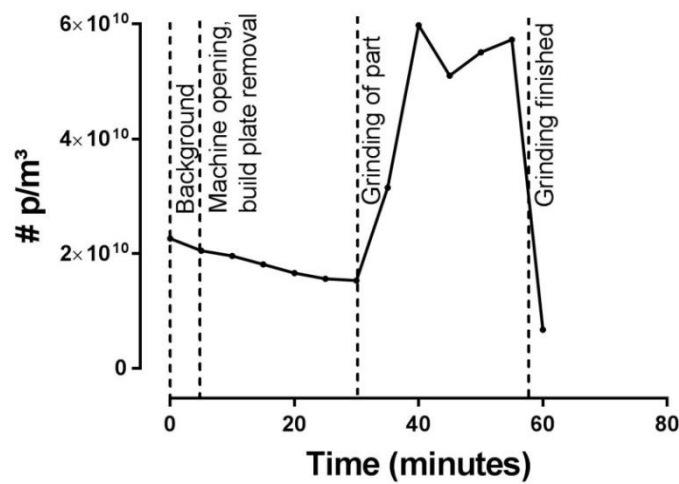
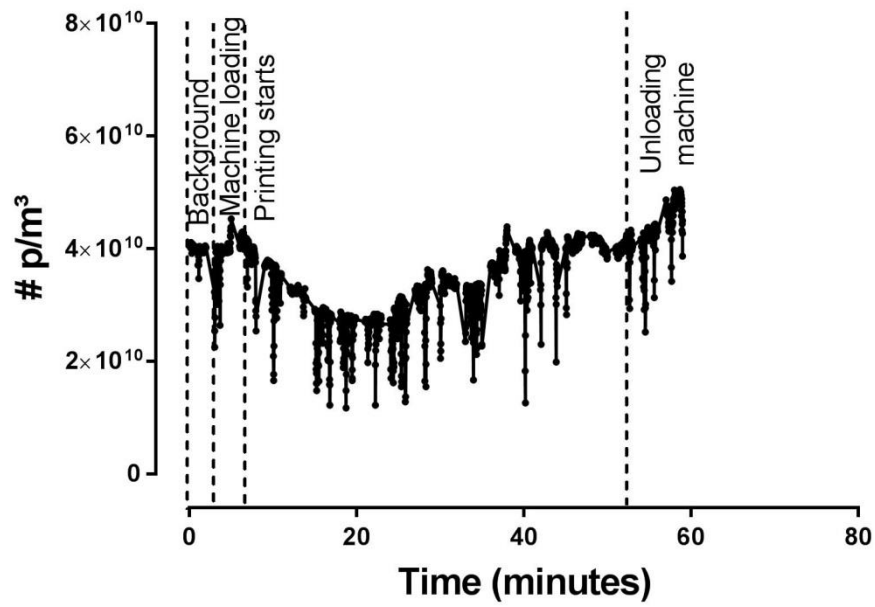


Figure 2: Particle number concentrations (0.01 to $>1 \mu\text{m}$) at Facility A during the Pre-processing (A1), Processing (A2) and Post-processing (A3) phases of PBF.

B1



B2

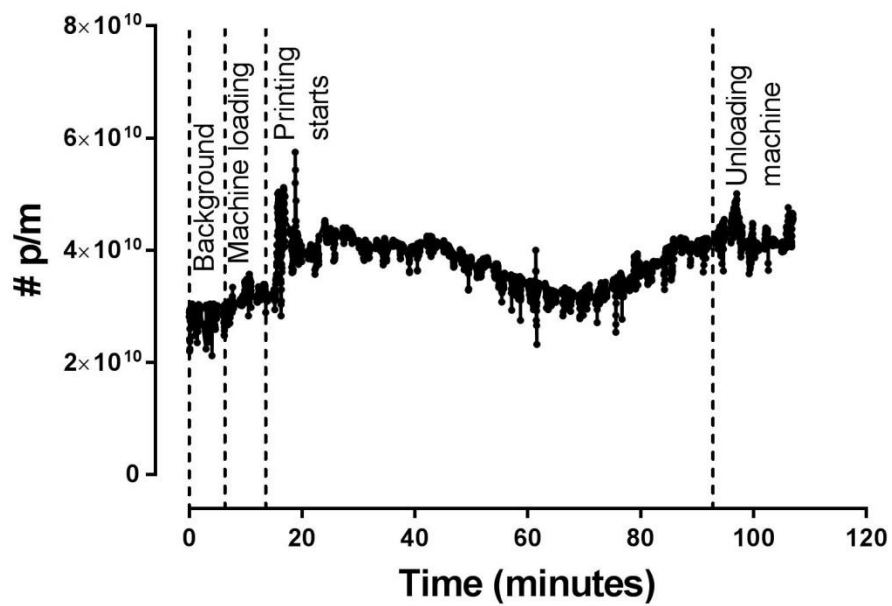
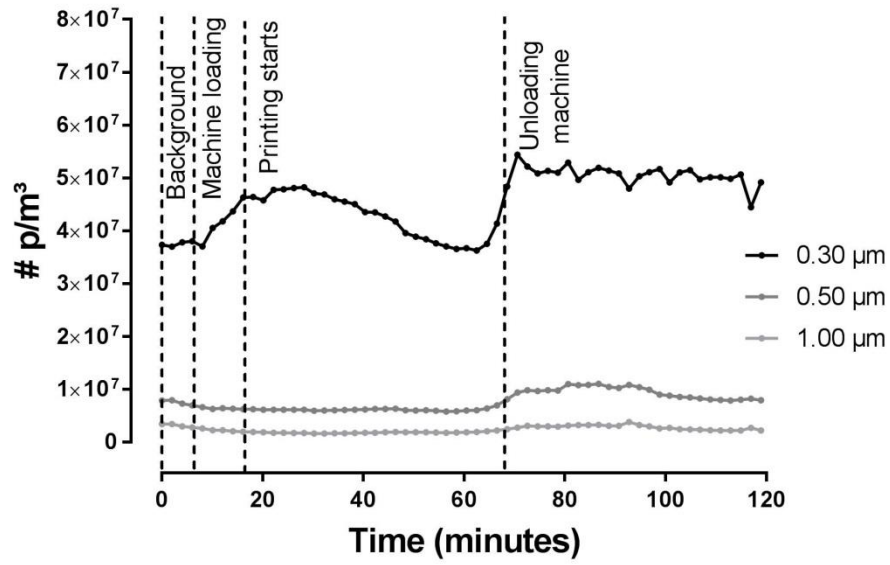


Figure 3: Particle number concentrations (0.01 to $> 1 \mu\text{m}$) at Facility B during DED print cycle 1 with stainless steel I (B1) and print cycle 2 with stainless steel I (B2).

B1



B2

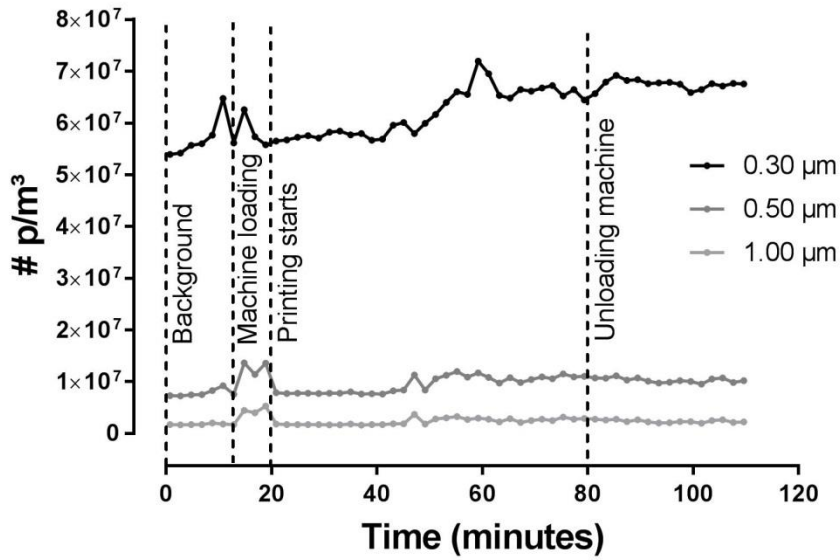


Figure 4: Particle number concentrations (0.30, 0.50 and 1.00 µm) at Facility B during DED print cycle 1 with stainless steel I (B1) and print cycle 2 with stainless steel II (B2).

Table 3: Metal concentrations in AM areas during all phases of AM at Facility A and B

Facility	Powder	Phase	n	Time (min)	Metals ($\mu\text{g}/\text{m}^3$)						
					Al	Cr	Cu	Fe	Ni	Ti	V
A	Maraging steel	*Pre-processing and processing	1	285	BDL	BDL	BDL	26.69	8.33	0.83	0.25
		*Post-processing	1	80	BDL	BDL	BDL	14.81	BDL	BDL	BDL
	Maraging steel	Pre-processing	1	260	1.63	BDL	1.42	0.20	BDL	0.87	BDL
		Processing	1	400	0.67	BDL	BDL	1.53	BDL	0.27	BDL
B	Stainless steel I	Continuous	1	125	BDL	BDL	BDL	14.92	2.28	BDL	BDL
	Stainless steel I		1	280	9.00	8.21	8.14	765.86	119.43	BDL	BDL
	Stainless steel II		1	176	BDL	29.94	BDL	1915.91	11.28	BDL	BDL

n: number of samples, $\mu\text{g}/\text{m}^3$: micrograms per cubic meter, BDL: below detection limit, Aluminium (Al), Chromium (Cr), Copper (Cu), Iron (Fe), Nickel (Ni), Titanium (Ti), Vanadium (V).

*Pre-processing and processing were carried out on the same day in the same workplace area, the following day the post-processing of the printed part took place. For the second print cycle of the maraging steel only a pre-processing and processing phase could be monitored.

Table 4: AM operator's TWA personal exposure to metals during all phases of AM at Facility A and B

Facility	Powder	n	Time (min)	Metals (TWA $\mu\text{g}/\text{m}^3$)						
				Al	Cr	Cu	Fe	Ni	Ti	V
A	Maraging steel	1	110	3.10	2.63	5.19	72.87	16.77	6.81	-
	Stainless steel I	1	125	0.73	0.11	0.12	10.35	2.20	0.16	BDL
B	Stainless steel I	1	214	1.02	0.41	1.04	7.54	0.58	0.23	0.14
	Stainless steel II	1	176	0.34	0.47	0.12	4.02	0.66	0.16	0.10
TWA OEL				10000	500	1000	1000	500	10000	-
ACGIH TLV [®]				1000	500	1000	1000	200	10000	-

n: number of samples, $\mu\text{g}/\text{m}^3$: micrograms per cubic meter, BDL: below detection limit, Aluminium (Al), Chromium (Cr), Copper (Cu), Iron (Fe), Nickel (Ni), Titanium (Ti), Vanadium (V). TWA OEL South African Eight-hour Time Weighted Average Occupational Exposure Limit, ACGIH: American Conference of Governmental Industrial Hygienists, No OEL for Vanadium.

*Note: The South-African TWA - OELs are in accordance to the Hazardous Chemical Substances Regulations (HCSR, 1995)^[33].

Table 5: AM operator's TWA personal exposure to < 300 nm metals during all phases of AM at Facility A and B

Facility	Powder	n	Time (min)	Metals (TWA $\mu\text{g}/\text{m}^3$)		
				Al	Cr	Ni
A	Maraging steel	1	360	0.69	0.46	2.41
	Stainless steel I	1	125	BDL	0.45	0.08
B	Stainless steel I	1	213	BDL	0.28	0.25
	Stainless steel II	1	280	BDL	0.28	0.42

n: number of samples, $\mu\text{g}/\text{m}^3$: micrograms per cubic meter, BDL: below detection limit, Aluminium (Al), Chromium (Cr), Nickel (Ni). TWA: Time Weighted Average.

SUPPLEMENTAL TABLES

Table S1: Particle number concentrations (0.01 to > 1 µm) during all phases of AM at Facility A and B

Facility	Powder	Phase	Particle number concentrations (x 10 ¹⁰ p/m ³)			
			0.01 to > 1 µm			
			Background concentration		Process concentration	
			Mean ± SD	Max	Mean ± SD	Max
A	Maraging steel	Pre-processing	2.53 ± 0.01 ^{a,A}	2.60	1.49 ± 0.01 ^{a,C,D}	2.40
		Processing	0.27 ± 0.01 ^{b,A,B}	0.30	0.13 ± 0.01 ^{b,C}	0.21
		Post-processing	0.20 ± 0.01 ^{c,B}	0.26	3.19 ± 0.02 ^{c,D}	5.98
B	*Stainless steel I		3.93 ± 0.26 ^d	4.53	3.52 ± 0.67 ^d	5.05
	#Stainless steel I		2.89 ± 0.16 ^e	3.05	3.78 ± 0.44 ^e	5.75

^{a-e} indicate significant ($p \leq 0.05$) differences between the means of background and phase concentration within each size range. Values with common superscript differ significantly. ^{A-D} indicate significant ($p \leq 0.05$) differences between the means of the phases (pre-processing, processing and post-processing). Values with common superscript differ significantly. *Stainless steel I (Print cycle 1), #Stainless steel I (Print cycle 2).

Table S2: Particle number concentrations (0.30 µm, 0.50 µm and 1.00 µm) during DED at Facility B

Facility	Powder	Particle number concentrations (x 10 ⁷ p/m ³)											
		0.30 µm				0.50 µm				1.00 µm			
		Background concentration		Process concentration		Background concentration		Process concentration		Background concentration		Process concentration	
		Mean±SD	Max	Mean±SD	Max	Mean±SD	Max	Mean±SD	Max	Mean±SD	Max	Mean±SD	Max
B	*Stainless steel I	3.80 ± 0.13 ^a	4.05	4.76 ± 0.53 ^a	5.85	0.71 ± 0.06	0.79	0.79 ± 0.17	1.10	0.29 ± 0.13 ^b	0.34	0.23 ± 0.05 ^b	0.37
	*Stainless steel II	5.70 ± 0.01 ^c	6.47	6.40 ± 0.47 ^c	7.19	0.78 ± 0.07 ^d	0.92	0.99 ± 0.15 ^d	1.36	0.17 ± 0.01 ^e	0.20	0.24 ± 0.07 ^e	0.53

^{a-e} indicate significant ($p \leq 0.05$) differences between the means of background and phase concentration within each size range. Values with common superscript differ significantly. *Stainless steel I (Print cycle 1), *Stainless steel II (Print cycle 2).

Table S3: AM operator's personal exposure to maraging steel during all phases of AM at Facility A

Facility	Powder	Phase	n	Time (min)	Metals ($\mu\text{g}/\text{m}^3$)					
					Al	Cr	Cu	Fe	Ni	Ti
A	Maraging steel	Pre-processing	1	40	BDL	8.38	BDL	204.00	50.13	8.75
		Processing	1	40	BDL	BDL	BDL	BDL	BDL	5.13
		Post-processing	1	30	0.48	BDL	19.83	112.67	22.00	15.83
	Maraging steel	Pre-processing	1	90	BDL	BDL	38.88	27.33	96.11	4.16
		Processing	1	210	BDL	BDL	BDL	6.76	BDL	BDL

n - number of samples, $\mu\text{g}/\text{m}^3$; - micrograms per cubic meter; BDL: below detection limit. Aluminium (Al), Chromium (Cr), Copper (Cu), Iron (Fe), Nickel (Ni), Titanium (Ti).

Table S4: AM operator's personal exposure to < 300 nm metals during all phases of AM at Facility A and B

Facility	Powder	Phase	n	Time (min)	Metals ($\mu\text{g}/\text{m}^3$)		
					Al	Cr	Ni
A	Maraging steel	Pre-processing and processing	1	280	0.57	0.49	0.71
		Post-processing	1	80	BDL	1.23	2.50
	Maraging steel	Pre-processing	1	120	BDL	2.15	BDL
		Processing	1	395	BDL	0.35	BDL
B	Stainless steel I	Continuous process	1	125	BDL	1.74	0.32
	Stainless steel I	Continuous process	1	213	BDL	0.65	0.56
	Stainless steel II	Continuous process	1	280	BDL	0.49	0.71

n – number of samples, $\mu\text{g}/\text{m}^3$ – micrograms per cubic meter, BDL: below detection limit. Aluminium (Al), Chromium (Cr), Nickel (Ni), Titanium (Ti), Vanadium (V). *Pre-processing and processing were carried out on the same day in the same workplace area, the following day the post-processing of the printed part took place. For the second print of the maraging steel only a pre-processing and processing phase could be monitored.

Chapter 6: CONCLUSIONS, RECOMMENDATIONS, LIMITATIONS AND FUTURE STUDIES

In this concluding chapter, the conclusions of this thesis, its limitations as well as recommendations for adequate control measures and future studies, are provided. Specific reference is made to the aims, objectives and hypotheses, as stated in Chapter 1. Recommendations are made to AM facilities (employers) and AM operators (employees) stating the control measures necessary to eliminate or reduce hazardous chemical substances (HCS) (particles and metals) emissions from and exposure of AM operators to HCS associated with/applicable to AM process categories investigated in this thesis as well as other metal powder based AM technologies. Finally, the limitations of this thesis as well as potential future studies are addressed.

6.1 Conclusions

6.1.1 Physico-chemical characteristics of metal powders

There are only two studies that have investigated particle sizes of AM metal powder feedstock used in industrial AM machines and the possible health risks associated with these powders.^[1,2] The physico-chemical characteristics of feedstock material can assist in identifying possible health implications prior to use.^[3] Particle size determines whether particles are inhalable, and when inhalable, where deposition may take place in the respiratory tract.^[4,5] The purpose of a safety data sheet (SDS) is to provide information on chemical safety, potential hazards (health, fire, reactivity and environmental) and safe work practices for a specific chemical product. SDSs should be used as a guide in the workplace and it should highlight health effects associated with powder exposure. Studies from Graff *et al.*^[1] and Mellin *et al.*^[2] have found variances regarding particle size with the manufacturers' statements in the SDSs indicating their results. The first objective as listed in Chapter 1 of this thesis was to establish the physico-chemical characteristics (particle size, shape and elemental composition) of virgin and used metal powders, used during powder bed fusion and direct energy deposition, and the relevance thereof to AM operators' health. All the feedstock powders were collected in order to compare their information with the corresponding information as stated in the SDSs of these powders.

Chapter 3 of this thesis presents the particle size distribution (PSD), shape and elemental composition of virgin and used (recycled) titanium (Ti) powders and their respective SDSs collected from three AM facilities in South Africa utilising powder bed fusion (PBF), and has been accepted for publication in *The South African Journal of Industrial Engineering*

(16 October 2018, acceptance letter is shown in Appendix A). In Chapter 5, virgin and used maraging steel and two used stainless steel powders were collected from two AM facilities, and the PSD, shape and elemental composition was also compared to their respective SDSs. All powders have been obtained from AM facilities located in South Africa.

The findings from both Chapter 3 (Article I) and Chapter 5 (Article III) is summarised in Table 1. The PSD analysis of virgin powders indicated particle size conformance to that stated in the SDS for only one (Ti64 powder) of the four powders. The SDSs of collected powders lacked detailed information on particle sizes of the collected powders. The SEM images indicated the presence of respirable sized ($< 4 \mu\text{m}$) particles and thoracic sized ($< 10 \mu\text{m}$) particles, which is of concern since respirable particles can penetrate the unciliated airways, while thoracic sized ($< 10 \mu\text{m}$) particles can penetrate beyond the larynx.

Table 1: Summary of particle size and elemental composition comparison between analysed findings from Chapter 3 and Chapter 5 of virgin powders to their respective SDSs

Chapter	Powder	Particle size (μm)	Elemental composition (%)
Chapter 3	Ti64	✓	x
	Ti ₆ Al ₄ V	x	x
	CL41TiEL	x	x
Chapter 5	Maraging steel	x	x

Elemental composition analysis of virgin powders (with XRD analysis) differed from the composition in terms of percentages and constituents disclosed in the SDS. The elemental composition of the powders suggests the potential to induce respiratory health effects. Health effects may not immediately be experienced by AM operators, however, repeated inhalation of these metal containing particles have the potential to cause adverse health effects.

Only used (recycled) stainless steel I and stainless steel II powders were collected from the facility as described in Chapter 5 because this was the preferred feedstock used by the AM facility for DED. Therefore, limited comparisons could be made. However, it was established that the SDS of the virgin stainless steel I powder used at the facility did not state a minimum or maximum particle size.

The objective has been achieved and physico-chemical characteristics (particle size, shape and elemental composition) of virgin and used metal powders, used during PBF and DED, and the relevance thereof to AM operators' health have been established. In Chapter 1 it was hypothesised that: *there is inadequate information regarding particle size and elemental*

composition of AM powders in the SDS documents as supplied by the manufacturers/suppliers which places AM operators' health at risk. This hypothesis can only be partially accepted. This partial acceptance is based upon the findings that only one of the four virgin powders size (as supplied by manufacturers/suppliers) conformed to the size range stated, while elemental composition analyses was different from the SDSs and found that SDSs did not report all constituents found in all four powders. Unfortunately, no virgin stainless steel I and stainless steel II powders could be analysed limiting further comparisons. An SDS should serve as an essential starting point for the development of a comprehensive health and safety programme in the workplace.^[6] If insufficient information is provided, an SDS may place AM operators' health at risk unintentionally.

6.1.2 Particle emissions during pre-processing, processing and post-processing phases

The PBF process is the most researched technology in terms of the feedstock materials used and technology development, however, research on particle emissions from and AM operators exposure to HCS and potential health risks remain limited.^[7,8] There is extensive literature available that has provided a better understanding on particle emissions from fused deposition modelling (FDM™) three dimensional (3D) printers, although most of these studies have been conducted in controlled environments, with only one study that has investigated emissions from a large industrial AM machine.^[1,8-10] From the results discussed in Chapter 4 (Article II) and Chapter 5 (Article III) it was evident that increases in particle number concentrations were associated with specific manual tasks performed by the AM operator. Manual tasks such as grinding, machine cleaning, wire cutting and cleaning of the part during post-processing led to an increase in particle number concentration especially in the 0.01 to > 1 µm particle size range.

The second objective of this thesis was to assess particle emissions and respiratory metal exposure of AM operators when using three titanium powders and maraging steel during the pre-processing, processing and post-processing phases of AM at three AM facilities utilising PBF. This objective is twofold and therefore, two hypotheses were postulated. In the first place the second aim and second hypothesis will be addressed, followed by the third hypothesis in Section 6.1.3.

In Chapter 4, particle emissions from and AM operators' respiratory exposure to metals were assessed during the pre-processing, processing and post-processing phases of PBF at three AM facilities using Ti powders. Similarly in Chapter 5, particle emissions from and AM

operators' exposure to maraging steel during the pre-processing, processing and post-processing phases of PBF were investigated. The findings from the comparisons made between the mean particle number concentrations during the three different process phases is summarised in Table 2, and are based upon the results from Chapter 4 (Table S1, page 99) and Chapter 5 (Table S1 page 143). The maximum detectable size of a Condensation Particle Counter (CPC) used in Chapter 4 and Chapter 5 is generally anywhere from 1 μm to 3 μm . However, particles larger than approximately 1 μm are very easily lost due to inertial impaction, (nanoparticles are essentially unaffected by this loss mechanism) and these supermicron sized particles cannot penetrate through the CPC flow path to the detection region, and is therefore unlikely to be measured.^[11] Furthermore, no particles emissions > 1 μm was detected by the Airborne Particle Counter (APC) indicating that particles detected by the CPC were most likely $\leq 1 \mu\text{m}$ in size.

Table 2: A summary of the mean particle number concentrations during three different process phases from Chapter 4 (Table S1, page 99) and Chapter 5 (Table S1 page 143)

Powder	0.01 to > 1 μm	0.30 μm	0.50 μm	1.00 μm
Ti64	post > pro > pre	pre > pro = post	pre = post = pro*	post = pre > pro
Ti ₆ Al ₄ V	post > pro > pre	pro > post > pre	pro > pre = post	pre = post > pro
#Maraging steel	post > pre > pro	-	-	-

pre: pre-processing, pro: processing, post: post-processing.

*No statistical significant differences between the three phases in the 0.50 μm particle range.

#Particle number concentration was only established in the 0.01 to > 1 μm size range.

It was, hypothesised *that the mean particle number concentrations are the highest during the post-processing phase followed by the pre-processing phase, with the lowest particle number concentrations during the processing phases of PBF*. Particle emissions from the CL41TiEL powder was excluded from the hypothesis testing, since particle number concentration for the pre-processing phase could not be collected. Therefore, conclusions can only be drawn where workplace scenarios entailed all three process phases. The abovementioned hypothesis is rejected based on the following: (i) Based on the APC size fractions mean particle number concentrations were in no instances the highest during the post-processing phase, followed by the pre-processing phase, with the lowest during the processing phase. (ii) Although mean particle number concentrations in the 0.01 to > 1 μm size range, as detected by the CPC, were the highest during the post-processing phase for all the three powders, the pre-processing phase only had the next (second) highest mean particle number concentration for one of the powders (maraging steel). (iii) It is evident from

the emission data collected during this study (Chapter 4, Figure 1 and Figure 2; Chapter 5 Figure 2) that the particle number concentrations emitted during each phase depends on the specific individual tasks being performed and that individual tasks performed during the pre-processing and post-processing phases leads to the emissions of particles. Findings also indicate high particle number emissions possible during the processing phase, however, this resulted from high particle emissions during the pre-processing phases (still present during the processing phase).

The investigated size fractions of the 0.01 to > 1 μm and 0.30 μm to 1.00 μm may easily penetrate to the unciliated airways of the lungs.^[12] Occupational exposure to fine particles (< 2.5 μm) has been associated with the development of cardiovascular diseases and cancer.^[13]

6.1.3 Respiratory exposure during processing and post-processing phases

AM machines are designed to operate unattended, however, all powder handling is performed manually by the AM operator and potential occupational exposure can occur during the three phases of AM, namely the pre-processing, processing and post-processing phases. Inhalation of materials used during AM can take place during manual sieving and powder loading during pre-processing, if particles are not properly removed by exhaust ventilation during processing and finally during post-processing techniques on the finished part.^[1,14-16]

Graff *et al.*^[1] investigated selective laser melting, which is a PBF technology utilising Inconel 939 feedstock powder. In their study, personal exposure monitoring was performed during activities such as opening the AM machine, vacuuming the build/base plate and handling of the build/base plate and it was found that AM operators were exposed to detectable levels of metals during AM. The authors also demonstrated that cobalt, chromium, and nickel containing particles < 300 nm were present in AM workplace air.^[1]

It was hypothesised *that there is respiratory exposure of AM operators to metals during all three process phases of PBF using titanium and maraging steel powders with the highest exposure during the post-processing phase followed by the pre-processing phase and the lowest exposure during the processing phase.* For the purpose of this hypothesis personal respiratory exposure was only considered where all three process phases took place therefore, CL41TiEL was excluded. The hypothesis is partially accepted. The total metal concentration was determined as the concentration of the sum of the quantified metals. By

summarising the results of the total detected metal concentrations obtained from three powders, metal concentration during post-processing was the highest for two out of the three powders (Table 3).

Table 3: A summary of AM operators' personal exposure to titanium metal powders and maraging steel during phases of AM

Powder	Phase	Metals $\mu\text{g}/\text{m}^3$								Total metal concentration $\mu\text{g}/\text{m}^3$
		Al	Co	Cr	Cu	Fe	Ni	Ti	V	
Ti64	Pre-processing	2.50	0.71	0.82	0.87	9.76	0.65	10.91	0.71	26.92
	Processing	4.06	1.15	1.32	170.91	4.87	16.23	1.94	1.15	201.63
	Post-processing	7.75	1.81	2.09	2.23	19.53	2.43	206.65	10.51	252.99
Ti6Al4V	Pre-processing	5.42	1.53	1.77	18.50	47.67	9.67	483.67	21.50	589.72
	Processing	1.08	0.31	0.35	1.63	5.87	0.28	0.52	0.31	10.35
	Post-processing	84.73	1.24	1.43	1.53	37.70	1.15	1352.16	57.03	1536.97
Maraging steel	Pre-processing	4.07	1.15	8.38	1.41	204.00	50.13	8.75	1.15	279.03
	Processing	4.07	1.15	1.33	1.41	1.33	1.06	5.13	1.15	16.61
	Post-processing	5.42	1.53	1.77	19.83	112.67	22.00	15.83	1.89	180.94

Aluminium (Al), Cobalt (Co), Chromium (Cr), Copper (Cu), Iron (Fe), Nickel (Ni), Titanium (Ti), Vanadium (V). For metal mass below the analytical detection limit (DL), metal mass was calculated using the DL mass divided by the square root of two method.^[17]

Each of the three processing phases involved manual tasks performed by the AM operator which led to AM operators being exposed to low concentrations of metals. Pre-processing tasks involved machine cleaning, sieving of powder and hopper loading of powder, followed by the processing phase not having as many manual tasks but requires the AM operator to regularly check on the progress of the build. The higher metal concentrations during the post-processing phases was ascribed to tasks that included grinding of the part, manual cleaning of the part and vacuuming the inside of the AM machine.

6.1.4 Particle emissions and AM operator exposure during DED

DED is one of the more complex AM processes mostly used to repair or add additional material to existing components.^[18] Laser cladding is a widely applied AM technology of DED, where metal powder feedstock is fed layer-by-layer through a nozzle onto an existing substrate base, and a laser beam is focused on the substrate to create a melt pool on the surface.^[19,20] Once laser cladding is initiated, the process is operated continuously and is not separated into distinct phases as for instance pre-processing, processing and post-processing. There is, however, limited emission and exposure information available for AM process categories other than material extrusion, and no published literature to date available on emissions from or exposure assessment studies related to DED or more specifically laser cladding.

The third objective of this thesis was to assess particle emissions and respiratory metal exposure of AM operators when using two types of stainless steel powders during DED at an AM facility. In Chapter 5 particle emissions from and exposure to metals during DED, more specifically laser cladding AM using stainless steel powders was investigated. Peak number concentrations of approximately 5.75×10^{10} p/m³ in the 0.01 to > 1 µm size range and 7.19×10^7 p/m³ for the 0.30 µm sized particles were detected, while no particles > 1 µm were detected. Initially when printing started particle number concentrations were high and declined after a while, with a slight increase once unloading of the machine took place. It was found that AM operators utilising two types of stainless steel were exposed to seven quantifiable metal concentrations (Al, Cr, Cu, Fe Ni, Ti and V) during DED. The Al and Cu that was found during DED with stainless steel I and stainless steel II were not listed in the respective SDSs. These deviations may be due to cross contamination as AM operators work with a variety of metal powders at each facility. The lowest TWA-OEL exposure was to V at 0.10 µg/m³ and highest to Fe at 10.35 µg/m³ during the use of stainless steel I. The Fe concentrations in stainless steel powders ranged from 4.02 µg/m³ to 10.35 µg/m³ respectively (no OELs were exceeded). No Co was detected during the use of stainless steel I or stainless steel II, and AM operators were only exposed to < 300 nm Cr (0.28 to 0.45 µg/m³) and Ni (0.08 to 0.42 µg/m³).

The hypothesis stated that *particles are emitted from and AM operators are exposed to metals during DED when using stainless steel*. This hypothesis is accepted based on the data reported in Chapter 5. When printing of stainless steel I commenced, the particle number concentration decreased in the 0.01 to > 1 µm size range but increased at the end of processing when unloading of the part took place. Particle number concentrations increased in the 0.30 to 1.00 µm size ranges during machine loading and unloading of stainless steel indicating that task specific activities leads to higher emissions of particles. No particles > 1 µm were detected during DED of stainless steel. Very low concentrations of Al, Cr, Cu, Fe and Ni were detected in the workplace areas during DED when using stainless steel. Although no OELs were exceeded, AM operators were exposed to seven detectable metals, with two of these metals < 300 nm.

6.2 Summary

The South African AM industry holds great potential for future developments in the AM of metal parts. However, there was a need to investigate AM feedstock and to address the emissions of and AM operators' occupational exposure to HCS (particles and metal dust). The findings from this thesis are the first in South Africa to give insights into particle

emissions from and AM operators' exposure to metals during PBF and DED in industrial AM facilities. It was found that SDSs contained inadequate information regarding particle size and elemental composition of AM powders as supplied by the manufacturers/suppliers which place AM operators' health at risk. Particles $\leq 1 \mu\text{m}$ were identified during PBF and DED and the increase in particle number concentrations depended on the specific pre- and post-processing tasks carried out by the AM operators. Low concentrations of metals were found in the workplace air and were ascribed to cross contamination of the various metal alloys used by the AM facilities. PBF utilising three different Ti powders and a maraging steel powder found that AM operators were exposed to detectable, but low concentrations of various metals during the three different process phases. DED was operated as a continuous process and quantifiable concentrations of metals were detected in the workplace air. AM operators were also exposed to low concentrations of metals including metals $< 300 \text{ nm}$ in size at all three facilities during PBF and DED.

In conclusion the general aim of the thesis, namely to assess the emissions of and occupational exposure to hazardous chemical substances (particles and metals) associated with two metal powder based AM process categories (powder bed fusion and direct energy deposition) at three South African institutions utilising AM, has been achieved.

6.3 Recommendations

Recommendations based on the findings reported in Chapters 3 to 5 are provided in the following text. In an effort to reduce particle emissions from and AM operators' respiratory exposure to metals the recommendations related to all three Chapters and will contain similarities, however, exceptions will be discussed separately. The recommendations are presented in no specific order.

❖ Recommendation 1:

Chapter 3 and Chapter 5 indicated inadequate information with regards to particle size and elemental composition to what was declared in the SDSs for three of the four investigated powders. It is therefore, recommended that manufacturers should provide more accurate and comprehensive information in SDSs on, in particular, the particle size and elemental composition of the AM powders. An SDS should be a primary resource for the employer (at the AM facility), to enable the employer to assess the risk, and to reduce or eliminate the risk (Section 8). The AM operator should also be able to refer to the SDS as guidance for safe powder handling, and should be informed of the potential health risks involved. Effective powder characterisation can contribute towards a better

understanding of potential health effects and assist in implementing controls at AM Facilities. According to Section 10 of the South African Occupational Health and Safety (OHS) Act (Act 85 of 1993)^[21] manufacturers should ensure that the supplied substance, if properly used, is safe and contains no risk to the health of the person using it. If a manufacturer chooses to withhold information regarding the composition of the feedstock due to trade secrets of the feedstock, the manufacturer should undertake to disclose specific information regarding the risk associated with the substance.^[21]

❖ *Recommendation 2:*

Due to a lack of detailed information in SDS's as reported in Chapter 3 and Chapter 5, it is recommended that a health risk assessment should be conducted in advance for each powder, since an inaccurate/incomplete SDS could create a false sense of protection of AM operators' health. The SDS's and operating manuals needs to be investigated, and any shortcoming needs to be identified such as a lack of safe operating guidelines or a lack of information on elemental composition and powder size. The Hazardous Chemical Substances Regulations (HCSR) 1995;^[22] Regulation 5 (1) (3) states that an employer should ensure that a risk assessment is conducted to determine if any employee might be exposed. During this assessment record should be kept of what the HCS the employee may be exposed to, the health effect thereof as well as where the HCS may be present and in what physical form is likely to be. The route of intake by which and the extent to which an employee (AM operator) can be exposed should be noted as well as the nature of the work, process and reasonable deterioration in of failure of control measures at the facilities. When an AM Facility identifies a lack of information in the SDSs of a powder in future, it is recommended that each facility should determine the physico-chemical characteristics (particle size, shape and elemental composition) of each metal feedstock used at their premises. Powder characterisation should be performed for both virgin and recycled powder. An inventory (list) should be drawn up of every feedstock powder, the respective SDS, PSD and elemental composition. Powder characterisation can be performed at the North-West University and comprehensive reports and feedback in this regard can be provided to an AM facility.

❖ *Recommendation 3:*

AM operators were exposed to detectable concentrations of metals. Although concentrations was well below the respective OELs, where the inhalation of an HCS is concerned, an employer shall ensure that there is a measurement programme of the airborne concentrations of the HCS to which an employee is exposed in accordance to Regulation 6 (1). It is important for an employer to note that there are two types of

exposure limits, namely an occupational exposure limit control limit (OEL-CL) and an occupational exposure recommended limit (OEL-RL) as listed in Annexure A of the HCS Regulations. The main difference between the two limits is that the OEL-RL is set at a level which there is no indication of risk to health at the level set and for the OEL-CL a residual risk to health may exist at the level set. In accordance to Regulation 6 (2) (b) of the HCSR^[22] representative measurement (air monitoring) should be carried out for a HCS with a control limit every 12 months and every 24 months for a HCS with a recommended limit. From Chapter 4 Al, Cu, Fe, Ni, Ti and V was detected during PBF. The findings of Chapter 5 indicated that the AM operators were exposed to six metals during PBF (Al, Cr, Cu, Ni, Fe and Ti), and seven metals during DED (Al, Cr, Cu, Ni, Fe, and Ti). HCS that need to be measured every 24 months include Al, Co, Cu, Fe, Ti and V, while HCS with control limits such as Cr and Ni need to be monitored every 12 months. The employer of the AM facility should obtain the service of an approved inspection authority to conduct the monitoring of HCS.

The results from static area monitoring as found in both Chapter 4 and Chapter 5 indicated different metal components to what was stated in the respective SDS documents. The results could be ascribed to unintentional transfer of metal elements between different AM workplace locations. AM operators may work with different metal powders at one facility in different workplace locations which contributes to cross contamination of metal powders. An employer shall ensure that the exposure of an employee is either prevented or, where this is not reasonably practicable, adequately controlled and shall further establish what precautionary measures should be taken and provide the necessary means to apply such precautionary measures. In order to ensure good occupational hygiene practice and due to differing production rates and environmental conditions, it is recommended that area monitoring also be performed in AM work areas.

Depending on the facility or the part that is being processed, the three AM processing phases can be performed in one work area or separate work areas. It is therefore recommended that distinctive features of each work area should be noted, along with the AM operators involved in the area, the duration of the AM operator being in the work area and source of exposure linked to the phase of processing in the area. Static area sampling will assist the employer to determine the distribution of HCS throughout the work area, and thereby identifying higher risk areas.

❖ *Recommendation 4:*

Based on the results in Chapter 4 and Chapter 5 an engineering control such as flushing the build chamber twice with non-flammable or reaction gases such as nitrogen or argon can be implemented. This can be done during the post-processing phase to assist in depowdering of final metal parts before they are removed from the build chamber. This measure can assist to reduce emissions from and exposure to particles and metals during the post-processing phase. This recommendation is dependent on the type of AM machine at the AM Facility, and the machines capabilities.

❖ *Recommendation 5:*

AM operators were exposed to particles $\leq 1 \mu\text{m}$ during specific process phases. According to these findings, it is clear that there is a need for standardised health and safety operating procedures for AM operators for task-based activities which occurred during pre-processing and post-processing phases. The employer at the AM facilities is responsible for providing AM operators with safe work procedures regarding the use, handling and storage of HCS in the workplace as stated in Regulation 3 (j) of the HCS regulations.^[22] Pre-processing tasks entailed machine cleaning, powder sieving and hopper loading, and post-processing consisted of tasks such as vacuuming, dry sweeping of the part to remove excess powder and part cleaning. At Facility A and Facility C (Chapter 4, Article II) post-processing tasks are carried out in different work areas than the pre-processing and processing work areas. These post-processing work areas are not equipped with local extraction ventilation systems. AM operators perform a variety of post-processing tasks such as grinding and part cleaning that may produce metal dust and metal shavings in the workplace atmosphere.

From the results of Chapter 5, it is clear that AM operator exposure to the individual metals was $< 3.60\%$ of the respective TWA-OELs and $< 9.01\%$ of TLVs[®]. These individual metals included Al, Cr, Cu, Fe Ti and V which might be a risk to the respiratory health of the AM operator. The individual metal with the highest exposure was Ni, which is human carcinogen. As FFP1 respirators only provide protection against low toxicity substances and dust, they cannot be recommended for AM operators. Elastomeric half-mask respirators with class N95 and P100 filters have been found to provide protection against particles $< 300 \text{ nm}$ ^[23]. Effective performance of a respirator is not only dependent on filter performance but also on the conduction of a fit test. Only when a respirator is worn (used) correctly it can provide adequate protection. AM operators who are required to wear respirators should be informed, instructed and trained in the use of respiratory protective equipment in accordance with Regulation 11 of the HCSR^[22].

When an employer provides PPE they should also provide separate containers or storage facilities for when PPE is not in use as required in terms of Regulation 11(3) (b) of the HCSR^[22]. This should be done to avoid contamination of the inside of respirators that could result in contaminant inhalation. The containers should be impermeable and should be able to seal properly. The employer should also ensure that PPE is in good working condition (Regulation 11 (2) (d)). In Regulation 11 (4) (a) it is also stated that an employer should ensure that where contaminated PPE that is cleaned on the workplace premises, care shall be taken to prevent contamination during handling, transport and cleaning of the PPE. It is also necessary for the employer to ensure that the provided PPE is maintained and in a good working order as stated in Regulation 12 (a). It is important to note that PPE is recommended as the last resort in the hierarchy of controls, however, PPE can be recommended along with existing controls. PPE should never be the only method to reduce exposure, as PPE only minimises the hazard.

❖ *Recommendation 6:*

The good housekeeping practices should be maintained at Facility A and Facility C to ensure that all working areas are in a clean condition to limit the amount of dust that can be resuspended in air. A lack of housekeeping can lead to metal dust build up creating a secondary exposure source. Cleaning schedules should be adapted to operating schedules. At Facility B metal dust build-up on work surfaces such as AM door handles and on the AM machine was evident in the work areas as well as tea rooms close to the work areas. Metal dust build-up on structures and on the floor should be limited by cleaning the areas thoroughly before and after processing has taken place. It is necessary to ensure that all AM facilities performing metal AM processes uses an immersion separation vacuum cleaner which neutralises the intake air and dust in a liquid form. Metals such as Ti are combustible and a small amount of static can ignite with the powder and cause an explosion.^[20] The pressure by which the powder material enters the vacuum enables these wet systems to capture and submerge the powder dust into water which quenches the ignition source. The filters inside the vacuum cleaners only return clean air into the workplace.

It is important to follow the correct disposal of and HCS (metal dust) from the contaminated filters, as stated in the HCSR^[22] in terms of Regulation 15 of the disposal of HCS. Filters from AM machines are removed in the work areas where AM operations take place, and filters from the vacuum are cleaned by AM operators. The employer should as far as is reasonably practicable ensure that all collectable HCS waste is placed into containers that will prevent the likelihood of exposure during handling as

stated in Regulation 15 (b). According to Regulation 15 (e) the employer should also ensure that all employees occupied in the collection, transport and disposal of HCS waste, in this case the AM operators that remove the filters from the vacuum for cleaning and may be exposed to that waste, are provided with suitable PPE such as elastomeric half-mask respirators with class N95 and P100 filters to provide protection against particles < 300 nm.^[23]

❖ *Recommendation 7:*

During this study it was noticed that Facility C did not have designated storage facilities for PPE. Therefore, it is recommended that separate, clean containers or storage facilities should be provided for PPE when not in use, as required in terms of Regulation 11(3) (b) of the HCSR.^[22] Please refer to Recommendation 5 for a more detailed discussion on legislation that is relevant to this recommendation.

❖ *Recommendation 8:*

According to Regulation 3 of the HCSR,^[22] before an employee (AM operators) is exposed or can become exposed to a HCS in this case metal powders and dusts, operators in the AM work environment should be properly and comprehensively trained at intervals which includes initial training and refresher training with respect to, amongst others:

- The source of exposure.
- Potential health risks associated with their tasks/activities.
- Measures necessary for protection from exposure, including wearing of personal protective equipment and clothing.
- The correct use of and maintenance of provided PPE.
- The correct use handling, storage and labelling of HCS in the workplace.
- Importance of good housekeeping and personal hygiene.
- The use of existing engineering control measures used to reduce/eliminate exposure.

In accordance to Regulation 3 (2) an employer should provide written instructions in the event of an emergency regarding HCS to the employees.

❖ *Recommendation 9:*

AM is a fast paced technology, with new features and improvements to AM machines and feedstock powders. In terms of Regulation 5 of the HCSR,^[22] if new processes or tasks are introduced, or if existing processes or tasks are changed or modified, the employer at the facility should inform the relevant health and safety representative of

health and safety committee to arrange an assessment of the potential exposures (risk assessment). This is of particular importance where AM facilities introduce new feedstock powders, new AM machines or during machine (routine) maintenance such as filter replacements. If during the assessment it is indicated that an employee (AM operator) might be exposed the employer should in terms of Regulation 6 of the HCS carry out exposure monitoring by an approved inspection authority or by a person whose ability to do the measurements is verified by an approved inspection authority.^[22]

❖ *Recommendation 10:*

As the AM industry in South Africa is expanding, it is recommended that if a facility acquires a new AM machine, proper planning of the design and operations layout of a production area is necessary. Planning should consider separating the process phases, by placing certain tasks in different rooms. By separating the process phases, the potential risks in an area can be minimised and spreading of airborne particles to adjacent processes can effectively be prevented. Separation of phases may also include isolation of sources of exposure by making use of enclosures where possible for certain tasks or process phases. When separating the process phases ventilation systems should be included in each of the work areas in and consultation with a ventilation expert.

❖ *Recommendation 11:*

Due to each AM facility that had different AM machines, different feedstock and their own workplace layout it can be difficult to implement one standard safe work procedure for all facilities, therefore, it is recommended that a mobile application can be developed, containing all seven AM process categories, their relevant technologies and feedstock applicable to the process/technology. The purpose of such an application should form part of information and training of the AM operator with regards to the safe work procedures and should be relevant to the process/technology and feedstock along with standard AM terminology. This will enable AM operators to easily access each AM process/technology that their facility has available and take reasonable care for their health and safety and also other persons that may be affected (exposed) by their acts.^[21] This will also enable the employer at the AM facility to be informed of the AM process/technology before a new AM machine is installed at the facility.

6.4 Limitations

In retrospect, the following limitations related to the assessment of emissions from and AM operator's respiratory exposure to HCS associated with/applicable to AM process categories investigated in this thesis have been identified:

❖ *Limitation 1:*

Studies carried out with polymer AM feedstock are usually able to repeatedly print/manufacture the same object (in size and mass). These “test runs” are conducted at the same printing speeds and printing time only using different polymer feedstock materials.^[24,25] This enables effective comparisons between feedstock materials, particles emitted and operator exposure. The manufacturing of metal AM parts is mostly consumer specific entailing one/two large production (processing) runs or small batch printing (processing). Therefore, repeatable manufacturing (printing) of the same part during metal AM processing is impractical, and also too expensive. This limits repeatable measurements of particle emissions and AM operator respiratory exposure. It is essential to understand operation variables, particle emissions and AM operator exposure to quantitatively compare results between studies.

❖ *Limitation 2:*

When investigating FDM™ printers, locations mostly include libraries, makerspaces and accessible (controlled) research facilities.^[9,26,27] During this study the three AM facilities were industrial facilities, where AM metal parts produced for clients are classified in certain circumstances, limiting access to study emissions or AM exposure, also limiting comparative studies. Also due to the large size of the industrial AM machines investigated in this thesis, these AM machines cannot be practically placed inside a controlled environment for chamber based studies. Studies were not performed in a controlled environment (chamber studies), this study was dependent on real-life working conditions that took place. This limitation may also be seen as an advantage in the sense that the results were a true representation of real-life AM working environments thus providing a true reflection of the actual emissions from and AM operator exposure to HCS in industrial AM workplaces.

❖ *Limitation 3:*

When this study was conducted, the NRD sampler was used as per manufacturer guidance, containing nylon mesh as the substrate to collect < 300 nm particles. A recent study has reported that the nylon mesh used in the NRD sampler contains Ti from the titanium dioxide (TiO₂), used to whiten the nylon material, and the presence of the Ti in the substrate which interferes with the exposure assessment of Ti.^[28,29] In the study by Mines *et al.*^[28] experimental adaptations was made to the NRD sampler by replacing the nylon mesh with polyurethane foam, and also differentiated the background metal in the substrate. Mines *et al.*^[28] used an experimental setup to generate metal fume particles, and NRD samplers with polyurethane foam and NRD samplers with nylon mesh was used at a flow rate of 2.5 l/min to measure collection efficiency. SEM imaging was also undertaken to investigate both the polyurethane foam and nylon mesh used. From the findings of the study the polyurethane foam was found to be more suitable than the nylon mesh used in the NRD, in terms of elemental content, particle collection by size and pressure drop. However, to my knowledge the NRD with polyurethane foam is at present not commercially available to purchase or use.

6.5 Future studies

At the completion of this thesis, several opportunities for possible future studies have been identified. These possible studies include the following:

- ❖ Steel is most commonly used as engineering material, also making it of high interest to the AM industry.^[30] Extensive research on the development of new AM metal powders such as platinum, vanadium and tungsten alloys as well as the expansion of current metal AM powders is underway.^[31,32] Two of the AM processes that are powder-based and commercially used for the production of metal parts are PBF and DED.^[31] Based on the findings on the physico-chemical characteristics of feedstock materials from this thesis, future studies may include a wider variety of AM metal powders used during PBF and DED AM processes. This may include physico-chemical characterisation of new powders. Studies may also include the emissions and exposure monitoring during the developmental process of these new powders when experimental processes (test runs) are performed at facilities.
- ❖ The Titanium Centre of Competence is currently in process of developing a Ti metal production plant to produce Ti metal powder in South Africa, which will enable larger scale of AM parts are produced. Once the Ti metal production plant is fully operational,

and producing Ti powders for AM, in depth powder characterisations of this locally produced titanium powder can be performed, as well as emission studies during the production of the powder.

- ❖ AM powder feedstock material can be recycled and reused, creating a powder blend consisting of virgin (new/unused) powder and used (recycled) powder.^[33] The findings from Chapter 3 indicated that thoracic sized ($< 10 \mu\text{m}$) and respirable sized ($< 4 \mu\text{m}$) particles were present in the virgin and used powders.^[34] The information contained in SDSs refer to virgin powders and not to used powders. Therefore, there is a lack of knowledge on the PSD and elemental composition of the used powders. Future studies may involve investigating the impact that recycling may have on powder characteristics, and how that may contribute to AM operator exposure to possibly different sized particles.
- ❖ Polymer feedstock studies performed have effectively compared emissions from different FDMTM printers. These studies also included printing (processing) the same object, and the same print speed and durations.^[24,25] As mentioned in Limitation 3 of this thesis, studies on polymer feedstock have enabled effective comparisons between AM machines and similar/different feedstock materials. Therefore, future studies should include different PBF machines conducting the exact pre-processing, processing and post-processing tasks and producing the exact same part, using the same feedstock material or different feedstock materials.
- ❖ AM facilities investigated during this thesis either collaborate or function as extensions of engineering facilities. These facilities will most likely invest in the smaller metal desktop printers that are gaining interest in the AM industry. Smaller metal desktop printers will be able to produce smaller metal parts and this may also entail mass production of metal AM parts. As these facilities are expanding they will in future also include AM technologies such as binder jetting and material extrusion in the work environments. This will lead to AM environments becoming more heterogeneous in terms of emissions and exposure due to a variety of manufacturing processes that may take place in close proximity to each other. Therefore, future studies may include concurrent exposure monitoring for a variety of HCS which may include metal feedstock and polymers.
- ❖ Although all AM personal exposure was far below the OELs, exposure to particles $\leq 1 \mu\text{m}$ should not be discarded as unimportant. Real-time monitoring has proven effective during AM for the investigation of particle emissions.^[35,36] Instruments used to

measure particle emissions should include the ability to measure particle concentration and particle size. Future studies may include a wider variety of real-time instruments such as a scanning mobility particle sizer (SMPS), a GRIMM optical particle counter and an electrical low-pressure impactor (ELPI). These instruments can measure particle size and number concentration spanning the total scale nanometre to micrometre. Depending on the model of the instrument the SMPS has 13 size fractions and can measure particles in the 3 nm to 300 nm size range, the GRIMM can measure in the 0.25 µm to 32.00 µm size range and the ELPI can measure in the 0.02 µm to 9.38 µm size range.^[25,37-39] Including more real time instruments will assist in characterisation of a wide variety of particle sizes.

- ❖ From Limitation 3, future studies may include the use of the NRD sampler with the polyurethane foam to assess respiratory exposure to < 300 nm Ti particles.

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APPENDIX A

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Dr. Bernhard
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27/4/2018

Dear Ms. du Preez,

Herewith we give permission to publish pictures from Roland Berger publications
with regard to Additive Manufacturing as part of her Dr.-thesis.

Best regards

A handwritten signature in black ink, appearing to read 'B. Langefeld'.

Dr.-Ing. Bernhard Langefeld
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APPENDIX B

Proof of acceptance of Article I to the respective journal.

Article I

16 October 2018

Mrs Sonette du Preez:

Your article "TITANIUM POWDERS USED IN POWDER BED FUSION: ITS RELEVANCE TO RESPIRATORY HEALTH" has been considered and deemed suitable for publication in The South African Journal of Industrial Engineering.

Your file ID for the manuscript is 1975-7871-1-CE.

Prof Thorsten Becker

Section editor: SAJIE

APPENDIX C

Proof of submission of Article II to the respective journal.

Article II

17 November 2018

Dear Mrs. du Preez:

Thank you for submitting manuscript "Particle emissions and metal exposure during Powder Bed Fusion Additive Manufacturing using titanium powders" to the Journal of Occupational & Environmental Hygiene.

The ID number for this manuscript is "JOEH-18-0454". Please reference this ID number in all future correspondence with the Editorial Office regarding this manuscript.

You may track the Manuscript Central operational status of this manuscript in your Author Center. If you have any questions about the review of your manuscript, you may email me at jennifer-j-patterson@uiowa.edu.

We welcome feedback about our manuscript submission and review process. If you have any comments or suggestions for our consideration, please email them to me at jennifer-j-patterson@uiowa.edu.

You may contact me if you have any questions about your manuscript submission now or in the future.

Thank you again for your submission to the Journal of Occupational & Environmental Hygiene.

Sincerely,

Jennifer Patterson

Editorial Office

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APPENDIX D

Declaration of language editing.

Woorde wat werk / Working Words

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LANGUAGE EDITING STATEMENT

2018-11-19

I, Jannetje Levina De Kock hereby declare that the thesis

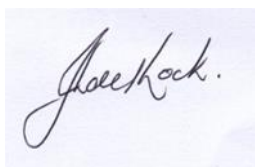
Emission of and exposure to hazardous chemical substances from selected additive manufacturing technologies

by
Sonette du Preez

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

APPENDIX E

Ethics approval certificate:



NORTH-WEST UNIVERSITY
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2016/05/26

ETHICS APPROVAL CERTIFICATE OF STUDY

Based on approval by Health Research Ethics Committee (HREC) on 09/06/2016, the North-West University Institutional Research Ethics Regulatory Committee (NWU-IRERC) hereby approves your study as indicated below. This implies that the NWU-IRERC grants its permission that provided the special 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: Exposure to hazardous chemical substances associated with selected additive manufacturing technologies																														
Study Leader/Supervisor:	Prof JL du Plessis																													
Student:	S du Plessis																													
Ethics number:	<table border="1"><tr><td>N</td><td>W</td><td>U</td><td>-</td><td>0</td><td>0</td><td>0</td><td>0</td><td>4</td><td>-</td><td>1</td><td>6</td><td>-</td><td>A</td><td>1</td></tr><tr><td colspan="4">Institution</td><td colspan="4">Study Number</td><td colspan="2">Year</td><td colspan="4">Status</td></tr></table> Status: S = Submission; R = Re-Submission; P = Provisional Authorisation; A = Authorisation	N	W	U	-	0	0	0	0	4	-	1	6	-	A	1	Institution				Study Number				Year		Status			
N	W	U	-	0	0	0	0	4	-	1	6	-	A	1																
Institution				Study Number				Year		Status																				
Application Type:	Single Study																													
Commencement date:	2016-06-09																													
Risk:	Minimal																													
Continuation of the study is dependent on receipt of the annual (or as otherwise stipulated) monitoring report and the concomitant issuing of a letter of continuation up to a maximum period of three years.																														

Special conditions of the approval (if applicable):

- Translation of the informed consent document to the languages applicable to the study participants should be submitted to the HREC (if applicable).
- Any research at governmental or private institutions, permission must still be obtained from relevant authorities and provided to the HREC. Ethics approval is required BEFORE approval can be obtained from these authorities.

General conditions:

While this ethics approval is subject to all declarations, undertakings and agreements incorporated and signed in the application form, please note the following:

- The study leader (principle investigator) must report in the prescribed format to the NWU-IRERC via HREC:
 - annually (or as otherwise requested) on the monitoring of the study, and upon completion of the study
 - 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.
- Annually a number of studies may be randomly selected for an external audit.
- The approval applies strictly to the proposal as stipulated in the application form. Would any changes to the proposal be deemed necessary during the course of the study, the study leader must apply for approval of these amendments at the HREC, prior to implementation. Would there be deviation from the study proposal without the necessary approval of such amendments, the ethics approval is immediately and automatically forfeited.
- The date of approval indicates the first date that the study may be started.
- In the interest of ethical responsibility the NWU-IRERC and HREC retains the right to:
 - request access to any information or data at any time during the course or after completion of the study;
 - to ask further questions, seek additional information, require further modification or monitor the conduct of your research or the informed consent process.
 - 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 HREC or that information has been false or misrepresented,
 - the required amendments, annual (or otherwise stipulated) report and reporting of adverse events or incidents was not done in a timely manner and accurately,
 - new institutional rules, national legislation or international conventions deem it necessary.
- HREC can be contacted for further information or any report templates via Ethics-HRECApply@nwu.ac.za or 018 299 1206.

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

Yours sincerely

Linda du Plessis

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Prof Linda du Plessis

Chair NWU Institutional Research Ethics Regulatory Committee (IRERC)