

Particle emission and respiratory exposure to platinum metal powders during additive manufacturing: A pilot study

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*“You started off as an infant, with no legs to stand on. Now you have grown,
run to the corners of the world - ZYL”*

SUMMARY

Title: Particle emission and respiratory exposure to platinum metal powders during additive manufacturing: A pilot study

Background: Additive manufacturing (AM) utilising metal powder is associated with the emission of airborne particles of various sizes, which may result in respiratory exposure of the AM operator to this powder. Research involving platinum in AM is non-existent and the aim of this pilot study was to provide an initial understanding of the characteristics of platinum powder particles and emissions during the different process phases of AM as well as personal exposure of the AM operator to metal powders.

Methods: This study was conducted over two print cycles of powder bed fusion (PBF) with platinum powder as feedstock at an AM facility. Particle size selective counting instruments were used to investigate the emissions of airborne particulates during the different phases of PBF AM in the workplace atmosphere. The particle number concentrations were used to calculate the particle emission rate during the AM process. Personal exposure to inhalable, respirable and < 300 nm sized particulates was measured and analysed using inductively coupled plasma-mass spectrometry to investigate possible metal exposure during AM.

Results: In this pilot study the highest concentration of $0.01 > 1 \mu\text{m}$ sized particles was emitted during the pre-processing phase, followed by the post-processing phase and lastly the processing phase. Particles of $0.3 \mu\text{m}$ in size had the highest peak particle number concentration of $7.71 \times 10^7 \text{p/m}^3$ during the first print cycle and $3.02 \times 10^8 \text{p/m}^3$ in the second print cycle, followed by $0.5 \mu\text{m}$ and $1 \mu\text{m}$ sized particles. Emission rates indicated that during pre-processing, the highest concentrations of particles were emitted ($7.95 \times 10^6 \text{p/min}$) followed by the processing phase and lastly the post-processing phase. Personal exposure concentrations for inhalable and < 300 nm sized platinum particles were below that of the detection limit for platinum metal analysis. However, operators were exposed to inhalable sized metals such as

arsenic, cobalt, copper, lead and nickel among which cobalt, copper and nickel exceeded occupational exposure limits.

Conclusion: Concentrations of particles ranging from 0.01 to 10 μm were emitted during all three AM phases. The highest emission concentration was in the pre-processing phases of print cycle 1 and print cycle 2. Emission rates were highest in the pre-processing phase over both print cycles. This pilot study indicates that future studies should focus on particle emissions rather than on personal exposure of the AM operators to platinum metal powders. Personal respiratory exposure to platinum metal powder was below the detection limit but attention should be directed to other detected insoluble metals such as arsenic, cobalt and copper of which the presence was likely engendered by workplace cross-contamination. It is the duty of the AM employer at the facility to educate AM operators to any risks that may be associated with the PBF AM process or any other workplace risk. These employers further need to implement control measures, to eliminate or reduce the risk to an acceptable level.

Key terms: Powder bed fusion; selective laser sintering; health and safety

AUTHOR'S CONTRIBUTION

This study was conducted by a team of researchers. The contribution of each individual is described briefly below:

Dr. S.J.L Linde: Supervisor of the project. Assisted with the design and planning of the study. Played an integral role in reviewing and interpreting the results of the study.

Dr. S. du Preez: Co-supervisor. Assisted with the planning of the methodology and data capturing.

Prof. J.L. Du Plessis: Assistant supervisor. Provided considerable insight into exposure and emission studies which helped mould the direction of the study.

The following statement from the co-authors regards the individuals' role in this study:

I declare that I have approved the article and that my role in this study as indicated above is a reflection of my actual contribution and that I hereby give my consent that it may be published as part of Z.Y Lambat's M.Sc. (Occupational Hygiene) dissertation.



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PREFACE

The outline of this mini-dissertation is as follows:

- Chapter 1 – General introduction which gives a shortened background as well as the problem statement, hypothesis, aims and objectives of this study.
- Chapter 2 – Literature study which provides background to the study.
- Chapter 3 – Article: “Particle emission and respiratory exposure to platinum metal powders during additive manufacturing: A pilot study.”
- Chapter 4 – Provides key discussions such as those around conclusions, recommendations and limitations of the study.

This study will be submitted to the journal of *Safety and Health at Work (SH@W)*. SH@W is an international, peer-reviewed, interdisciplinary journal. This journal requires formatting instructions to be applied to the Article section of the study, that is, Chapter 3. The journal is aimed at providing grounds for the exchange of ideas and data developed through research experience in the broad field of occupational health and safety. Articles may deal with scientific research to improve workers' health and safety by eliminating occupational accidents. Its abbreviated title is *Saf Health Work*. Technical aspects of this document were tended to accord the SH@W format. The language preference was English UK.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	I
SUMMARY	II
AUTHOR'S CONTRIBUTION	IV
PREFACE	V
 CHAPTER 1	 11
1.1 General introduction	11
1.2 General aim:	13
1.3 Specific objectives:	14
1.4 Hypothesis.....	14
1.5 References	15
 CHAPTER 2 Literature study	 17
2.1 Introduction.....	17
2.2 The rapid increase of AM.....	17
2.3 Classification of AM	18
2.4 Powder bed fusion	18
2.5 Three phases of PBF	19
2.6 Selective laser sintering	19
2.7 Metal powders used in AM.....	20
2.8 The respiratory system	21
2.8.1 Anatomy of the respiratory system.....	21
2.8.2 Nose	21

2.8.3	Pharynx, larynx and trachea	22
2.8.4	Bronchi, bronchioles and alveoli	22
2.8.5	Gaseous exchange and circulation	22
2.8.6	Deposition of particles in the respiratory system	23
2.9	Platinum and the risk to health.....	23
2.10	Particle emissions and emission rates	24
2.11	Particle size	25
2.12	Morphology of particles.....	26
2.13	Conclusion.....	27
2.14	References	28
CHAPTER 3		32
Manuscript		32
1. ABSTRACT		36
2. INTRODUCTION.....		38
3. METHODOLOGY.....		41
3.1. Site and AM operators.....		41
3.2. Particle and metal emissions.....		42
3.3. Personal metal exposure monitoring		44
4. STATISTICAL DATA ANALYSIS		44
5. ETHICS APPROVAL		45
6. RESULTS		45
6.1. Particles 0.01 to > 1 µm		45
6.2. Personal respiratory exposure monitoring		51

7. DISCUSSION	52
8. CONCLUSION	57
9. REFERENCES	59
10. ANNEXURES	63
ANNEXURE A: SAMPLING SITE AND ROOM LAYOUT	63
ANNEXURE B: STATIC AREA AND PERSONAL EXPOSURE CONCENTRATIONS FOR ICP – MS DETECTED METALS	64
ANNEXURE C: TABLE 1A: PARTICLE SIZE CHANNELS (0.3 - > 10 µM) AND TOTAL PARTICLE COUNT FOR APC AND GRIMM COUNTING INSTRUMENTS	65
Chapter 4 66	
4.1 Main findings	66
4.2 Further discussions.....	68
4.3 Limitations	71
4.4 Recommendations.....	71
4.5 Future studies.....	72
4.6 References	73
ANNEXURE A: ETHICS CLEARANCE CERTIFICATE	74
ANNEXURE B: LANGUAGE EDITING CERTIFICATE	75

LIST OF TABLES

CHAPTER3	32
Table 1: Particle number counts and emission rates for print cycle 1 and print cycle 2	47
Table 2: Cumulative particle number count per size channel (0.3 - 10 µm)	49
Table 3: Calculated 8-hour time weighted average concentrations for metals (mg/m³) detected with ICP – MS analysis	51

LIST OF FIGURES

CHAPTER 2	LITERATURE STUDY	17
Figure 1:	Diagrammatic representation of the powder bed fusion process [5].....	18
CHAPTER3		32
Figure 1:	Particle number concentration of $0.01 > 1 \mu\text{m}$ sized particles emitted during each phase of a) print cycle 1 and b) print cycle 2.....	46
Figure 2:	Emission rates of particles during AM phases. $n=2$; the average of the emission rate was calculated using print cycle 1 and print cycle 2, $n=1$; the emission rates of data obtained during print cycle 2).....	48
Figure 3:	APC and GRIMM particle concentrations for size channels $0.25 \rightarrow 10 \mu\text{m}$ during a) print cycle 1 and b) print cycle 2 Error! Bookmark not defined.	

CHAPTER 1

1.1 General introduction

Additive manufacturing (AM) is the process of joining materials together to make objects from three-dimensional model data, usually layer upon layer, as opposed to subtractive manufacturing methods [1, 2]. AM is applicable to numerous classes of materials including metals, ceramics, polymers, composites and biological systems. The interest in AM has been on the rise in recent years with its greatest impact on the industrial market as AM provides a “part on demand” approach [3]. It has now become possible to reliably manufacture objects using materials such as aluminium, titanium and steel [4]. During the early development of AM, the technology was only applied to design items to reproduce visualisation models. As technology developed further, the use of AM was implemented in the aerospace industry, automotive industry, healthcare and consumer products [5]. Since then, the advancement in the field has been on the rise. AM is now in its fourth decade of technological development and in this period a vast number of significant changes have led to improving it in terms of accuracy, product properties, a larger range of applications concomitant with reduction in overall cost [5]. Many changes have also occurred regarding the range of materials used, including the recent introduction of platinum as an AM material.

AM consists of multiple different processes, which vary due to methods of application as well as materials used and machine technology. There are seven AM manufacturing processes: powder bed fusion (PBF), vat photo polymerisation, material extrusion, material jetting, binder jetting, sheet lamination and direct energy deposition. These processes can be further subcategorised depending on the technology applied (ASTM International, 2012). According to Kellens et al. [6], the five most applied metal AM technologies are selective laser sintering (SLS), selective laser melting (SLM), electron beam melting (EBM), stereo lithography (SL) and fused deposition melting (FDM). SLS, SLM and EBM technologies make use of powder bed fusion (PBF) as the AM process.

This study focuses on SLS as the technology and PBF as the process utilising platinum powder to create platinum objects, products and components.

The EOSINT M 280 PBF machine process (designed by EOS, München, HRB, Germany) utilises a container that is filled with a powder as the feedstock material to be processed selectively using a laser as the energy source. The laser is programmed to deliver energy to the surface of the powder bed, sintering the powder into the desired shape [3]. PBF-SLS AM consists of three phases of production. These are (i) the pre-processing phase, during which the PBF machine is prepared and supplied with the necessary powder for the build, (ii) the processing phase, which is fully automated and results in the production of the object by means of SLS and (iii) the post-processing phase involving the removal and refinement of the object produced. The composition of the platinum metal powder is unknown due to confidentiality held by the AM facility.

During the different process phase of AM emissions of and exposures to hazardous chemical substances have been reported to occur. However, the emissions of and respiratory exposure to platinum powders used during these three phases is not known and emissions and exposures associated with each phase could possibly differ from each other. It is necessary to identify during which of these three phases, that is, pre-processing, processing and post-processing, the highest concentration of emissions and exposure will be prevalent in order to protect the health of the AM operator.

Platinum is a chemical element that is dense, ductile, malleable and highly unreactive. It is resistant to corrosion and is a noble metal [7]. Exposure to metallic platinum has not been linked to any health effects, while exposure to soluble platinum may cause sensitisation [7] as it is classified as a respiratory sensitiser and increases the risk for development of rhinitis and asthma [8].

Graff et al. [9] carried out a study regarding the presence of airborne Inconel powder (an alloy consisting of cobalt and nickel) during AM operations. They focussed on particulate

number, mass and size of the Inconel powder to identify the metal particulate emissions. Their study indicated that particles 300 nm to 10 µm were detected and this raised a health concern for AM operators handling these powders. These smaller particles ranged from 0.3 µm to 10 µm while particles < 300 nm were emitted. There is a need for information regarding the emissions and exposure of platinum in the AM industry, as platinum metal powder is a new material used in AM. It is also important to assess if the exposure exceeds the occupational exposure limits (OEL) to protect the health and safety of AM operators involved in the process. It is incumbent to identify whether particles emitted are inhalable, thoracic or respirable, as this will influence their toxicity. Inhalable particles are defined as the mass fraction of particles which can be inhaled and can enter the nose and mouth. Thoracic particles are the mass fraction of particles that passes the larynx. Respirable size fractions of particles are those particles with the ability to reach the alveoli of the lungs [10]. AM machine operators need to be educated in handling and disposal of these materials. With the increase in application of platinum in AM, exposure to airborne particulates needs to be closely monitored as information regarding platinum metal powder in AM is non-existent and the emissions thereof are unknown.

As the AM field tends to broaden there is a need to seek knowledge and a better understanding regarding the possible emissions and exposure to airborne particulates as well as other hazardous chemical substances (HCS) and whether these may pose a risk to the health of AM operators.

1.2 General aim:

To assess the emissions and personal respiratory exposure associated with PBF using platinum metal powders.

1.3 Specific objectives:

- To quantify particle emissions associated with PBF AM utilising platinum metal powders by means of area monitoring and particle size selective counting instruments during the different phases of AM.
- To determine the personal respiratory exposure of AM operators to metal particulates during the AM print cycle by following the standardised MDHS 46/2 method.

1.4 Hypothesis

- Graff et al. [9] conducted research on Inconel metal powders (an alloy consisting of cobalt and nickel) during PBF AM, and they have identified that particles ranging from 300 nm to 10 µm have been emitted during PBF AM. It is therefore hypothesised here that metal PBF AM is associated with particle emission ranging from 300 nm to 10 µm and is likely to be the same or similar for platinum metal powder. This is substantiated by the similarities of emission and exposure concentrations found in AM studies not directly related to PBF AM using platinum metal powder.
- Due to the emission of particles during the AM process, it is hypothesised that there is a personal exposure of the AM operator to platinum metal particles.

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CHAPTER 2 LITERATURE STUDY

2.1 Introduction

This literature study will discuss the following: the rapid increase of additive manufacturing (AM), classification of AM processes with focus on powder bed fusion (PBF) and its selective laser sintering (SLS) technology, the different phases of AM and the powders used as feedstock, the risk platinum exposure poses to health, particle emissions and emission rates during PBF, the respiratory system and deposition of particles, particle size and morphology, emission of ultrafine particles and the requirements concerning occupational exposure limits related to platinum.

2.2 The rapid increase of AM

A general description that suits AM is that it consists of a family of processes used to produce objects by successively adding material in a layered fashion [1]. AM has now surpassed traditional means of machining design and production due to technological advancement and a decrease in limitations posed by traditional machinery and subtractive methods. Traditional machining methods limited the design of objects to certain geometrical shapes: machining methods limited the freedom of design. AM allows the designer to produce an item starting from the centre of the object to consequently add layers until the final product has been created. Therefore, AM is transforming the way in which we can design and produce components [1,2].

Metal products are indispensable for a multitude of functions such as structural support, electrical conduction and heat dissipation. Based on these functions extensive research is going into the development of AM utilising metals, that is, metal powders [1]. The present research intends to identify and understand AM operator exposure and hence to develop AM utilising platinum metal powders further by improving areas of the AM cycle that pose health related risks to the AM operator.

2.3 Classification of AM

AM consists of seven processes and a variety of technologies which are applied differently to each process, depending on the material used and the desired outcome. The seven processes are material extrusion, powder bed fusion (PBF), direct energy deposition (DED), material jetting, binder jetting, sheet lamination and vat photo-polymerisation [3]. AM processes can be classified further into laser-based AM and non-laser-based processes. Laser AM provides a high intensity and a highly concentrated beam of light, moving in a controlled manner. The main purpose of laser in AM is heating. Heating is used either to cut through solid material (known as a subtractive process) or to melt powdered material together (known as an additive process) [2]. According to a study by Mahamood et al. [4], the commercially available laser AM technologies are stereo lithography, selective laser sintering (SLS), laminated object melting and laser metal deposition, whilst non-laser-based AM technologies include inkjet printing and fused deposition modelling.

2.4 Powder bed fusion

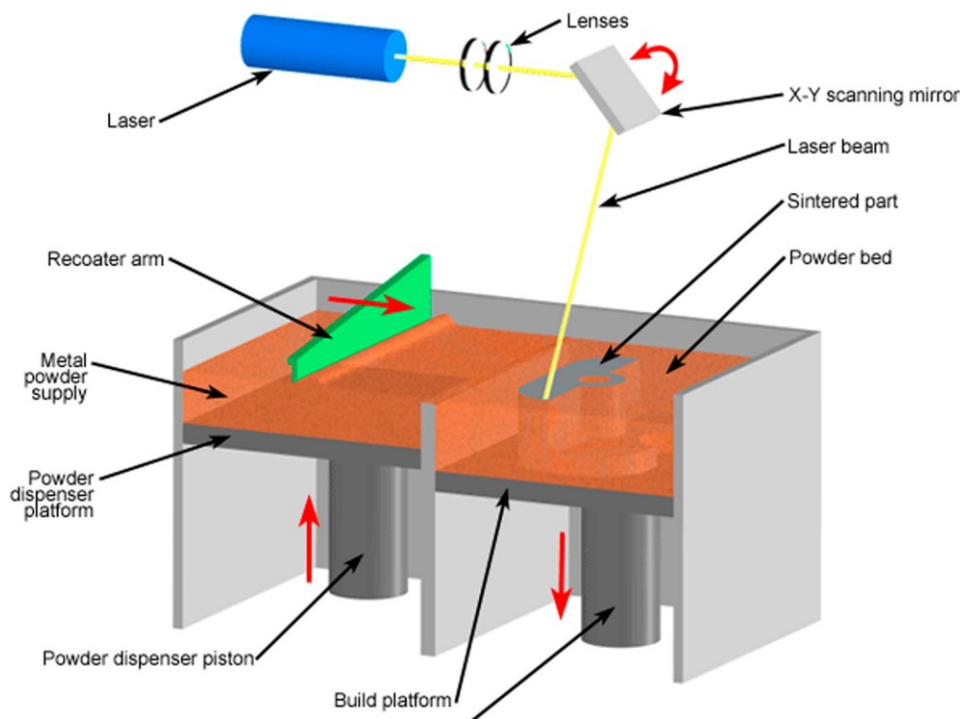


Figure 1: *Diagrammatic representation of the powder bed fusion process [5]*

PBF includes all processes where energy is focused and is used selectively to sinter or melt desired areas of a powder bed [5]. A 3D object is formed through multiple repeated cycles. As shown in Figure 1, two chambers are present: the first chamber (feedstock) stores the virgin powder and the second chamber (build) contains the building platform and houses the sintered or melted powders that form part of the final object. The powder is transferred from the feedstock chamber to the build chamber by means of a rake. The build chamber is situated below the laser that is used to sinter or melt the powder. Periodically, the rake will sweep across the build chamber, providing it with a new layer of virgin powder to be sintered [6].

2.5 Three phases of PBF

PBF comprises three distinct phases. The first is the pre-processing phase and involves designing the object that is to be manufactured by use of computer aided design (CAD) software [7] as well as preparing the AM machinery, acquiring and sieving the powders and filling the feedstock dispenser of the machinery with powders [8]. The second is the processing phase during which the powder is sintered to form the desired product. This phase includes the laser sintering process from the first layer of virgin powder raked across the build chamber up to and including the last layer of powder sintered to complete the product. The third is the post-processing phase in which the final product is refined [7] and involves the removal of the product as well as cleaning and refinement to ensure good product quality. As part of post-processing, the powders that have not been sintered in the product are commonly recycled, which involves the removal of these unsintered powders [8]. Depending on the discretion of the AM operator, machine cleaning may take place either after post-processing or prior to pre-processing.

2.6 Selective laser sintering

The use of the selective laser technologies can be categorised into two types: melting and sintering. During PBF AM, SLS is used for partial melting of the material and selective laser

melting is used for complete melting [5]. The purpose of melting is to allow the material particles to join to build a product. Kruth et al. [9] states that SLS can be divided into four categories according to its binding mechanisms: solid state sintering, chemically induced binding, liquid phase sintering and full melting. Solid state sintering is a thermal process that occurs at the melting temperature of the material, leading to various chemical and physical reactions. Solid state sintering offers an advantage because it can be used on a wide variety of materials. Chemically induced binding heats the material powder to a high temperature after which the material powder particles encounter a binder to form bonds between the powders resulting in a final product. Liquid phase sintering can be described as the heating of a material in a such a manner as to maintain its solid state with a partial liquid state occurring, to bind the powder material. Full laser melting is of two types: selective laser melting (SLM) and the selective laser sintering process (SLS). Full melting results in the melting of powdered material by means of a laser to form a product. It is primarily used for metal powder materials [9].

2.7 Metal powders used in AM

Metals commonly used in AM are titanium, aluminium and steel, as these were mainly used in traditional machining. Apart from commercially pure titanium, AM parts are fabricated from the alloy Ti-Al₆-V₄, which is widely used in commercial fabrication. Aluminium alloys are rather limited in application since they cannot be welded. Therefore, it is less frequently preferred for commercial use, even though it is considerably less expensive. Steel alloys are still the most common engineering materials and are of high interest to the AM industry. PBF and DED are the main metal powder-based AM processes that are commercially used today [10]. The set of common commercially used metal powders are limited to pure titanium, Ti-Al₆-V₄, 316 stainless steel, 174PH stainless steel, 18Ni300 steel, AlSi, CoCrMo, Inconel 718 and Inconel 625. This range is continually expanding with new entrants such as gold, silver and platinum [10].

Platinum is a novelty metal, only setting its roots in AM recently. Not much is known about platinum metal powder when it comes to AM including its characteristics, applications and commercial appeal.

2.8 The respiratory system

The respiratory system has the primary function for gaseous exchange. Through the process of breathing, oxygen is inhaled and diffuses into the bloodstream while carbon dioxide is exhaled as a by-product of this metabolism. The diffusion of oxygen into the blood stream is extremely important as it results in energy production required for cells to function [21,22].

2.8.1 Anatomy of the respiratory system

The respiratory tract is divided into two parts: upper- and lower respiratory tract. The upper respiratory tract includes the nose, mouth and upper trachea and the lower the trachea, bronchi, bronchioles and the alveoli, all of which form part of the gaseous exchange region of the lung [21]..

The respiratory tract begins at the entrance to the nasal cavity and continues through the pharynx, larynx, trachea, bronchi and the bronchioles. In addition to delivering oxygen to the lungs, the conducting passages warm and humidify the air which protects the alveoli from debris and foreign bodies by maintaining the airway surface fluid that evaporates under the influence of cold air. As the air reaches the alveoli, most foreign bodies and debris have been removed as part of the body's natural defence mechanism [21].

2.8.2 Nose

Air enters the respiratory system via a pair of nostrils, which then open into the nasal cavity. The nasal vestibule is the area within the cavity consisting of coarse hairs to protect the nasal cavity from large airborne particles such as sand, dust and other foreign materials. As the air leaves the nasal vestibule it enters the nasopharynx area. During this transition, air

encounters mucus that coats the nasal cavity, which provides additional filtration. The nasal area also contains cilia that sweep debris into the pharynx [21, 24].

2.8.3 Pharynx, larynx and trachea

The pharynx, also known as the throat, forms part of the respiratory system as well as the digestive system. It lies primarily between the nasal cavity and the larynx. Air leaves the pharynx and enters the larynx, via the glottis, and thereafter passes on to the trachea, which in turn allows it to pass on to the bronchi. The pharynx, larynx and trachea serve only as a pathway of gaseous exchange in the lungs [21, 24].

2.8.4 Bronchi, bronchioles and alveoli

The trachea branches off into two regions, the right and left primary bronchi, which respectively lead to the right and left lung. These further segment into the secondary bronchi and then the tertiary bronchi which finally lead to the bronchioles. These control the airflow and distribution of air in the lungs. Respiratory bronchioles open into alveolar ducts and then into the alveoli. Each lung comprises an abundance of alveoli. It is here that gaseous exchange occurs between the alveoli and blood. Within the alveoli macrophages are found that seek out and remove dust and debris [21].

2.8.5 Gaseous exchange and circulation

The respiratory exchange surface consisting of alveoli receives blood from the arteries of the heart. These pulmonary arteries enter the lungs and branch into the bronchi, bronchioles and then the alveoli. The alveoli are surrounded by capillaries. At this point the alveoli are supplied with oxygen from the bronchioles which then diffuses into the capillaries while carbon dioxide enters the alveoli as part of the gaseous exchange. Subsequently the capillaries lead to the pulmonary venules, pulmonary veins and then the left atrium to supply the body with oxygenated blood. Even though this entire process is designed to prevent the entrance of foreign particles into the body, particles which are small enough such as those smaller than 300 μm may enter the blood stream [21, 22].

2.8.6 Deposition of particles in the respiratory system

Inhaled particles are transported with air through the respiratory system, but forces such as gravity, inertia and collisions cause these particles to behave according to the laws of motion. Particles are thus transported to the surfaces of the respiratory tract by sedimentation, impaction and diffusion, also known as Brownian motion [25, 26]. Impaction is the inertia that a particle possesses that deviates the particle from the air flow. Impaction is more pronounced when the particle is larger than 1 μm and moves at high velocity. Sedimentation is the settling effect that a particle will possess due to gravity acting upon it (0.1 – 1 μm). It is pronounced when a particle is larger and has a slower velocity. Diffusion is the random motion of small particles due to collisions occurring with airborne particles. Particles of a size < 0.1 μm are transported through diffusion. It is more pronounced in smaller particles [26].

2.9 Platinum and the risk to health

Platinum is a chemical element that is dense, ductile, malleable and highly unreactive. It is resistant to corrosion and is a noble metal [11]. Exposure to metallic platinum has not been linked to any health effects, while exposure to soluble platinum may cause sensitisation [11]. Soluble platinum is regarded as a respiratory sensitiser and increases the risk for the development of rhinitis and asthma ([12]). In the Hazardous Chemical Substances Regulations (HCSR) [13], metallic platinum is listed with an 8-hour time weighted average occupational exposure limit and recommended limit (TWA-OEL-RL) of 5 mg/m^3 while soluble platinum is listed with an 8-hour TWA-OEL-RL of 0.002 mg/m^3 and a sensitiser notation. According to the HCSR, exposure to sensitisers should be prevented and if this is not possible, it should be kept as low as reasonably practicable.

The OEL-RL designates the concentration of an airborne substance averaged over a reference period of 8-hours, at which time there should be no evidence that the substance may be injurious to health should an AM operator be exposed to that concentration by inhalation day after day. If the OEL-RL is exceeded, steps should be taken to reduce

exposure levels by implementing control measures [13]. Symptoms of exposure to soluble platinum includes lacrimation, irritation of the nasal cavity and throat, rhinitis and coughing. Sensitisation may develop immediately or over a period of weeks, years or months, depending on the level of exposure [14]. Sensitisation is a major factor influencing the body's reaction to exposure and may cause an individual to display extreme symptoms even to a low concentration of exposure, even if the latter have been considered as a safe level for the average individual. Long-term exposure could possibly result in respiratory- and skin allergies [11].

2.10 Particle emissions and emission rates

The pre-processing phase involves designing the final product that is to be manufactured by use of CAD software [7] as well as preparing the AM machinery, purchasing the powders, sieving and distributing the powders to the feedstock dispenser of the machinery [8]. During this phase, exposure to powder dust is most likely to occur during handling and loading of the powders into the machine. During the processing (build) phase, the process is fully automated and may carry on without stringent supervision [15]. This phase can be assumed to have the lowest level of exposure due to the automated process in which the building chamber is sealed. The post-processing phase in which the final product is refined [7] involves the removal of the part as well as subsequent cleaning and refinement to ensure good product quality. As part of post-processing, the unsintered powders are commonly recycled, which involves the removal of these excess powders [8]. Even though many steps of the processing phases are automated and require minimal supervision, the activities performed by the operator during each phase differs and therefore the potential exposure experienced by the operator during these phases will likely differ [16].

A study by Stabile et al. [17] state that all environments are likely to have a concentration of particles in the workplace atmosphere, whether it be offices or manufacturing facilities. These particles are usually generated from a source, such as welding, grinding or AM processing.

The source of emission can be monitored by using real-time particulate emission instruments to calculate a rate of emission. These emission rates thus provide an understanding as to the number of particles that are emitted (particles/min) and the phases of the print cycle where increased numbers of particles are emitted in the workplace atmosphere.

A study carried out by Graff et al. [14] indicate that during SLM using a nickel Inconel powder, the highest level of exposure to particles smaller than 300 nm occurred during the handling of the powders, which comprises both pre-processing and post-processing phases. A study carried out by Bours et al. [18] indicate that hazards occurring during FDM AM were most prevalent during the processing phase. They go on to state that these hazards encompassed environmental hazards, physical hazards, volatile organic compounds and particulate emissions, including the emission of particles smaller than 300 nm. They mention that identifying and understanding these risks and hazards will result in the ability to reduce the prevalence and impact of exposure by providing AM operators with the necessary engineering control measures and personal protective equipment. It is unclear as to which processing phase of AM will have the highest level of exposure.

Ultrafine particles (UFPs) are described as particulate matter showing an aerodynamic diameter of < 100 nm in size. UFPs are unique to other particles due to physical and chemical characteristics such as particle size, surface area, charge, shape and solubility. UFPs represent the largest and fastest growing group of emitted particles, resulting in human and environmental exposure occurring, and emissions are predicted to increase dramatically due to the rapid growth [19]. Studies report increased toxicity of UFPs when compared to larger particles [20].

2.11 Particle size

Different particle sizes may cause different bodily reactions in different anatomical areas of the respiratory system [27]. Those that may deposit in the nose may be cleared by the body's response of sneezing or entrapment by the ciliated airway. Particle sizes are of four main

categories, depending on the ability to penetrate the different areas of the respiratory system:

(i) deposition of respirable particles occurs in the alveolar region of the lungs.

-(ii) Deposition of thoracic particles occurs in the tracheobronchial region.

-(iii) Deposition of inhalable particles occurs in the mouth and nose region [27].

-(iv) UFPs have an aerodynamic diameter less than 100 nm [28] and deposits throughout the respiratory system.

Toxicological studies confirm that UFPs penetrate the alveoli and may produce inflammatory responses, headaches and cardiovascular effects since they can be absorbed into the blood and translocated to other parts of the body [29, 30, 31]. In addition to this, they also have a larger effective surface area, which may allow them to act as carriers of harmful chemicals [20]. From a toxicological point of view, all particles smaller than 10 μm have the potential of being biologically active in susceptible individuals [26].

2.12 Morphology of particles

Particle morphology plays a significant role in the level of hazard the particle may pose. The morphology of particles found in AM is spherical although, in certain instances, the presence of non-spherical and quasi-spherical morphologies are found to be present [33]. The differences in morphologies are of critical importance when it comes to elucidating the behaviour of particles and the risk they may pose. Particles that are spherical in nature as well as rod-like particles are more likely to be taken up in the human body than other particles with other shapes [32]. A study conducted by Mellin et al. [33] states that inert spherical TiO_2 particles do not cause a serious response when inhaled, even though the particle size falls within the unfavourable nanoscale range: but such particles may nonetheless cause serious consequences depending on their shape. Mellin et al. [33] further states that the shape of the particle poses a greater health risk if it is needle shaped, like that of fibres found in asbestos and quartz. A study conducted by Du Preez et al. [34] on titanium alloys used in PBF AM states that the powders that were used were inhalable and a fraction of particles were able to penetrate beyond the larynx and reach the unciliated airways. SEM

revealed that all particles were smooth-surfaced, spherical particles. Regardless of composition of the powders, repeated inhalation over a long duration is hazardous. Due to the confidentiality held regarding the composition of the platinum metal powder, particle morphology falls out of the study scope.

2.13 Conclusion

Concluding this literature study, the following has been identified as regards AM: the usage of AM applications has increased, PBF AM consists of three phases of production and the phases differ from each other regarding particle emission and respiratory exposure, the range of AM metal powders is continuously expanding and studies indicate and support the notion that during AM utilising metal powders, particle emission occurs. Due to the size of particles emitted adverse health effects around respiratory exposure to the AM operator is possible. Previous studies regarding AM therefore prompt a study such as the present one, since extant findings demonstrate that powder handling phases, especially pre-processing, are of high risk. The emissions associated with this phase could have a major impact on the concentration of airborne particles and the personal exposure of the AM operator. Particles which are ultrafine in nature, proven to be emitted in other studies, may cause health related risks as they may penetrate the airways and enter the bloodstream.

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CHAPTER3

MANUSCRIPT

Instructions to authors

Safety and Health at Work (SHAW stylised as SH@W) is an international peer-reviewed interdisciplinary journal published quarterly in English since the beginning of 2010. The journal aims at providing grounds for the exchange of ideas and data developed through research experience in the broad field of occupational health and safety. Articles may deal with scientific research to improve workers' health and safety by eliminating occupational accidents and diseases, pursuing a better working life and creating a safe and comfortable working environment. The journal focuses primarily on original articles across the whole scope of occupational health and safety, but also welcomes up-to-date review papers and short communications and commentaries on urgent issues and case studies on unique epidemiological survey, methods of accident investigation and analysis. High priority is given to articles on occupational epidemiology, medicine, hygiene, toxicology, nursing and health services, work safety, ergonomics, work organization, engineering of safety (mechanical, electrical, chemical, and construction), safety management and policy and studies related to economic evaluation and its social policy and organizational aspects. Its abbreviated title is *Saf Health Work*.

Author guidelines

Formatting requirements:

The manuscripts should be created using MS Word. It must be double-spaced and written in an A4 page format. Do not leave a space between paragraphs. Only a single font should be used in 11 point with margin of 2.5 cm. Latin origin words should not be italicized and all pages including the title page should be paginated consecutively. All numbers should be written in Arabic numerals throughout the manuscript except for the first word of the

sentence. Texts should be justified on both sides and not hyphenated, and headings should be in bold letters, aligned in the centre. If possible, avoid using abbreviated words in the beginning of sentences. Original articles report the results of basic and practical SHAW researches and investigations that are sufficiently and thoroughly documented to be acceptable to critical readers. Section headings should be written in the following format: title page; abstract and keywords; introduction; materials and methods; results; discussion; conclusions (if any); acknowledgements; references; and tables and figures.

Figures and tables:

Tables should be simple, self-explanatory, and supplemental, and should not duplicate the text or figures. Each table must be on a separate page, not exceeding one page when printed and have a concise and informative title. The tables should be numbered with Arabic numerals in consecutive order. Each column should be appropriately headed with units in parentheses if numerical measures are given. All units of measurements and concentrations must be indicated.

References:

In the main text, tables, figure legends and references should be identified using Arabic numerals in squared brackets, in the order they appear in the text (Vancouver style) and be placed at the end of referenced text. References cited in tables or figure legends should be included in sequence at the point where the table or figure is first mentioned in the main text. Do not cite abstracts unless they are the only available reference to an important concept. Uncompleted work or work that has not yet been accepted for publication (i.e., "unpublished observation", "personal communication") should not be cited as references. Example in Korea, the industrial revolution began in the 1970s, and the first occupational cancer was mesothelioma due to asbestos, reported in 1993 [5]. In the references list References should be limited to those cited in the text and listed in the order in which they appear in the text. References should include, in order, authors' surnames and initials, article title, abbreviated

journal name, year, volume and inclusive page numbers. The last names and initials of all author names should be included. Abbreviations for journal names should conform to those used in MEDLINE. If citing a website, provide the author information, article title, website address and the date you accessed the information. Reference to an article that is in press must state the journal name and, if possible, the year and volume. Those not shown in the below examples should be cited according to 'Uniform Requirements for Manuscripts Submitted to Biomedical Journals' and 'style of NLM (the National Library of Medicine).

Particle emission and respiratory exposure to platinum metal powders during additive manufacturing: A pilot study

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1. Abstract

Title: Particle emission and respiratory exposure to platinum metal powders during additive manufacturing: A pilot study

Background: Additive manufacturing (AM) using metal powder is associated with the emission of airborne particles of various sizes, which may result in respiratory exposure of the AM operator. No research exists that involves platinum in AM and the aim of this pilot study was to assess particle emissions and personal respiratory exposure of the AM operator as well as assessing the risk to health that these particles may pose.

Methods: This study was conducted over two print cycles at an AM facility. Particle size selective counting instruments were used to investigate the emissions of airborne particulates during the different phases of powder bed fusion (PBF) AM in the workplace atmosphere. The particle number concentrations were used to calculate the particle emission rate during the AM process. Personal exposure to inhalable and < 300 nm sized particulates was measured and analysed using inductively coupled plasma-mass spectrometry to identify concentrations of metal exposure during AM.

Results: In this pilot study particles 0.3 μm in size showed the highest peak particle number concentration of $7.71 \times 10^7 \text{ p/m}^3$ during the first print cycle and $3.02 \times 10^8 \text{ p/m}^3$ in the second print cycle, followed by 0.5 μm and 1 μm sized particles. Emission rates indicated that the highest concentration of particles, $7.95 \times 10^6 \text{ p/min}$, were emitted during pre-processing. Personal exposure concentrations for inhalable and < 300 nm sized platinum particles were below that of the detection limit for platinum metal analysis. However, operators were exposed to inhalable sized metals such as arsenic, cobalt, copper, lead and nickel while cobalt, copper and nickel exceeded the respective occupational exposure limits.

Conclusion: Particles ranging from 0.01 to 10 μm were emitted during all three AM phases. The highest peak emission concentrations and emission rates took place during the pre-

processing phases of the print cycles. Static area and personal exposure concentrations of platinum particles were below the limit of detection but, as indicated, other insoluble metals were detected and were likely the result of contamination. This pilot study therefore finds that future studies should focus on particle emissions rather than on personal exposure of AM operators to platinum metal powders. This study indicated a risk to health of the AM operator through respiratory exposure to arsenic, cobalt, copper, lead and nickel.

Key terms: Powder bed fusion; selective laser sintering

2. Introduction

Additive manufacturing (AM) is the process of joining materials together to make objects from three-dimensional model data [1, 2]. It is applicable to numerous classes of materials including metals, ceramics, polymers, composites and biological systems. Given the increased interest in AM and technological advancements, metals such as aluminium, titanium, and steel are increasingly used [3] and has been implemented in various industries and products [4, 5]. More recently, powder bed fusion (PBF), selective laser sintering (SLS) and AM with platinum metal powder were introduced as a novelty material within South Africa. Since this is a new application, no literature is available on the emissions and exposures associated with AM of platinum metal powder.

Based on the tasks of the operator and the specific processes applied, AM can be categorised into three distinct phases: pre-processing, processing and post-processing. Pre-processing requires an AM operator to sieve and load the powders into the feedstock chamber of the AM machine which is followed by warming up the machine in preparation for processing. The processing phase is fully automated and PBF AM machines are designed to operate with minimal supervision from the AM operator [6]. During post-processing, printed objects are removed from the build chamber and undergo final refinement followed by removal of unsintered powder and the cleaning of the AM machine. Cleaning of the machine is performed at the discretion of the AM operator and may occur during either pre-processing or post-processing. Activities performed during each phase by the AM operator differ, therefore, operator exposure levels during these phases will likely differ and operators are most likely exposed to metal powders during activities such as machine cleaning, loading of the powders into the machine chamber, removal of printed objects and the final phase refinement of the project [6].

As mentioned, the present article focuses on the metal of platinum. It is a chemical element that is dense, ductile, malleable, highly unreactive, resistant to corrosion and is considered a

noble metal. Due to its properties of strength and resistance to corrosion, it makes an excellent resource to be used in AM applications as it is widely preferred in many industrial applications [7]. Exposure to metallic platinum has not been linked to any adverse health effects, while exposure to soluble platinum may cause sensitisation [8]. Sensitisation to platinum increases the risk for development of asthma [9]. Clinical symptoms of allergic reactions include irritation of the eyes, nose, coughing, dyspnoea, wheezing and cyanosis [10]. Soluble platinum is classified by the South African Department of Employment and Labour, under the Hazardous Chemical Substances Regulations, as a respiratory sensitiser with an occupational exposure control limit (CL) of 0.002 mg/m³[11]. Metallic platinum has been listed with a recommended occupational exposure limit (RL) of 5 mg/m³ [11], whilst international organisations such as the National Institute for Occupational Safety and Health (NIOSH), the American Conference of Governmental Industrial Hygienists (ACGIH) and the Occupational Safety and Health Administration (OSHA) list it with an exposure limit five times lower, at 1 mg/m³ [10, 11].

As AM is being increasingly implemented, efforts are required to identify risks and hazards that may negatively influence the health of the AM operator. Particle emissions from AM are an important factor when exposure and operator health are considered [14] as increased particle emissions will lead to a higher risk of respiratory exposure and health of the AM operator [15].

Research contests the phrases “release of particles” and “emission of particles” and these should therefore be clarified for the purpose of the present project. The release of particles is linked to the AM phase in which sintering is not involved and is observed in the pre-processing phase where machine cleaning, powder loading, and warm-up takes place. Emission occurs during processing when sintering of the powder take place. The accumulation of particles in the build chamber throughout processing contributes to the emission of particles in the post-processing phase when the chamber is opened.

The post-processing phase is included in the emission of particles as the concentrations of particles observed are a by-product of the processing phase and includes the removal of the object and final refinement thereof. In this study the term emissions will be used to describe the release and emission of particles during all three phases of the AM print cycle.

To provide an indication of particle emission during AM, emission rates can be calculated. These reflect real-time particle concentrations to provide concentrations of particles emitted per minute. Extant studies around metal AM emission rates are minimal and this pilot study will be the first to examine platinum particle emission rates. Area emission sampling facilitates monitoring of particles that are emitted throughout the AM process, irrespective of the location of the AM operator. It includes the monitoring of particles emitted per minute and the size of these emitted particles. Area emission thus elucidates the overall emission of airborne particulates to which the AM operator may be exposed.

Graff et al. [6] investigated particle emissions and exposure to airborne nickel-based Inconel powder during PBF AM. They found that particles ranging in size from 0.30 μm to 10 μm were emitted. They also stated that the highest exposure risk was present when the AM operators handled the powders, which emphasises the phases during which AM operators are in direct contact with the powders, namely during pre-processing and post-processing phases, where handling of the powders is a requirement [6]. A study conducted by Stefaniak et al. [17] illuminates the matter of emissions and exposures during industrial scale AM, stating that it is reasonable to expect exposure to particles and emissions occurring in occupational settings. Based on a review of literature, they indicate that insufficient understanding prevails around the magnitude and characteristics of emissions and exposure resulting from industrial scale AM processes.

The aim of this pilot study was to assess particle emissions and personal exposure to airborne platinum during the three phases of PBF using platinum powder and to assess the risk that these particles may pose to the health of the AM operator.

3. Methodology

This study was carried out following standardised occupational exposure monitoring methods to determine respiratory exposure of the AM operator. The emission of particles during PBF AM was determined by using real-time particulate counting instruments.

3.1. Site and AM operators

This study was performed at a Rapid Prototyping Centre, located at a tertiary institution in South Africa. The facility used one operator involved in platinum AM, working with an EOSINT M 280 machine from EOS, München, HRB, Germany. The AM process was conducted in an enclosed room measuring 4.11 m x 4.37 m x 3.35 m with a ductless split-level air-conditioning unit located inside the room, as well as a cooled environment created by means of an air-cooling chiller to maintain the EOSINT M 280 at an optimum temperature: see Annexure A – Sampling site and room layout. Prior to machine loading, the AM operator transferred the powder to a hopper, baked the powder in an industrial oven to achieve maximum dryness and then loaded the AM machine with platinum powder. The composition of the powder was not disclosed, as this is proprietary information. The AM operator was monitored over two print cycles, referred to as print cycle 1 and print cycle 2. Print cycle 1 comprised a single PBF print of a platinum object with cylindrical dimensions of 45 mm diameter and a height of 3 mm. Baking of the powder only took place prior to print cycle 1. Print cycle 2 comprised a test conducted to identify the best finishing quality that could be achieved by the laser to sinter the powder.

Print cycle 1 consisted of pre-processing and processing and no post-processing as the print failed at a height of 3 mm so that the printed part was removed, and processing terminated prior to the need of post-processing. Print cycle 2 consisted of all three process phases. During this cycle, the post-processing phase gave an indication of the level of particle emissions associated with the opening of the build chamber after a print had been completed and did not include any final refinement of the printed object, as it was not required.

3.2. Particle and metal emissions

The AM processes were monitored to determine particle emissions during platinum PBF AM. The process consisted of three phases, each of which was monitored individually to identify the one that presented the highest emission of particles. Particle number concentrations (p/m^3) were measured by means of an Airborne Particle Counter (APC, Model 9310, TSI incorporated, MN, U.S.A.), a Condensation Particle Counter (CPC, Model 3007, TSI incorporated, MN, U.S.A.) and GRIMM spectrometer (Model 11-A, Aerosol Technik Ainring GmbH, Germany). The APC was used to detect particles emitted in the following size channels: 0.30 μm , 0.50 μm , 1.00 μm , 3.00 μm , 5.00 μm and 10.00 μm . The CPC detected the total numerical concentration, real-time, of particles in a size range of 0.01 to $> 1 \mu\text{m}$. The design of the CPC allows the instrument to effectively count the smallest of particles. The maximum range for detection is between 1 μm and 3 μm . Particle larger than 1 μm in size are not effectively collected due the particles being lost due to inertial impaction and does not affect particle smaller than 1 μm . These 1.00 μm sized particles, including particles smaller than 1 μm tended to follow the airstreams because they were most resistant to gravitational pull found in the immediate environment, thus causing them to remain airborne [16]. The GRIMM spectrometer detected particles through 31 different size channels, from 0.25 μm up to and including 32 μm . For this study only 24 size channels were used, from 0.25 μm to 10 μm to keep uniformity between the CPC and GRIMM. The duration of monitoring varied due to the tasks that had to be performed during the different process phases. Data was recorded in 1-second intervals and were presented as particle number concentrations per minute. Emissions monitoring was performed as closely as possible to the AM workstation, that is, within a 1-meter radius from the source and 1 meter above floor level. The instruments were placed on a workbench, adjacent to each other and located in front of the AM machine. Background measurements were taken early morning, in a room parallel to the platinum AM room, where no AM machines were present and the AM machines in the adjacent rooms were not yet turned on.

These measurements provided a comparable baseline environment free from particles emissions resulting from AM activities within the room. Emission rates were calculated by using the particle number concentration in accordance with a formula engendered by He et al. [19] and Stabile et al. [18]:

$$ER = V \cdot \left[\frac{C_{peak} - C_{out}}{\Delta t} + \overline{AER + k} \cdot \bar{C}_{in} - AER \cdot C_{out} \right] \quad \text{Equation 1.}$$

where V (m^3) = the room volume, C_{peak} (p/m^3) = peak concentration of the particles emitted during the processing phase, C_{out} (p/m^3) = the outdoor concentration of the particles during processing (assumed to be equal to the ambient indoor background concentration), Δt (min) = the time difference between C_{peak} and C_{out} , $\overline{AER + k}$ = average total removal rate of the particles (AER 2/h) = air exchange rate in the room, k (constant) = rate of contaminant loss due to deposition onto surfaces and is assumed for indoor environments to be approximately 1/hr [19]), and $\bar{C}_{in}$ (p/m^3) = the average concentration of the contaminant. The ER is reported as number of particles emitted per minute (p/min). The average air exchange (AER) value used in this calculation is taken as 2 air exchanges per hour as identified after consultation with the engineers at the AM facility. The AER information provided by the engineers were estimated and not calculated and results in this being a limitation.

The concentration of inhalable metals in the workplace air was measured according to the National Institute for Occupational Safety and Health (NIOSH) method 7300 by using an IOM sampler with foam insert. Static area monitoring was performed for the AM process phases on the same workstation as the particle counting instruments. Specifications regarding samplers, flow rates and calibration can be found under personal metal exposure monitoring. Inductively Coupled Plasma-Mass Spectrometry (ICP – MS) analysis was performed by an SANAS accredited analytical laboratory. One field blank also underwent analysis. Static area samples were obtained over the duration of the entire print cycles with 269 minutes in print cycle 1 and 160 minutes in print cycle 2.

3.3. Personal metal exposure monitoring

Personal exposure monitoring involved the simultaneous use of an inhalable dust sampler (IOM) (SKC Pennsylvania, USA) and a nano particle respiratory deposition (NRD) (Zefon International, USA) sampler throughout the duration of the entire AM print cycle. The inhalable dust sampler was fitted with a 25 mm MultiDust foam disc to simultaneously sample for inhalable and respirable particles. The NRD sampler contained 7 nylon filters and was designed to selectively collect particles smaller than 300 nm in size in a manner mimicking the deposition in the respiratory tract [20]. Each sampler was placed in the breathing zone of the AM operator. Gilian Gilair Plus (Sensidyne, Florida, USA) sampling pumps were calibrated to a flow rate of 2 l/min and 2.5 l/min, for the IOM and NRD samplers respectively, before sampling and verified after sampling by a Gilibrator Airflow calibrator (Sensidyne, Florida, USA) [21]. A total of 6 personal exposure samples (IOM and NRD) were collected and were analysed with three media blank samples (2 IOM and 1 NRD). These 6 samples were used throughout the duration of the entire print cycle (3 samplers for each print cycle). The samples also underwent ICP – MS analysis by an accredited analytical laboratory to determine the mass of metals present in each. The volume of air sampled, and the duration of the print cycle were used to calculate the time-weighted average (TWA) exposure concentration for each metal and comparison was made with occupational exposure limits for each metal. Personal exposure samples were obtained over the duration of the entire print cycles with 269 minutes in print cycle 1 and 160 minutes in print cycle 2.

4. Statistical data analysis

Statistical analysis software SPSS version 25 (IBM Corporation, USA) was used for this purpose. Multiple methods of analysis, including cross-tabulation and statistical significance ($p \leq 0.05$) testing was used to determine the meaningfulness of the data acquired from the airborne particle emission data, as well as to identify when the highest level of risk was

present. Cross-tabulation was simulated between each particle size category and its concentration in each phase and cumulative concentrations over the entire print. The results of these tests were used to indicate significant differences between selected data sets, to identify the highest emission phase and the most prevalent particle sizes emitted during PBF AM. Figures were plotted to visually represent the data by means of GraphPad Prism version 8.1.0 (GraphPad Software Inc, CA, USA). Statistical analysis was not performed on the static and personal exposure monitoring data.

5. Ethics approval

This study was approved by the Health Research Ethics Committee of the North-West University (NWU-00007-18-A1). The participant was recruited and thereafter informed consent was obtained. The AM operator was recruited as the participant as the AM operator is the only individual capable of operating the AM machine.

6. Results

In the following section, the particle emissions are reported per print cycle followed by the process phase and then categorised by particle size range. Subsequently, the personal exposure of the AM operator is presented.

6.1. Particles 0.01 to > 1 μm

The particle number concentration (p/m³) emitted during Print cycle 1 is best explained using Figure 1A, which shows the concentrations of the number of emitted particles during the cycle phases. This cycle showed an average ambient background particle number concentration of 7.37 x10³ p/m³. The print cycle, including pre-processing and processing, took a total duration of 269 minutes. The pre-processing phase was monitored for 151 minutes and showed the highest concentration of particle emissions for the print cycle.

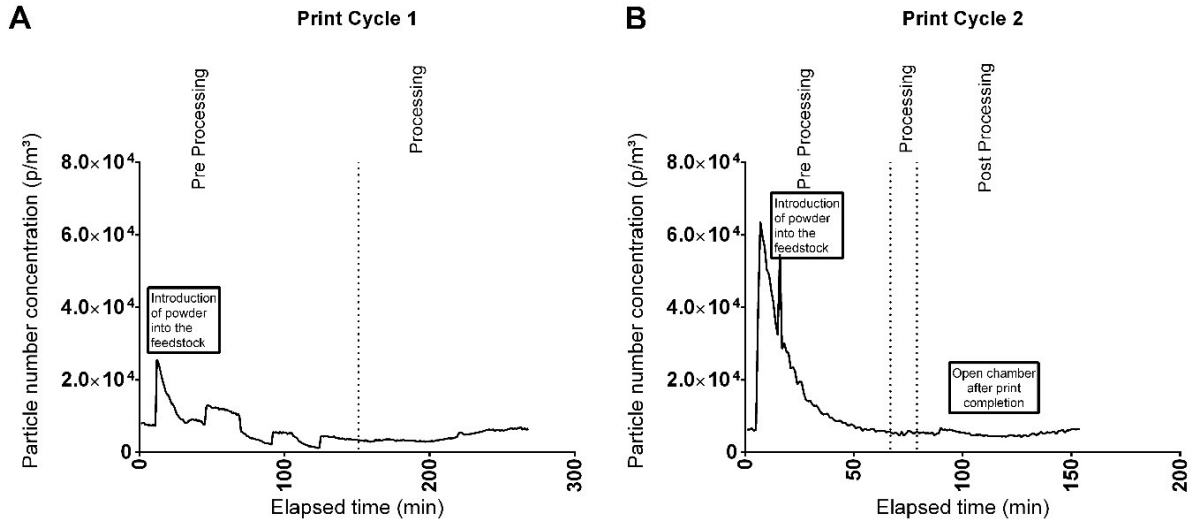


Figure 1: *Particle number concentration of 0.01 to > 1 µm sized particles emitted during each phase of a) print cycle 1 and b) print cycle 2*

A peak in particle emissions was found 12 minutes after the start of the pre-processing phase, which occurred during the transfer of the platinum metal powder from its packaging into the machine; this in fact presented the highest particle number concentration of the entire print cycle 1 at $2.56 \times 10^4 \text{ p/m}^3$. Subsequently, a gradual decline in concentration of emitted particles occurred, followed by smaller repetitive peaks throughout the pre-processing phase, after which the emitted concentration of particles stabilised towards the end of the pre-processing phase and onto the processing phase. Table 1 categorises the particle number count and emission rates observed. In the processing phase the highest particle concentration was $6.90 \times 10^3 \text{ p/m}^3$.

Table 1: Particle number counts and emission rates for print cycle 1 and print cycle 2

			AM process phase			Total particle number count (p)
			Pre-processing	Processing	Post-processing	
Average ambient concentration for both print cycles (p.m³)			7.37 x10³			
Print cycle 1	Total particle number count (p/m³)	*	264.00 x10⁶	65.60 x10⁶	*	329.60 x10⁶
	Duration (min)	6	151	118		275
	Particle emission rate (p/min)	*	5.11 x10⁵	N.A.*		*
Print cycle 2	Total particle number count (p/m³)	-	63.10 x10⁶	8.76 x10⁶	18.40 x10⁶	90.20 x10⁶
	Duration (min)	6	70	20	65	166
	Particle emission rate (p/min)	*	7.95 x10⁶	1.02 x10⁵	3.35 x10⁴	*

(*; Could not calculate)

Figure 1B shows the particle number concentration for emitted particles during all three phases of Print cycle 2. This cycle took 160 minutes and had an average ambient background particle number concentration of 7.37x10³ p/m.³ The transfer of the platinum metal powder from its packaging into the machine engendered an immediate peak 7 minutes into the process, showing the highest peak concentration value of the entire cycle, namely

$6.37 \times 10^4 \text{ p/m}^3$. A decline in concentration of emitted particles followed, and subsequently a second peak and an exponential decline occurred extending into the processing phase. The post-processing phase particle number concentration 90 minutes peaked at $6.91 \times 10^3 \text{ p/m}^3$ after 90 minutes.

The particle emission rates were calculated for print cycles 1 and 2 by using a formula created by He. et al [19] using particle number concentrations. Print cycle 1 yielded an emission rate for pre-processing and presented insufficient data for the processing phase as the particle number concentration was below the ambient concentration. The average particle emission rate over both print cycles was used to represent the pre-processing phase whilst the processing phase and post-processing phase contained emission rate data derived from print cycle 2.

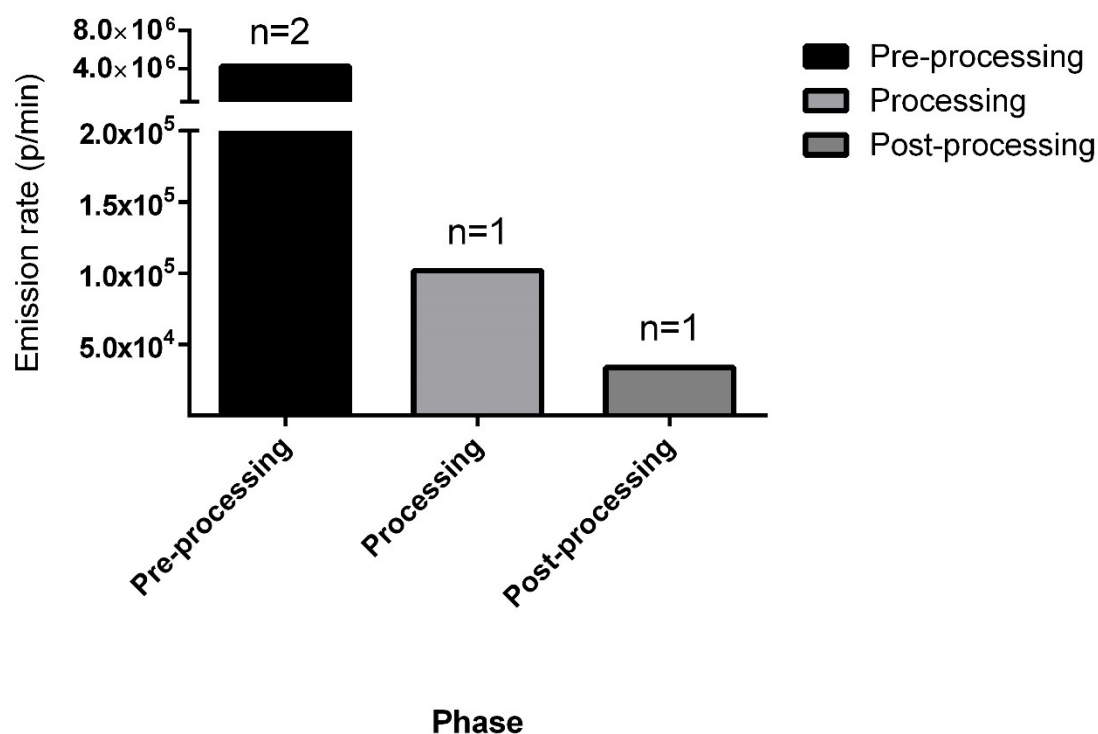


Figure 2: *Emission rates of particles during AM phases. n=2; the average of the emission rate was calculated using print cycle 1 and print cycle 2, n=1; the emission rates of data obtained during print cycle 2)*

As seen in Figure 2, pre-processing presented a particle emission rate higher than that of the other phases: particles were emitted at an average rate of 4.22×10^6 p/min, which is nearly 40 times the rate observed in the processing phase of 1.02×10^5 p/min. Since capturing of post-processing only took place to represent emissions from the print chamber without final refinement, the post-processing emission rate of 3.35×10^4 p/min was nearly a third that of the processing phase at 1.02×10^5 p/min.

Table 2 provides a size summary of the particle counts for each of the particle sizes (0.3 μm - 10 μm). It provides an indication of the size channel that registered the highest number of particles over the entire duration of the print. Particles emitted over each print cycle were predominantly in the 0.3 μm size channel presenting 85.40% in print cycle 1 and 91.45% in print cycle 2. The size channel with the next highest particle number counts was the 0.5 μm channels with 11.65% in print cycle 1 and 7.39% in print cycle 2, with the remaining size channels showing lower percentages.

Table 2: Cumulative particle number count per size channel (0.3 - 10 μm)

		Particle size (μm)					
		0.30	0.50	1.00	3.00	5.00	10.00
Print cycle 1	Number of particles (p)	7.71×10^7	1.05×10^7	2.46×10^6	1.77×10^5	1.97×10^4	2.69×10^3
	Percentage of total particles (%)	85.40	11.65	2.73	0.20	0.02	0.00
Print cycle 2	Number of particles (p)	3.02×10^8	2.44×10^7	3.55×10^6	2.55×10^5	3.89×10^4	4.45×10^3
	Percentage of total particles (%)	91.45	7.39	1.07	0.08	0.01	0.00

Size channels 1 to 10 μm presented a total average cumulative count over both print cycles of 2.05% suggesting that most emitted particles were found in the smaller size channels, $< 1\mu\text{m}$. Statistical analysis performed on the data sets for print cycles 1 and 2 indicated that the number of particles for each size channel differed from the number of particles of the other size channels ($p \leq 0.05$).

Figure 3 presents particle emission counts detected by the APC and GRIMM particle counting instruments. The GRIMM captures particle number counts over 31 size channels but only key channels were used in this data set (0.25 - 10 μm). Due to the 31 size channels offered by the GRIMM, the range of counts was spread over more of the channels when compared to the APC. A caveat should be expressed around this: when comparing data generated by these instruments, particle counts are distributed over different ranges. The APC detected higher concentrations for the size channels that matched the GRIMM (see Annexure C – Table 1A) but the GRIMM detected the highest particle number counts in the 0.25 μm and 0.30 μm size channel. Similarly, in print cycle 2 (as presented in Figure 3B) a higher particle concentration was detected by the APC in all the size channels that corresponded with GRIMM.

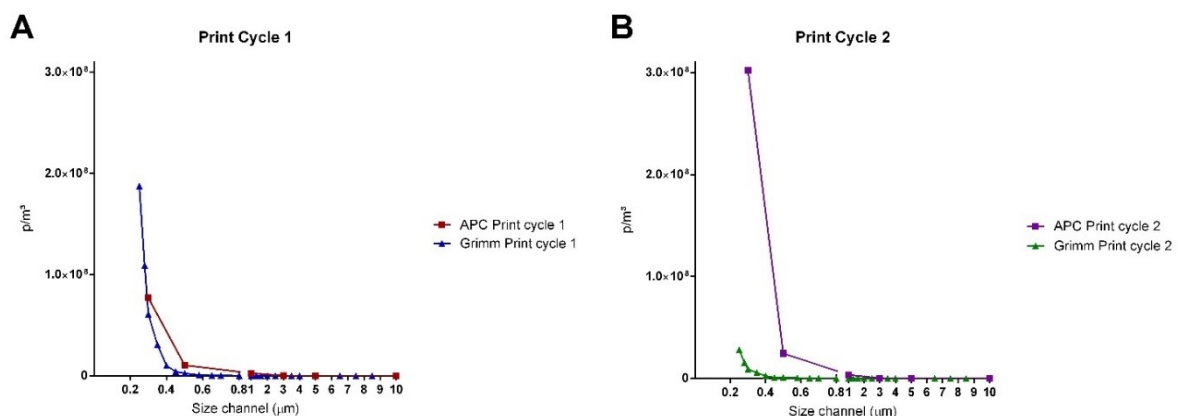


Figure 3: *APC and GRIMM particle concentrations for size channels 0.25 to 10 μm during a) print cycle 1 and b) print cycle 2*

Static area samples of platinum particles presented concentrations below the analytical detection limit for gravimetric and ICP – MS analysis (0.005 mg/m³). During the AM cycle, static area concentrations to inhalable metals such as arsenic (0.017 mg/m³), cobalt (0.015 mg/m³ and 0.063 mg/m³), copper (0.042 mg/m³) and nickel (0.06 mg/m³ and 0.348 mg/m³) were detected. Cobalt and nickel were detected during both print cycles whilst arsenic and copper were only detected during print cycle 1.

6.2. Personal respiratory exposure monitoring

Table 3: Calculated 8-hour time weighted average concentrations for metals (mg/m³) detected with ICP – MS analysis

	Personal exposure (mg/m ³)		TWA OEL (mg/m ³)
	Print cycle 1 Sampling duration:269 minutes	Print cycle 2 Sampling duration:160 minutes	
Arsenic, As	0.035	BDL	0.1 (CL)
Cobalt, Co	0.374*	0.063	0.1 (RL)
Copper, Cu	1.119*	BDL	1.0 (RL)
Lead, Pb	0.019	BDL	0.15 (LR)
Nickel, Ni	0.973*	0.145	0.5 (CL)
Platinum, Pt	BDL	BDL	5 (RL)

* Concentrations of exposure that exceeded the occupational exposure limits, CL; control limit, RL; recommended limit, LR; lead regulations.

All personal exposure samples for inhalable and < 300 nm particles, a concentration below that of the analytical detection limit for platinum ICP – MS analysis was found. Even though

platinum was not detected in the ICP – MS analysis of the inhalable samples, insoluble metals such as arsenic, cobalt, copper, lead and nickel were detected while cobalt, copper and nickel exceeded their occupational exposure limits as shown in Table 3.

Results engendered around the NRD (< 300 nm) personal exposure samples reported concentrations below the analytical detection limit for platinum and other metals.

7. Discussion

PBF AM machines have been designed in such a manner that the physical print cycle of the process requires minimal AM operator intervention and supervision, whilst the preparation of the machine and removal of the printed object requires the AM operator to carry out a variety of tasks to ensure completion of the print. This pilot study was conducted to assess particle emission and personal respiratory exposure that may have occurred during PBF AM utilising platinum powder.

The AM phase with the highest particle number concentration (0.01 to > 1 μm) was the pre-processing phase (see Figure 1). The reason for the higher particle number concentrations found during the pre-processing phase is likely the operator's involvement and movement in the AM process [6]. Pre-processing required the AM operator to handle and load the powder into the feedstock of the AM machinery which increased emission levels compared to the processing and post-processing phases. During print cycle 1 and print cycle 2 continuous emission of particles (0.01 to > 1 μm) occurred, which is statistically significant and above the ambient concentration throughout the pre-processing phase of the AM process. Nonetheless, the concentration was below ambient concentrations in the processing and post-processing phases (see Figure 1). Statistical analysis of the data obtained for the emission of particles between 0.3 and 10 μm indicated that during the AM phases significant differences occurred in particle number concentrations among all six size channels (Table 2). The general trend observed around particle sizes was that the smaller the particle size, the higher the particle number concentrations was observed for each of the print cycles. Particle number counts

during all three phases of AM were higher in the 0.3 μm and 0.5 μm size channels while lower counts were distributed among the remaining size channels (Table 2). In the present study it was indeed observed that most particle counts were found in the smaller size channels ($<1 \mu\text{m}$) (see Annexure C, Table 1A). A study conducted by Graff et al. [6] shows that particles $< 300 \text{ nm}$ were present in the workplace air during PBF AM where Inconel powder was used. This is confirmed by GRIMM spectrometer particle number concentration, which indicated that particles were found in the 0.25 μm - 0.3 μm size range. The particle number concentration of $1.08 \times 10^8 \text{ p/m}^3$ that falls within the 0.25 μm size channel and an average particle count of $3.50 \times 10^7 \text{ p/m}^3$ in the 0.30 μm channel indicated that during PBF AM an emission of particles of $<300 \text{ nm}$ occurred. Graff [6] has found that during processes where AM operator involvement is needed such as chamber opening, sieving of powders, vacuuming and cleaning around pre-processing and post-processing, an increase in particle emission concentrations occurred. This study confirmed the finding: the 0.25 μm and 0.3 μm size fraction was the highest emitted particle size throughout the AM process examined here, especially in phases where powder handling was required.

Particle emission rates showed that the pre-processing phase was a high-risk phase presenting emission rates of $7.95 \times 10^6 \text{ p/min}$ in print cycle 2 and a combined average over both print cycles of $4.23 \times 10^6 \text{ p/min}$. Static area monitoring showed concentrations below the analytical detection limit for platinum. Nickel and cobalt exposure presented a static area concentration during both print cycles. Nickel exposure had concentrations of 0.348 mg/m^3 during print cycle 1 and 0.006 mg/m^3 during print cycle 2 Cobalt exposure showed concentrations of 0.166 mg/m^3 and 0.063 mg/m^3 . Both these metals therefore posed a risk to the AM operator's health. Health effects and symptoms are subsequently briefly discussed in further detail.

Due to automation of the process, the AM operator was not always present at the machine during the print and this resulted in limited respiratory exposure to metal powder during the processing phase. Personal respiratory exposure monitoring for inhalable and $<300 \text{ nm}$

particles showed concentrations that were below the detection limit for platinum and, therefore, below the South African OEL for platinum of 5 mg/m³ and international limits set by ACGIH, OSHA and NIOSH at 1 mg/m³. Studies conducted by Stefaniak et al [17] state that during personal exposure monitoring, AM operators were performing tasks besides AM during an eight-hour shift which led to lower personal exposure concentrations. The AM operator in this study similarly was also involved in other tasks besides platinum AM. He carried out office duties and administration tasks whilst not busy with the AM print.

Even though this study indicated concentrations of respiratory exposure to other inhalable insoluble metals such as arsenic, cobalt, copper, lead and nickel, platinum exposure above the detection limit was not present. Copper, nickel and cobalt exposures presented TWA concentrations of 1.119 mg/m³, 0.973 mg/m³ and 0.374 mg/m³ respectively. Copper has been listed by NIOSH and OSHA and the South African HCSR with a 1 mg/m³ recommended limit (RL), while nickel has been listed by the HCSR with a 0.5 mg/m³ limit and by OSHA with a 1 mg/m³ control limit (CL); in its turn, cobalt has been listed by NIOSH and the HCSR with an OEL of 0.1 mg/m³ (RL): see Table 3 for South African OELs.

Exposure routes for copper include inhalation, ingestion, skin and mucous membranes with health risks identifiable by irritation of the eyes, nose, and pharynx, while the metal may cause perforation of the nasal septum [24]. Negative health effects associated with the exposure to nickel includes sensitisation, allergic asthma and pneumonitis [25]. Nickel is a known occupational group 1 carcinogen which may lead to nasal and lung cancer [25]. Arsenic is associated with the following negative health effects: ulceration of nasal septum, dermatitis, skin cancer, respiration irritation and hyperpigmentation of skin as a consequence of exposure occurring through inhalation or skin- or eye contact [26]. The presence of these metals indicates a likely cause of workplace cross contamination. The AM operator moved between the work areas located at the facility where other AM processes may have taken place and may also be a form of contamination by the AM operator. Due to the confidentiality held regarding the composition of the powder, it cannot be assumed to be pure platinum

metal powder. These metals detected by ICP – MS analysis posed a risk to the health of the AM operator and is suspected to have occurred due to contamination of the AM print room.

The static area concentrations for arsenic, cobalt, copper, lead and nickel exposure indicates that prior to the first print cycle other metals were present in the workplace environment. The AM operator was performing office duties whilst not involved in the platinum AM print cycle. The other print cycles that were simultaneously taking place involved nylon and alumide but these were isolated from the other print rooms. The most likely causes for exposure were cross-contamination and surface settling of airborne particulates in areas the AM operator frequented. Secondary exposure to these insoluble metals needs to be reduced or prevented.

Occupational exposure limits are based on exposure-effect relationships where the exposure is directly proportionate to the duration of exposure. Depending on the half-life of the substance, daily exposure could increase the concentrations found in the body. Exposure to substances such as cobalt, copper and nickel over a period could cause health problems for the AM operator, specifically those substances that are carcinogenic as these pose a cancer risk.

Personal exposure below the OEL does not mean that the AM operator is protected, and caution should still be advised [27]. The NRD exposure samples were below the analytical detection limit in that particles < 300 nm was not detected in the personal exposure sample. Even though the real-time counting instruments detected large amounts of particle number counts in the 0.25 µm – 1.0 µm range, the NRD sampler did not detect any of these particles. Thus, partial emission concentrations are dominant over exposure concentrations due to the AM operator's absence during the entire print cycle may have decreased the personal exposure concentration found on the filter of the sampler.

This study took place during initial platinum AM developmental stages and it was the first time that platinum was used at this facility. The newly implemented AM novelty material was

in the initial stages of its use and limited the study to some degree. The high cost of PBF AM in the case of platinum metal powder means that limited use is made of this process and technology, with the result that it was not possible to repeat measurements. The lack of such measurements prevented obtaining a larger dataset. Only limited access to the powder was possible and characterization of the platinum particles through microscopy could therefore not be undertaken. Confidentiality regarding the nature of the platinum metal powder that was used in this study prevented the investigation of particle size, shape and elemental composition.

As indicated, personal respiratory exposure to platinum was found to be below the limit of detection in the present study, but emission numbers indicated an airborne release of particles and the AM operator should be protected from these. Even though particles $>1\ \mu\text{m}$ were detected, many of the particles counted were in the smaller size ranges, as indicated: see Annexure C Table 1. Regarding detected metals such as cobalt and nickel, which pose risks to human health, a much more stringent approach should be taken in reducing the exposure of the AM operator. Exposure to these metals exceeded the TWA-OEL-CLs. Long-term exposure to nickel may cause cancer [24, 25, 26].

Engineering control measures such as machine isolation were already in place at the site studied. Each printing room at the facility was isolated and provided with its own air-conditioning unit serving as mechanical ventilation. The ventilation systems could however be improved by controlling the air exchange rates required for a room of that particular size. General housekeeping should be improved in such a way that surfaces and equipment are cleaned according to a specific schedule to reduce workplace cross-contamination. Surface contamination may give rise to secondary respiratory exposure due to the settled particles becoming airborne when direct or air contact is made with these. AM operators should be educated concerning the potential health risks that may be associated with the PBF AM process and the long-term effects of exposure. With engineering controls and administrative controls in place, personal protective equipment should accompany the AM operator and will

aid in providing the necessary protection especially during powder handling where the likelihood of exposure increases due to airborne particles. This however only provides a temporary solution and controls should always be evaluated for efficiency. Elastomeric half-mask respirators class N95 or P100 with a combined filter should provide protection against particles, including particles < 300 nm, which accounted for the majority of the airborne particles emitted in the AM process studied here.

This pilot study identified aspects that should be addressed in future research pertaining to AM utilising platinum metal powder. Future studies should be directed to reduce emissions of the PBF AM print cycle especially in phases where AM operator input, and handling of the powder are required. The physical and chemical characterisation of platinum metal powders would provide researchers with a better understanding of the nature of these emitted particles. Focus should also be placed on identifying the origin of personal exposure to insoluble metals such as nickel, copper and cobalt during AM, which increases the risk that the AM operator will be exposed to the effects of these metals including the carcinogenic nature of some of these metal powders.

8. Conclusion

This pilot study paves a way for future research involving PBF SLS AM utilising platinum metal powders and provides an initial elucidation of the characteristics of emitted particles during the three phases of AM including the personal respiratory exposure of the AM operator. Particles ranging from 0.01 to > 1 μm were emitted during all three AM phases with the highest emission concentration in the pre-processing phases of print cycle 1 and print cycle 2 where AM operator involvement and powder handling were required. Particle emission rates were the highest in the pre-processing phase with an emission rate of 7.95×10^6 p/min. Static area emission of platinum particles did occur but was below the analytical detection limit but copper, cobalt and nickel was detected. Personal respiratory exposure to

platinum particles was below the detection limit but other insoluble metals were detected and were likely the result of contamination. Particle emission data provided the most prominent illumination of PBF AM involving platinum powders and should be the focus of future studies. The findings made here serve as a way to assist AM facilities in recognising, identifying and resolving emissions caused by the platinum PBF AM process. The study found no personal exposure to platinum metal powders but ICP – MS analysis indicated the presence of other insoluble metals which exceeded the OELs, as indicated. It is the duty of the AM employer at the facility to educate operators around any risks that may be associated with the PBF AM process or any other workplace risk. Employers are further bound to implement control measures to eliminate or reduce the risk to an acceptable level.

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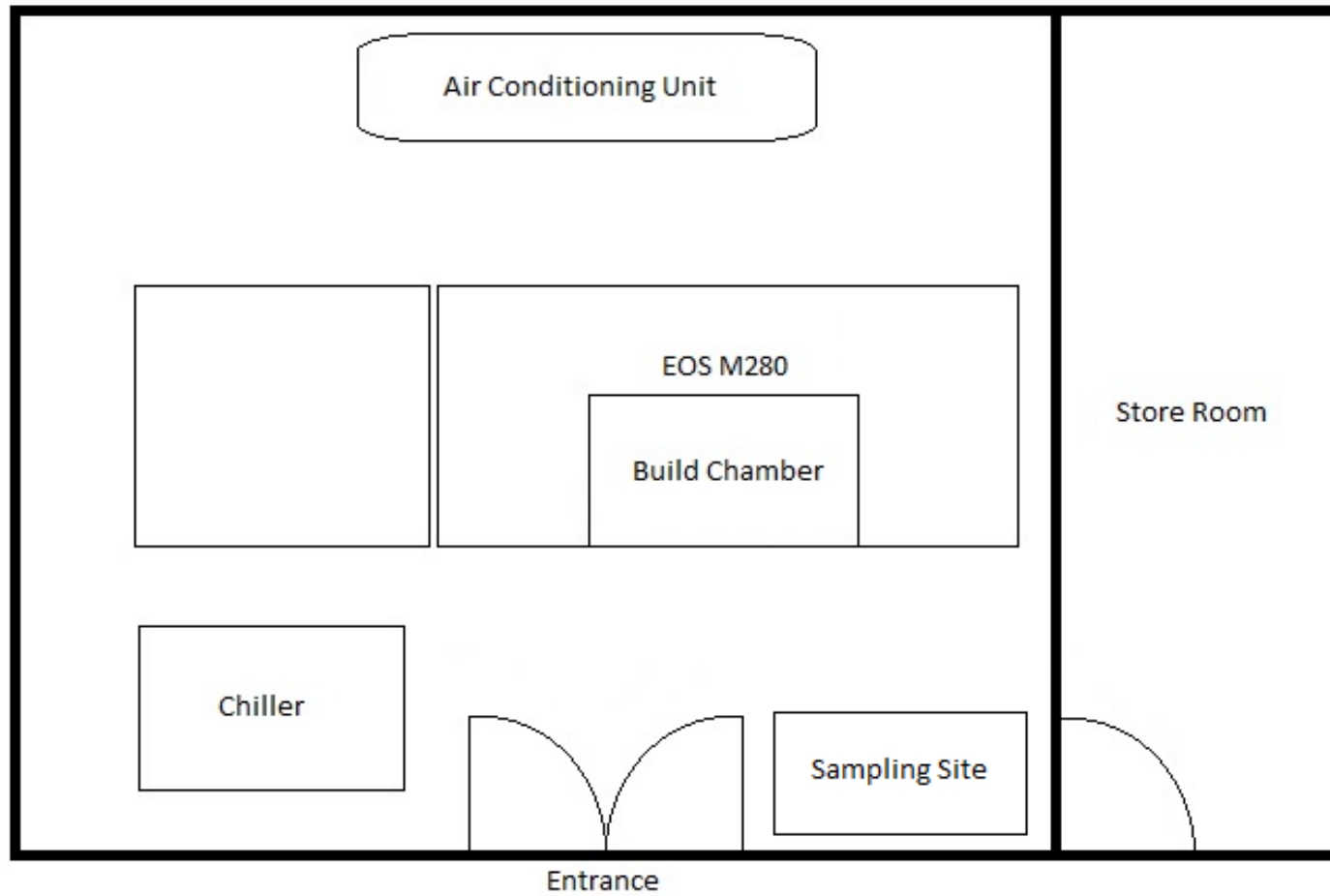
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10. Annexures

Annexure A: Sampling site and room layout



Annexure B: Static area and personal exposure concentrations for ICP – MS detected metals

	Print cycle 1			Print cycle 2			Print cycle	Print cycle 2	
	Area	Personal	Blank	Area	Personal	Blank	NRD	NRD	NRD
Metals	Concentration (mg/m ³)								
Osmium	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Iridium	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Platinum	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Gold	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Mercury	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Lead	BDL	0.059	BDL	BDL	BDL	0.011	BDL	BDL	BDL
Cobalt	0.514	1.159	BDL	0.028	0.177	0.011	BDL	BDL	BDL
Nickel	1.077	3.013	0.0011	0.011	0.268	0.018	BDL	BDL	BDL
Copper	0.129	3.465	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Arsenic	0.052	0.110	BDL	BDL	BDL	0.048	BDL	BDL	BDL
Ruthenium	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Rhodium	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Palladium	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Silver	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0,008

Note: The concentrations listed are not TWA concentrations.

Annexure C: Table 1A: Particle size channels (0.3 - > 10 µm) and total particle count for APC and GRIMM counting instruments

		Particle size channels (µm)											
		0.30		0.50		1.00		3.00		5.00		10.00	
APC	Cycle1	7.71x10 ⁷		1.05x10 ⁷		2.46x10 ⁶		1.77x10 ⁵		1.97x10 ⁴		2.69x10 ³	
	Cycle2	3.02x10 ⁸		2.44x10 ⁷		3.55x10 ⁶		2.55x10 ⁵		3.89x10 ⁴		4.45x10 ³	
		0.25	0.3	0.4	0.5	0.70	1.00	2.00	3.00	4.00	5.00	7.50	10.00
GRIMM	Cycle1	1.88x10 ⁸	8.05x10 ⁷	4.17x10 ⁶	0.36x10 ⁷	2.82x10 ⁵	0.19x10 ⁶	8.53x10 ⁴	0.20x10 ⁵	1.99x10 ⁴	1.29x10 ⁴	3.53x10 ³	3.51x10 ³
	Cycle2	2.81x10 ⁸	0.12x10 ⁸	2.29x10 ⁶	0.13x10 ⁷	1.04x10 ⁵	0.13x10 ⁶	2.41x10 ⁴	0.27x10 ⁵	2.76x10 ⁴	1.49x10 ⁴	2.85x10 ³	2.31x10 ³

CHAPTER 4

The present chapter contains a summary of the key findings of this study. It consists of a conclusion, discussion of limitations and recommendations for control measures as well as suggestions for future studies. The main aim of the study will be considered, and the formulated hypothesis will be assessed.

4.1 Main findings

This pilot study investigated particle emission and respiratory exposure to platinum metal powders during powder bed fusion (PBF) selective laser sintering (SLS) additive manufacturing (AM). Platinum metal powder that was used in this study is a novelty material used in AM and not much information is available regarding the emissions, respiratory exposure and health risks that it may pose in the AM workplace. Elucidating the behaviour of particles as well as the concentrations of particles emitted throughout the AM print cycle needed to be achieved. Not much is known regarding platinum AM, but studies related to AM with other materials provided an indication of how to identify possible high emission phases.

PBF AM consists of three main phases: pre-processing, processing and post-processing. During all these phases, particles ranging from 0.01 to > 1.00 μm were continuously emitted with higher peak emission concentrations occurring during the pre-processing phase where there was an increase in the operator's involvements in the AM print cycle, especially powder handling. Particles emitted were predominantly smaller, ranging from 0.25 μm , the highest emitted particle size throughout all the phases of the print cycle, followed by particles of sizes 0.30 μm , 0.50 μm and 1.00 μm . The number of concentrations for particles $\leq 0.30 \mu\text{m}$ indicated that smaller sized particles were being released into the workplace atmosphere, which increased the risk of respiratory exposure as these particles may have deposited in the alveoli of the

lungs. Particles emitted of $> 1 \mu\text{m}$ in size only accounted for 2% of all particles emitted across the entire study.

During print cycle 1 the cumulative count of particles over a period of 269 minutes was 329.60×10^6 with majority counts found in the pre-processing phase where the AM operator was involved in tasks such as machine cleaning, feedstock loading and closing of the build chamber. The pre-processing phase accounted for 80% of overall particle emission. The entire print cycle presented an 85.38% count of particles of $0.30 \mu\text{m}$ in size and 11.62% of particles of $0.50 \mu\text{m}$ in size. During this cycle, the peak particle number concentration was $2.56 \times 10^4 \text{ p/m}^3$ with an emission rate of $5.11 \times 10^5 \text{ p/min}$ in the pre-processing phase. The emission rate of the processing phase could not be calculated due to the fact that the ambient background reading was higher than the concentrations observed.

During print cycle 2 the number concentration of emitted particles over a period of 160 minutes was $90.20 \times 10^6 \text{ p/m}^3$ with majority counts found in the pre-processing phase. The pre-processing phase accounted for 57.36% of overall particle emission counts. During the print, 91.51% of the emitted particles were in the $0.30 \mu\text{m}$ particle size range and 7.93% were in the $0.50 \mu\text{m}$ size range. As illustrated in Figure 1B (see Chapter 3) the concentration of particles ranging 0.01 to $> 1.00 \mu\text{m}$ were pronounced in the pre-processing phase and post-processing phase, with the peak concentration ($6.37 \times 10^4 \text{ p/m}^3$) occurring as the AM operator introduced the powder into the feedstock of the machine. The emission rate for pre-processing was $7.95 \times 10^6 \text{ p/min}$, processing $1.02 \times 10^5 \text{ p/min}$ and $3.35 \times 10^4 \text{ p/min}$ during post-processing. It is evident that when the build chamber is sealed during physical processing of the object, emissions are lower than when powders are handled directly. Powder handling is the main cause of higher emission and particle counts found in the pre-processing phase. During activities that require powder handling, particles become airborne and depending on the size of the

particle, will either remain airborne for a while before settling on surfaces or will settle quickly for larger particles.

Static area metal concentrations were below the analytical detection limit for platinum. However, other insoluble metals such as nickel and cobalt were detected over both print cycles. Nickel had concentrations of 0.348 mg/m³ and 0.006 mg/m³ respectively. Cobalt had a static area concentration of 0.166 mg/m³ and had the concentration of 0.015 mg/m³ during the second print cycle.

Personal exposure monitoring samples were below the detection limit for platinum and the occupational exposure limits stipulated in the Hazardous Chemical Substance Regulations (HCSR) (Department of Employment and Labour, 1995) at 5mg/m³ and international standards set at 1mg/m³ (ACGIH, NIOSH and OSHA) [1] was not exceeded. However, the AM operator experienced personal exposure to insoluble metals other than platinum, as mentioned, namely, arsenic, cobalt, copper, lead and nickel. Metals such as arsenic and nickel are harmful to the AM operator and the concentrations observed for copper and nickel were of concern as they both exceeded occupational exposure limits while nickel and arsenic are known to be carcinogens [2, 3].

4.2 Further discussions

The aim of this study was to assess the emissions and respiratory exposure of AM operators during PBF using platinum metal powders. This general aim was achieved by completing two specific objectives.

The first objective was to quantify particle emissions associated with PBF AM utilising platinum metal powders by means of emission and area monitoring. This was achieved by using particle size selective counting instruments during the different phases of AM which, in turn, was achieved by means of real-time particulate counting

instrumentation. This was used to gather the particle number concentrations and emissions (0.01 to 10.00 μm). The particulates were then counted and classified (0.25 μm to 32 μm) according to specific size channels by another real time particle counting instrument. Ambient readings determined the background concentration prior to the print. As the AM process started, the pre-processing phase began with a large increase in particle concentration attributed to the loading of powder into the feedstock of the machine. As pre-processing continued, the concentration gradually declined and was intermittently observed to have an increase in concentration which once again decreased gradually. This could be attributed to the warmup stage of the machine where heat is applied to the build chamber to prepare the powder for the high intensity heat required for the build. As the pre-processing phase terminated, the processing phase began. The processing phase was automated, the build chamber was sealed, and particle emission concentrations were stable. After processing, post-processing required the opening of the build chamber which caused a slight increase in the concentration of emitted particles due to the release of accumulated particles in the build chamber during processing. Area exposure monitoring involved the use of a sampler designed to mimic normal respiration (IOM) which was placed in the vicinity of the AM machine to identify the area concentrations of platinum particles. The filter from the sampler underwent gravimetric and ICP - MS analysis and the results were below that of the detection limit for platinum but indicated the presence of other metals (arsenic, cobalt, copper, lead, nickel) in the AM workplace. The presence of these metals was likely caused by workplace cross contamination and a lack of housekeeping.

The second objective was to determine the personal respiratory exposure of AM operators to inhalable and $< 300\text{ nm}$ platinum particles during the different phases of AM. The emission results of this study elucidated the phases that cause a risk to the AM operator. Release of airborne particles throughout the AM print occurred mainly

during pre-processing, followed by the post-processing and lastly the processing phase. The higher the emission of particles occurring during these phases the higher the risk of respiratory exposure of the AM operator to these airborne particles. However, results engendered by the gravimetric analysis of the IOM as well as NRD sample results obtained from the accredited laboratory indicated that the detection limit for platinum had not been reached. Even though the aim was to assess platinum metal powder, the fact that there were other detected metals posing a known risk to health, should be investigated further. Therefore, the objectives set for this study were achieved.

Two hypotheses were formulated in this study. The first hypothesis of this pilot study was that particles ranging from 0.30 μm – 10.00 μm were emitted during PBF AM. Particles emitted throughout the entire print were most dominant in the smaller size ranges (0.25 μm – 1 μm) and concentrations of particles 0.01 μm to > 1 μm were detected throughout both the print cycles. Particles ranging from 1 to 10 μm were detected but only accounted for 2% of the total particle counts. These findings entail that the hypothesis can be accepted.

The second hypothesis was that there would be personal respiratory exposure to emissions of platinum metal particles that possibly arose during the AM print cycle. Although respiratory exposure samples were below the platinum detection limit for gravimetric analysis, which entails rejection of the hypothesis, other insoluble metals such as arsenic, cobalt, copper, lead and nickel were detected. Personal exposure to these metals exceeded the OEL and increased the AM operator's risk to health. It is thus contended that extra caution should be in place to prevent respiratory exposure of the AM operator.

4.3 Limitations

The high cost of PBF AM with platinum metal powder meant that limited use was made of this process and technology, resulting in the absence of repeat measurements. The high cost of PBF AM printing was not only factored by the novelty and cost of platinum as a material but also the high cost of the machine itself.

Confidentiality regarding the nature of the platinum metal powder used, significantly decreased the possibilities to investigate particle characterisation. This also factored in on whether the platinum powder was contaminated with other metals (arsenic, cobalt, copper, lead and nickel) or whether these metals may have been used in the production process of these powders. The air exchange rate provided by the engineers is seen as limitation as it was estimated and not calculated.

4.4 Recommendations

To protect the AM operator from respiratory exposure to particle emission, especially to metals other than platinum, namely arsenic, cobalt, copper, lead and nickel, certain control measures should be put in place. Engineering control measures such as machine isolation and ventilation were already in place but could be improved by the implementation of a local extraction ventilation system to remove airborne particles. Administrative controls should be in place to ensure good house-keeping practices, especially the cleaning of surfaces and tabletops in the vicinity of the machine. Cross-contamination may arise from other AM processes due to the movement of the AM operators, natural airflow and general lack of housekeeping. Contamination may result in airborne particles settling on floors and surfaces and these will become airborne once disturbed. Wet methods should be used to prevent particles that have settled to become airborne. Wet methods mean that the housekeeper should use cleaning apparatus that will trap particles without allowing them to become airborne such as a wet cloth, mop or dusting instrument. Housekeeping should be done daily to prevent

workplace contamination. Respirators should be used to ensure that general respiratory exposure does not occur for a variety of metals. However, as regards nickel and arsenic of which the latter is carcinogenic, an elastomeric half-mask respirator class N95 or P100 with a combined filter should provide protection especially against nickel and arsenic [4]. Extra caution should be advised during activities that involve direct contact with the powder, such as powder handling and machine loading, as these activities increased the exposure of the AM operator to airborne particulates.

4.5 Future studies

This pilot study provided an understanding of particle emission and respiratory exposure that occurred during PBF AM utilising metal powders.

Future studies should aim to investigate the characterisation of particles as well as the sampling of a variety of platinum AM prints to obtain more data and identify correlation between prints. Particle characterisation will provide a background around the morphology of particles and will facilitate improved understanding around the behaviour that the particle will undergo while being emitted into the airborne environment as well as how deposition in the respiratory tract will occur. Characterisation of virgin and recycled powder could provide information about the changes that occur in the powder after it has been exposed to the AM cycle. Repeat measurements will create a greater database to compare emissions and exposure during the AM print cycle.

The concentrations of other metals, especially copper and nickel, should be investigated to identify the source of exposure. As mentioned, presence of other metals in this environment is a reason for concern as these metals exceed the OEL without direct contact with these powders. A study should focus on identifying the source of these exposures during platinum AM and should reduce or remove the source entirely.

4.6 References

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ANNEXURE A: ETHICS CLEARANCE CERTIFICATE



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22 March 2018

Mr S.J.L. Linde
Occupational Hygiene-OHHRI

Dear Mr Linde

APPROVAL OF YOUR APPLICATION BY THE HEALTH RESEARCH ETHICS COMMITTEE (HREC) OF THE FACULTY OF HEALTH SCIENCES

Ethics number: NWU-00007-18-S1

Kindly use the ethics reference number provided above in all future correspondence or documents submitted to the administrative assistant of the Health Research Ethics Committee (HREC) secretariat.

Study title: Particle emission and respiratory exposure to platinum metal powders during additive manufacturing

Study leader: Mr S.J.L. Linde

Student: ZY Lambat-24222704

Application type: Single study

Risk level: Minimal (monitoring report required annually)

You are kindly informed that your ethics approval application has been successful and fulfils all requirements for approval. Your study is approved for a year and may commence from 22/03/2018. 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. A monitoring report should be submitted two months prior to the reporting dates as indicated i.e. annually for minimal risk studies, six-monthly for medium risk studies and three-monthly for high risk studies, to ensure timely renewal of the study. A final report must be provided at completion of the study or the HREC, Faculty of Health Sciences must be notified if the study is temporarily suspended or terminated. The monitoring report template is obtainable from the Faculty of Health Sciences Ethics Office for Research, Training and Support at Ethics-HRECMonitoring@nwu.ac.za. Annually, a number of studies may be randomly selected for an internal audit.

ANNEXURE B: LANGUAGE EDITING CERTIFICATE



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DECLARATION OF LANGUAGE EDITING

I, Christina Maria Etrecia Terblanche, hereby declare that I edited the
research study titled:

**Particle emission and respiratory exposure to platinum metal
powders during additive manufacturing: A pilot study**

for **ZY Lambat** for the purpose of submission as a postgraduate research
study. Changes were indicated in track changes and implementation was
left to the author.

Regards,

A handwritten signature in black ink, appearing to read 'CME Terblanche', is written over a circular stamp or watermark.

CME Terblanche

Cum Laude Language Practitioners (CC)

South African Translators Institute accr nr: 1001066

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