

Surface contamination from the use of metal powders at two additive manufacturing facilities

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Preface

This mini-dissertation is written in article format and according to the specifications outlined for the journal *Annals of Work Exposures and Health*. The literature is therefore referenced in accordance with the style used by the *Annals of Work Exposures and Health*, using the Vancouver style of abbreviation and punctuation. Examples of referencing:

- Simpson AT, Groves JA, Unwin J, Piney M. (2000) Mineral oil metal working fluids (MWFs)—Development of practical criteria for mist sampling. *Ann Occup Hyg*; 44: 165–72.
- Vincent JH. (1989) *Aerosol sampling: science and practice*. Chichester, UK: John Wiley. ISBN 0 471 92175 0.
- Swift DL, Cheng Y-S, Su Y-F, Yeh H-C. (1994) Ultrafine aerosol deposition in the human nasal and oral passages. In Dodgson J, McCallum RI, editors. *Inhaled Particles VII*. Oxford: Elsevier Science. p. 77–81. ISBN 0 08 040841 9 H.
- British Standards Institution. (1986). BS 6691: 1986. Fume from welding and allied processes. Part 1. Guide to methods for the sampling and analysis of particulate matter. London: British Standards Institution.
- Morse SS. (1995) Factors in the emergence of infectious diseases. *Emerg Infect Dis* [serial online] 1995 Jan–Mar;1(1). Available from: URL: <http://www.cdc.gov/ncidod/EID/eid.htm> (accessed 25 Oct 2010).

For uniformity, this referencing style is used throughout the entire mini-dissertation. A detailed description of the author guidelines for the *Annals of Work Exposures and Health* can be found at the beginning of Chapter 3. British spelling is used in this mini-dissertation except in direct quotes, titles of articles and journals, and names of organisations, that use American spelling. The outline of the mini-dissertation is as follows:

- Chapter 1: the general introduction which introduces the study and states the aim, objectives, and hypotheses of the study.
- Chapter 2: the literature review focusing on the information which is relevant to the study.
- Chapter 3: an article on surface contamination by stainless steel and maraging steel powders, presented in a format that meets the required specifications of the *Annals of Work Exposures and Health* journal.
- Chapter 4: an article on the surface contamination by Ti-6Al-4V powder, presented in a format that meets the required specifications of the *Annals of Work Exposures and Health* journal.
- Chapter 5: the conclusion of the study presented as a discussion and including recommendations, limitations, and suggestions for future research related to this study.

- Annexure: for brevity, only selected results were reported in the articles (Chapters 3 and 4). Therefore, a complete data set is provided in the annexure.

Authors' contributions

The study was planned and carried out by a team of researchers. The contributions of each researcher to the study are presented in Table 1 below.

Table 1. Contributions of the different authors.

Name	Contribution
Ms. RL Hyslop	• Planning the study. • Conducting literature research. • Conducting surface sampling. • Statistical analysis of the data. • Interpretation of data results. • Formulating recommendations. • Writing the mini-dissertation, including the article and short communication.
Mr. SJL Linde	• Supervisor. • Assisting with the planning and design of the study, approving the study protocol, selection of statistical analysis methods, and review of the mini-dissertation.
Prof. A Franken	• Co-supervisor. • Assisting with the planning and design of the study, approving the study protocol, selection of statistical analysis methods, and review of the mini-dissertation.
Mrs. S du Preez	• Assistant supervisor. • Assisting with the planning and design of the study, approving the study protocol, and review of the mini-dissertation.

The following is a statement from the co-authors that confirms each individual's role in the study:

I declare that I have approved the articles and that my role in the study as indicated above is representative of my actual contribution and that I hereby give my consent that it may be published as part of RL Hyslop's M.Sc (Occupational Hygiene) mini-dissertation.

Mr. SJL Linde (supervisor)

Prof. A Franken (co-supervisor)

Mrs. S du Preez (assistant supervisor)

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“For me to live is Christ, and to die is gain.” — Philippians 1:21 (ESV).

This mini-dissertation is the product of two years’ worth of lessons learned, battles fought, trials faced, and blessings received. To say that I did it alone would be the greatest act of foolishness I could ever commit. Every lesson I learned was taught to me by someone wiser, every battle was fought with an army by my side, every trial was faced with a panel of experts backing me, and every blessing received was a gift from God.

Firstly, I thank my Heavenly Father who has blessed me with more than I could ever comprehend. He has become my perspective and He has given me my purpose: to know Him and make Him known.

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Summary

Title: Surface contamination from use of metal powders at two additive manufacturing facilities.

Additive manufacturing (AM) of metal powders is a relatively new technology, especially in South Africa, therefore little information exists on the potential health hazards involved. Maraging steel, stainless steel, and titanium alloy powders are used in AM process, including the process categories of powder bed fusion (PBF) and directed energy deposition (DED). As such, these powders may contaminate workplace surfaces and contribute to overall inhalation, dermal, and ingestion exposure. Exposure to metal powders such as nickel, chromium, and cobalt, which are steel component metals, can lead to dermal or respiratory sensitisation.

Aims and objectives: To determine surface contamination caused by use of maraging steel, stainless steel, and titanium-6aluminium-4vanadium (Ti-6Al-4V) powders during PBF and DED at two AM facilities using a wipe sampling method.

Methods: Sampling took place at two AM facilities where maraging steel, stainless steel, and/or Ti-6Al-4V powders were used in PBF and/or DED. Surface wipe sampling was carried out in printing and non-printing areas using Ghostwipes™. Printing activities were divided into three printing phases (pre-processing, processing, and post-processing) and, where possible, samples were collected before and after activities in each of the phases. Even surfaces were wiped three times consecutively following an s-shaped pattern and using a 10 x 10 cm template. Uneven or irregular surfaces were also wiped three times consecutively and the area sampled was measured and used to adjust the results. The surface samples as well as the collected field and media blanks were subjected to inductively coupled argon plasma atomic emission spectroscopy (ICP-AES) analysis.

Results: Detectable concentrations of aluminium (below detection limit [BDL]-42.422 µg/cm²), calcium (BDL-22.553 µg/cm²), cadmium (BDL-0.051 µg/cm²), cobalt (BDL-66.741 µg/cm²), chromium (BDL-132.727 µg/cm²), copper (BDL-3.84 µg/cm²), iron (BDL-1072.28 µg/cm²), lead (BDL-0.311 µg/cm²), magnesium (BDL-0.351 µg/cm²), manganese (BDL-3.625 µg/cm²), molybdenum (BDL-22.943 µg/cm²), nickel (BDL-77.539 µg/cm²), tin (BDL-0.217 µg/cm²), titanium (BDL-8.0 µg/cm²), vanadium (BDL-0.538 µg/cm²), and zinc (BDL-1.175 µg/cm²) were found to be present on surfaces in both printing and non-printing areas at both of the AM facilities. Contamination occurred prior to as well as during the different printing phases. When comparing total metal concentrations, significant differences ($p \leq 0.05$) were found between the concentrations of contaminants on certain surfaces prior to specific printing phases and the concentrations of contaminants after those printing phases. Cross-contamination was found to

occur between AM printing rooms and within AM printing rooms where more than one type of metal powder was used in the printing rooms. Significantly higher metal powder concentrations were found on surfaces in the printing rooms compared to that of surfaces in non-printing rooms.

Conclusions: DED with stainless steel powder, and PBF with maraging steel powder and Ti-6Al-4V powder caused detectable levels of metal powder contaminants to be present on printing room surfaces and non-printing room surfaces at both AM facilities. Cross-contamination as a result of airborne and/or contact transfer was found to have occurred from previous print builds with different metal powders in the same room. Contaminated surfaces presented as potential secondary sources of worker exposure through inhalation, dermal contact, and ingestion. Some of the metals that were found to be present on AM surfaces are capable of eliciting toxic responses in humans, including hypersensitivity reactions and cancer, and potential surface contamination-related exposure may contribute to the development of the adverse health effects associated with these metals. While surface contamination occurred as a result of the AM activities, poor housekeeping contributed to the extent of surface contamination. The concentrations of metal powders found to be present on surfaces at the AM facilities is comparable to that found in other industries including the cemented tungsten carbide industry.

Key words: Surface sampling; maraging steel; stainless steel; Ghostwipes™; Ti-6Al-4V.

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List of symbols and abbreviations

α	alpha
$\pm$	approximately
β	beta
$^{\circ}\text{C}$	degrees Celsius
cm^2	square centimetre
g	gram
$\mu\text{g}/\text{cm}^2$	microgram per square centimetre
nm	nanometre
%	percent
3D	three dimensional
Al	aluminium
AM	additive manufacturing
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
BDL	below detection limit
Ca	calcium
CAD	computer-aided design
CCOHS	Canadian Centre for Occupational Health and Safety
Cd	cadmium
Co	cobalt
Cr	chromium
Cu	copper
DED	directed energy deposition
EOS	Electro Optical Systems
Fe	iron

FFP	filtering face-piece
GM	geometric mean
HCS	hazardous chemical substance
HSE	Health and Safety Executive
IARC	International Agency for Research on Cancer
ICP-AES	inductively coupled argon plasma atomic emission spectroscopy
ISO	International Organization for Standardization
MELISA®	memory lymphocyte immunostimulation assay
Mg	magnesium
Mn	manganese
Mo	molybdenum
MS	maraging steel
MSDS	material safety data sheet
Ni	nickel
NIOSH	National Institute for Occupational Safety and Health
OEL	occupational exposure limit
OSHA	Occupational Safety and Health Administration
Pb	lead
PBF	powder bed fusion
PPE	personal protection equipment
PR1	printing room 1
PR2	printing room 2
SANAS	South African National Accreditation System
SDS	safety data sheet
Sn	tin
SS	stainless steel

Ti	titanium
Ti-6Al-4V	titanium-6aluminium-4vanadium
V	vanadium
Zn	zinc

Chapter 1: General introduction

1.1 Introduction

Additive manufacturing (AM) is a technology that uses computer-aided design (CAD) data to guide the layer by layer construction of three dimensional objects (Wohlers and Caffrey, 2015). AM is taking its place on the frontline of modern technology (Wohlers and Caffrey, 2015; Ryan and Hubbard, 2016) by providing advantages that include more efficient use of materials, the ability to achieve greater design detail, and reduced time-to-market (Petrovic *et al.*, 2011; Wohlers and Caffrey, 2015). Factors such as the cost of feedstock, make AM impractical in industries reliant on mass production (Huang *et al.*, 2013; Wohlers and Caffrey, 2015). However, AM has found application in many areas including aerospace, engineering, architecture, biomedicine, and various consumer product industries that often require a small quantity of specialised objects to be manufactured (Wohlers and Caffrey, 2015; Ryan and Hubbard, 2016).

The popularity and relative newness of the AM industry give rise to a need for determination of the potential hazards and risks involved in AM processes. These processes are divided into seven standard categories and differ according to the specific operating principle, the feedstock that is used, and the physical form of the feedstock (powder, liquids, sheets, etc.). Binder jetting, powder bed fusion (PBF), and directed energy deposition (DED) are three types of AM process categories that use powdered materials as feedstock (ISO/ASTM, 2015; Wohlers and Caffrey, 2015). Powdered material, such as metal powders, may be released into the working environment from where it can contribute to worker exposure via inhalation, dermal contact, and/or ingestion (Afshar-Mohajer *et al.*, 2015). In addition, contamination may occur when the airborne powder settles onto surfaces in the workplace, and/or through spillage or deliberate application of powders to these surfaces. Contaminated surfaces in the workplace can result in the formation of secondary sources of exposure, which can potentially lead to further inhalation, dermal contact, and/or ingestion exposure (Schneider *et al.*, 1999).

Surface sampling is used to assess the importance of surface contamination as a secondary source of exposure in a particular workplace, and to provide information on the effectiveness of the housekeeping programmes and controls that are utilised in that workplace (Schneider *et al.*, 1999; Badenhorst, 2007). There are many different forms of surface sampling, of which wipe sampling is the most popular. There are also a number of different wipes available for use in different situations (Wheeler and Stancliffe, 1998; Byrne, 2000; Badenhorst, 2007).

The selected method and sampling media should be validated for the substances for which wipe sampling is being carried out, in this case: the iron-based alloys: maraging steel (EOS, 2011) and stainless steel (Baddoo, 2008), and titanium (titanium-6aluminium-4vanadium (Ti-6Al-4V), the most common titanium alloy (Bhola *et al.*, 2011)). Ghostwipes™ have been validated for use in sampling for 13 metals. These include the major maraging steel and stainless steel component

metals (iron, chromium, cobalt, nickel, manganese, molybdenum, vanadium), but exclude titanium and aluminium (OSHA, 2002).

The physical and chemical form of the metal powders, as well as the exposure route will determine the nature of the health effects caused by exposure. Stainless steel and Ti-6Al-4V metals are considered to be biologically inert and safe enough to be used in biomedical implants—one of the main target industries for AM (Dewidar *et al.*, 2006; Santos *et al.*, 2006; Rack and Qazi, 2006). This does not preclude the possibility of adverse health effects resulting from exposure to one or more forms of these metals (Sicilia *et al.*, 2008; Tokar *et al.*, 2013). In biomedicine, for example, leaching of ions from the metal can cause toxicity (Sicilia *et al.*, 2008; Vijayaraghavan *et al.*, 2012). Exposure to powdered alloys involves exposure to one or more of the individual alloying elements, but not necessarily to the complete alloy itself. For example, workers handling stainless steel powder may be exposed to iron particles or particles composed of both iron and chromium, but may not actually be exposed to the complete stainless steel alloy. Thus, the toxicity associated with each of the component elements must be investigated separately, as well as collectively (Santos *et al.*, 2006; Gu *et al.*, 2012). Reports of titanium-related illness are rare and relatively few studies have been conducted into titanium toxicity. This suggests that toxicity is unlikely, not impossible (Nohynek *et al.*, 2008; Fage *et al.*, 2016). Chronic exposure to aluminium has been associated with lung and bone toxicity, and exposure to vanadium can lead to bronchitis (Tokar *et al.*, 2013). The metals found in maraging steel and stainless steel (Tolosa *et al.*, 2010) are all capable of causing pathology, for example chromium and nickel are both well-known skin sensitisers capable of eliciting allergic contact dermatitis, and manganese has been associated with neurotoxicity (Tokar *et al.*, 2013).

Using powdered metals in AM may lead to surface contamination. Surface contamination needs to be evaluated in order to determine the contribution of this contamination to overall exposure (via the inhalation, dermal, and ingestion exposure routes), and also to provide information on the effectiveness of cleaning and control practices. The body of knowledge regarding exposure in AM is limited. The available literature is focused on emission exposure as opposed to dermal exposure, although a recent study by Creytens *et al.* (2017) published findings on the relationship between epoxy resin exposure in the AM industry and allergic contact dermatitis. Further research is required to gain a more comprehensive understanding of the hazards and risks to health that may arise during AM.

1.2 Research aims and objectives

The general aim of this study is:

- To assess surface contamination caused by use of metal powders at two AM facilities.

The specific objective of this study is:

- To determine the presence of surface contamination caused by use of maraging steel, stainless steel, and Ti-6Al-4V powders during PBF and DED at two AM facilities using a wipe sampling method.

1.3 Hypothesis

Powder bed fusion and directed energy deposition, two AM process categories, involve the use of powdered metals (Beese and Carroll, 2015; Wohlers and Caffrey, 2015). The two proposed AM facilities used maraging steel, stainless steel, and Ti-6Al-4V metal powders. Loose powder may be released into the workplace and cause direct and indirect surface contamination (Schneider *et al.*, 1999; Afshar-Mohajer *et al.*, 2015; Graff *et al.*, 2016). Therefore, it is hypothesised that detectable concentrations of metal powder, such as aluminium, chromium, cobalt, iron, manganese, molybdenum, nickel, titanium, and vanadium are present on surfaces which workers come into contact with at the AM facility.

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Chapter 2: Literature review

2.1 Introduction

This literature review will discuss the use of metal powders in additive manufacturing (AM); the properties and adverse health effects of managing steel, stainless steel, and titanium-6aluminium-4vanadium (Ti-6Al-4V); surface sampling, specifically surface wipe sampling in occupational settings; and the process, purpose, and importance of method validation.

2.2 Additive manufacturing

AM is the name given to a collection of process categories used to create three dimensional (3D) objects according to computer-aided design (CAD) data in an additive, as opposed to a subtractive manner; by building layer upon layer, not removing piece by piece (Wohlers and Caffrey, 2015). The possibilities of this technology are seemingly endless and AM is becoming increasingly more important and popular as an alternative to the more traditional manufacturing techniques (Gu *et al.*, 2012). Owing to the development of technologies such as electron beam AM, which is used in powder bed fusion (PBF) (Diegel *et al.*, 2010; Gong *et al.*, 2014), AM is no longer limited to use in fabrication of models and prototypes (Gu *et al.*, 2012; Frazier, 2014). It is now able to produce fully functional, full-strength or full-density metallic parts in a timeous fashion (Diegel *et al.*, 2010; Gong *et al.*, 2014). As such, AM finds application in a wide range of fields (Wohlers and Caffrey, 2015; Ryan and Hubbard, 2016).

AM provides many advantages over other manufacturing methods. The technology that it uses facilitates greater detail and geometric capability, increasing the flexibility of design and allowing the formation of customised parts (Diegel *et al.*, 2010; Huang *et al.*, 2013; Gong *et al.*, 2014). The formation of a complete part eliminates much of the tooling needed in traditional manufacturing, reducing both time-to-market and cost. Other methods by which cost is lowered in AM is through the effective utilisation of materials, the ability to recycle some of the feedstock, and the resultant minimisation of the amount of waste produced (Huang *et al.*, 2013; Gong *et al.*, 2014). However, AM is still limited in its application by factors such as the cost of feedstock, the fact that only a select number of materials are appropriate for use as feedstock in AM, and the size of the machines, which limits the size of the final products. These limitations are particularly applicable in industries reliant on mass production (Petrovic *et al.*, 2011; Wong and Hernandez, 2012; Huang *et al.*, 2013; Wohlers and Caffrey, 2015). Regarding the future of AM, Huang *et al.* (2013) suggest that it will not replace traditional manufacturing completely, but rather the two techniques will ultimately function together in a harmonious manner.

2.2.1 Applications

AM finds application in several sectors, out of which Wohlers and Caffrey (2015) identified the industrial, consumer, automobile, aerospace, and medical and dentistry fields as the largest markets. In the industrial sector AM is used to fabricate construction components, power tools, moulds, and dies (devices used to mould or cut metal into specific shapes). In the consumer goods sector, it is utilised in the production of electronic devices and kitchen appliances. AM is furthermore involved in design and production of customised parts to be used in the automobile and aerospace industries. In medicine and dentistry, the ability of AM to afford accuracy and complexity of design to the components is exploited during the production of implants, prostheses, and surgical tools (Venekamp and Le Fever, 2015; Wohlers and Caffrey, 2015). The significance of maraging steel, stainless steel, and titanium alloys as materials in the aerospace and/or biomedical sectors becomes apparent when reviewing literature on these metals (Tsay *et al.*, 2005; Dewidar *et al.*, 2006; Kostov and Friedrich, 2006; Lo *et al.*, 2009; Shaulov *et al.*, 2009; Cui *et al.*, 2010; Kempen *et al.*, 2011; Beese and Carroll, 2015). The role of AM in the application of these metals in these two industries is similarly evident (Tolosa *et al.*, 2010; Kempen *et al.*, 2011; Beese and Carroll, 2015; Wohlers and Caffrey, 2015; Lin *et al.*, 2016).

2.2.2 Occupational exposure

The same basic principle underlies all AM processes but each process differs according to the specific technology by which it operates (process categories), the feedstock that is used, and the physical form of the feedstock. The seven standard process categories are: binder jetting, directed energy deposition (DED), material extrusion, material jetting, PBF, sheet lamination, and vat polymerisation. Processes in these categories can use metals, plastics, ceramics, or other raw materials in the form of sheets, powders, liquids, filaments, pastes, or pellets (ISO/ASTM, 2015; Wohlers and Caffrey, 2015).

The potential for risk to health of workers exists in any workplace (Department of Labour, 1993); AM facilities are no exception. Despite the fact that the concept of AM has existed for decades, its practical application was delayed by a dependency on computer-based technologies, such as CAD, which were only developed years after the theoretical birth of AM (Wong and Hernandez, 2012; Ryan and Hubbard, 2016). As a result, AM is still considered to be a relatively new industry, especially in South Africa, and is still faced with the problems attached to emerging industries, including incomplete documentation and understanding of associated occupational hazards and risks (Campbell and De Beer, 2005; Wohlers and Caffrey, 2015). The potentially hazardous raw materials and byproducts involved with AM are of particular concern (Wohlers and Caffrey, 2015).

The operating technology and the resultant activities involved in the printing phases, as well as the identity and physical form of the feedstock influence the potential health effects associated with each of the different AM process categories. This is because these variables have an influence on important occupational hygiene-related factors. The operating technology and printing phase can affect the potential sources and opportunities for exposure (Wohlers and Caffrey, 2015), the physical state of material can affect potential routes of exposure (Afshar-Mohajer *et al.*, 2015; Ryan and Hubbard, 2016), and the type of material can affect the likelihood of toxicity following exposure (Lehman-Mckeeman, 2013).

PBF and DED are two examples of AM process categories which rely on different operating technologies but which are both used to create products from metal powders. PBF melts and fuses specific areas of a powder bed together using thermal energy and DED uses concentrated thermal energy to melt and fuse powdered materials together as they are being deposited (Wohlers and Caffrey, 2015).

AM can be divided into three phases: pre-processing, processing, and post-processing. Pre-processing prepares the system for performing the print job. The AM machine operator will perform activities such as cleaning the machine, preparing the CAD, importing the design into the machine, and loading the machine with raw material as well as any required support or binding material (Udroiu and Nedelcu, 2011; Wohlers and Caffrey, 2015). Processing involves workers operating the AM machines as the part is being printed. During post-processing, the operator may need to remove the part from the machine, separate the part from unused material, carry out a number of different finishing processes, such as infiltration and sanding, as well as clean the machine. Each of these phases present different opportunities for exposure to the AM machine operator (Udroiu and Nedelcu, 2011; Beese and Carroll, 2015; Wohlers and Caffrey, 2015).

2.2.3 Exposure routes

In occupational hygiene, there are three main routes of exposure: inhalation, dermal, and ingestion. Inhalation was traditionally considered to be the most important (Schneider *et al.*, 2000) but the mid-1960's discovery that the skin is not a perfect barrier prompted investigations into the dermal route of exposure (Sartorelli, 2002). Subsequently, research has found that in some cases, the contribution of dermal exposure to the total body burden may be greater than that of inhalation exposure, either due to the nature of the hazardous chemical substance (HCS) or as a result of the greater control measures in place to protect workers against inhalation exposure (Wheeler and Stancliffe, 1998; Sartorelli, 2002). Despite such discoveries, large sections of South African occupational health and safety legislation, such as the occupational exposure limits (OELs) for HCSs, still only apply to inhalation exposure (Department of Labour, 1995). OELs are

values describing acceptable risk levels rather than absolute safety limits and are used to control occupational exposure to HCSs (Perkins, 2008). Some HCSs are assigned a skin notation, indicating that they may be absorbed through the skin, but no numerical value has been determined (Department of Labour, 1995). Even less research has been done on ingestion exposure, possibly because ingestion has generally been considered to be either intentional or the result of extreme negligence. Additional reasons are the low bioavailability of most substances following ingestion and the assumption that the amount of material ingested is significantly smaller than that which is inhaled or absorbed through the skin (Cherrie *et al.*, 2006).

Processes such as PBF and DED, during which powder feedstock is used, introduce the risk of occupational exposure to these powders via inhalation, dermal contact, and/or ingestion (Afshar-Mohajer *et al.*, 2015; Wohlers and Caffrey, 2015). The importance of inhalation as an exposure route for a particular substance depends on a number of factors, including particle size, chemical properties, absorption versus deposition within the respiratory tract, and ventilation rate (Perkins, 2008). Particles of metal powders are generally small enough to become airborne, although the exact size of the particles will determine the length of time they remain suspended in the air as well as the location of deposition in the respiratory tract.

The contribution of dermal exposure to total body burden depends on factors such as the physical and chemical properties of the substance and the condition of the skin (Perkins, 2008). There are three main methods of dermal exposure: immersion (also known as direct contact), deposition, and surface contact. This means that potential causes of dermal exposure to metal powders in AM could result from direct handling of the metal feedstock and end products, deposition of airborne particulate matter onto exposed skin, and contact with surfaces contaminated with the powder (Schneider *et al.*, 2000). While titanium can accumulate and become trapped in hair follicles or skin folds in the stratum corneum, it cannot permeate through the skin (Mavon *et al.*, 2007). Certain metal components of maraging steel and stainless steel, including nickel and chromium, can permeate through the skin (Mäkinen and Linnainmaa, 2003; Tokar *et al.*, 2013) (as will be discussed in sections 4 and 5).

Ingestion may follow clearance of the powder particles deposited in the respiratory tract, contamination of food and drink, and transfer of the metal powders from objects or hands to the mouth (Cherrie *et al.*, 2006).

In addition to the possibility of direct exposure following the emission of a contaminant from the source, these emissions may result in contamination of surfaces in the workplace if airborne particles settle onto the surfaces and if the powders are transferred to the surfaces from the workers' skin or clothing. Such contamination may create secondary sources of exposure which

need to be considered when performing an occupational hygiene assessment (Schneider *et al.*, 1999).

2.3 Surface contamination

Contaminated surfaces can act as reservoirs and become secondary exposure sources (Schneider *et al.*, 1999). In the conceptual model for assessment of dermal exposure developed by Schneider *et al.* in 1999, these surfaces form a compartment known as the “surface contaminant layer”. As depicted in Figure 1, a simplification of this conceptual model, several transport processes contribute to the surface contaminant layer, these include direct emission from the source, deposition from the air, skin-to-surface and clothing-to-surface removal, as well as surface-to-surface redistribution.

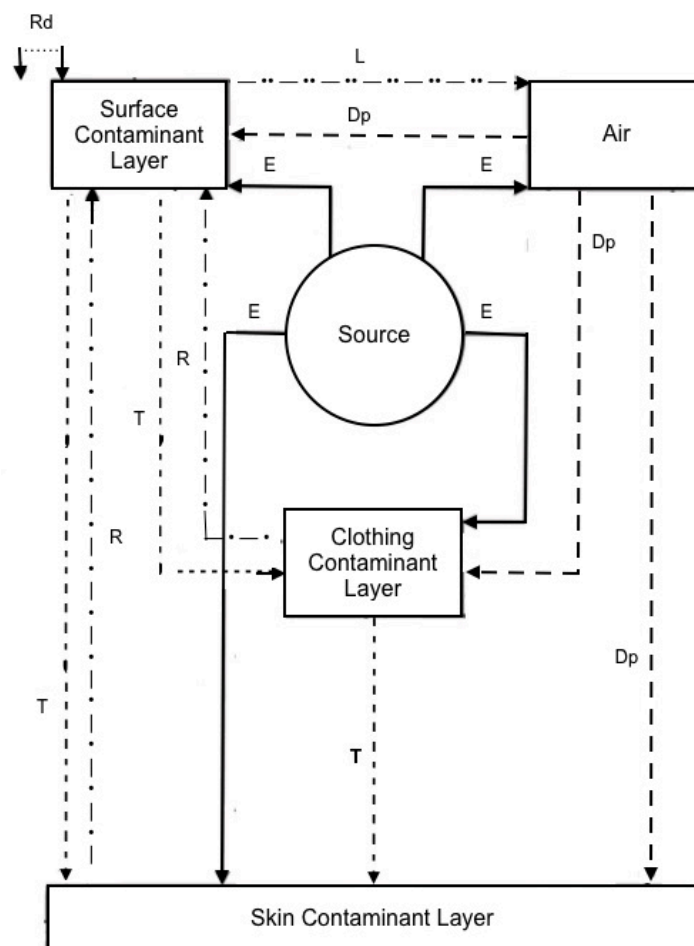


Fig. 1. The conceptual model, adapted from Schneider *et al.* (2000), depicting the transport processes that contribute to surface contamination as well as mechanisms by which this surface contamination can lead to exposure. E=emission (——), Dp=deposition (— — —), L=resuspension (— · —), T=transfer (- - -), R=removal (— · —), Rd=redistribution (.....).

Contaminated surfaces act as sources of exposure in different ways. Firstly, and arguably most significantly, direct contact with a contaminated surface can lead to dermal exposure. Secondly, handling food and drink after touching a contaminated surface, or after the food and drink have come into contact with a contaminated surface, can lead to ingestion of the contaminant. Thirdly, the disturbance of settled contaminant particulates can cause them to become airborne, from where they pose a risk to health via inhalation exposure, and also dermal exposure through deposition on the skin. Transfer of contaminants from contaminated surfaces to non-contaminated surfaces compounds the problem by increasing the number of surfaces acting as potential secondary sources of exposure and potentially creating hidden sources of exposure (Boeniger, 2006; Badenhorst, 2007).

There is also the possibility of the inner surfaces of personal protection equipment (PPE) and personal protection clothing becoming contaminated. Use of contaminated gloves, respirators, overalls, and hard-hats, among other PPE and personal protection clothing, can increase the risk of exposure. This contamination may be overlooked during cleaning and factors such as occlusion and sweating can facilitate greater dermal absorption (Rawson *et al.*, 2005).

Activities that occur during AM with metal powders, and which may contribute to surface contamination and therefore overall exposure, can be divided into pre-processing, processing, and post-processing activities, which will be discussed further (Udroiu and Nedelcu, 2011).

2.3.1 Pre-processing activities

The operator designs the parts using CAD. This is a computer-based pre-processing activity that does not generate surface contamination but exposure to contaminated surfaces may still be involved in this task, especially if it is performed in the printing room. After the part has been designed, the AM machine operator needs to load the raw material, support material, and/or binding fluids into the feed systems and powder bed. These activities represent some of the major opportunities for surface contamination during pre-processing. The surfaces onto which the operator deliberately adds the AM materials, such as the material containers, sieves, mixers, and powder beds, are directly contaminated, as are surfaces onto which the feedstock is accidentally spilled. Indirect surface contamination may result from deposition of airborne particulates onto surfaces and by contact transfer from contaminated hands and tools to other surfaces not previously contaminated (Schneider *et al.*, 1999; Udroiu and Nedelcu, 2011; Wohlers and Caffrey, 2015).

2.3.2 Processing activities

The actual processing phase is less likely to cause surface contamination because the printing is done within a closed machine. However, exposure to contaminated surfaces may still occur during operation of the machine as the workers come into contact with surfaces (such as door handles and machine panels) that could have been contaminated during other phases (Udroiu and Nedelcu, 2011; Wohlers and Caffrey, 2015).

2.3.3 Post-processing activities

Once the part is printed, the AM machine operator needs to remove it manually from the surrounding support material, which is often thick enough to cover and obscure the part. Removal from the baseplate, therefore, involves the use of vacuums, brushes, and/or compressed air, and can result in relatively large quantities of powder becoming airborne or depositing directly onto surfaces (Udroiu and Nedelcu, 2011; Beese and Carroll, 2015; Wohlers and Caffrey, 2015). Post-processing often involves the operator applying finishes to the part. Infiltration is a more complex finishing method aimed at reducing porosity of the final part. It involves incorporation of additional feedstock into the printed part (Wohlers and Caffrey, 2015) and thus may lead to direct and indirect surface contamination. In this situation, indirect contamination may occur as a result of touch transfer (contaminated hands and tools to non-contaminated surfaces) and/or airborne particles settling onto the surfaces (Petrovic *et al.*, 2011; Udroiu and Nedelcu, 2011; Afshar-Mohajer *et al.*, 2015). Simpler methods, designed to make slight geometric alterations or to improve the surface finish of the part, include sanding and polishing. These finishing processes primarily contribute to surface contamination indirectly as airborne particulates settle out of the air onto surfaces, and/or through touch transfer (Petrovic *et al.*, 2011; Udroiu and Nedelcu, 2011; Afshar-Mohajer *et al.*, 2015; Bours *et al.*, 2017).

The possibility of occupational exposure is not the only factor to consider. The route of exposure and the potential toxic effects following exposure are important for understanding the nature and degree of hazard existing in the workplace. The physical state of the material can affect potential routes of exposure and the potential toxic effects are dependent on the chemical nature or identity of the feedstock involved in the processes (Lehman-Mckeeman, 2013; Afshar-Mohajer *et al.*, 2015; Ryan and Hubbard, 2016). In AM, maraging steel, stainless steel, and Ti-6Al-4V are commonly used materials and so the toxic potentials of these metal powders are of interest.

2.4 Maraging steel

Maraging steel, MS1, is an iron-nickel alloy also known as 18Ni-300 steel (EOS, 2011; Kempen *et al.*, 2011). In addition to iron and nickel, the major metal components of maraging steel are cobalt, molybdenum, titanium, and aluminium (Kempen *et al.*, 2011). Maraging steel combines high strength and high toughness with good ductility, weldability, and machinability. In addition to these characteristics, maraging steel displays minimal dimensional changes following heat treatment and parts made from this metal are resistant to crack propagation (Würzinger *et al.*, 2004; Kempen *et al.*, 2011).

2.4.1 Uses

The mechanical characteristic profile of maraging steel makes it a highly desirable material for application in two main areas: the aircraft and aerospace sectors, and in tooling applications. Maraging steel is used as a raw material in AM in order to produce parts used in these areas of application (Kempen *et al.*, 2011; Wohlers and Caffrey, 2015).

2.4.2 Adverse health effects

Maraging steel powder may be inhaled, come into contact with the skin, or be ingested. Such exposure can cause mechanical irritation to mucous membranes and the respiratory tract (Afshar-Mohajer *et al.*, 2015), and adverse health effects associated with the individual alloying elements (Santos *et al.*, 2006; Gu *et al.*, 2012). The chemical nature of powdered alloys accounts for the importance of considering the adverse health effects caused by the individual alloying elements. Powdered alloys can be formed in two ways: by mixing the powdered alloying elements in the desired ratios or by powdering a pre-alloyed metal so that each particle contains one or more element, but not necessarily all of the elements of which the alloy is composed. Irrespective of the form of the metal powder (pre-alloyed or powder mixture), the workers are potentially exposed to the individual elements contained within the powdered alloy. Furthermore, these elements may influence which exposure routes are of toxicological concern (Santos *et al.*, 2006; Gu *et al.*, 2012).

2.4.2.1 Iron

One of the primary metals in stainless steel is iron, a physiologically essential metal that can be absorbed following ingestion. Ingestion of more than 0.5 g of iron will result in gastrointestinal symptoms, such as vomiting, but the damage may also extend to the liver. A general increase in the amount of iron in the body, regardless of exposure route, may contribute to the development of cardiovascular disease and may lead to oxidative stress through the Fenton reaction. Iron oxide dust is a threat to health via inhalation exposure, causing fibrotic and/or non-fibrotic damage

to the lungs (Tokar *et al.*, 2013). Iron nanoparticles (smaller than 10 nm) may permeate through the skin via the stratum corneum and the openings from which hair follicles grow (Baroli *et al.*, 2007).

2.4.2.2 Nickel

Nickel is the most common metal sensitiser (Lidén *et al.*, 2008). The most toxicologically significant exposure route for nickel is inhalation but dermal exposure is also important to consider. Dermal exposure to nickel causes allergic contact dermatitis and can elicit a hypersensitivity reaction through such minor contact as occurs with jewellery and zippers (Lidén *et al.*, 2008; Tokar *et al.*, 2013). The prevalence of nickel hypersensitivity is 10-20% (Tokar *et al.*, 2013). It has been suggested that concurrent exposure to both chromium and nickel can result in a synergistic hypersensitivity reaction (Day *et al.*, 2009). Inhalation of nickel can also cause cancer in the respiratory tract and in the nose (IARC, 2012; Tokar *et al.*, 2013). Nickel can be absorbed following ingestion. Once inside the body it may act as a carcinogen and teratogen, and in cases of chronic exposure, nickel can cause cardiovascular and respiratory system dysfunction (Denkhaus and Salnikow, 2001; Tokar *et al.*, 2013).

2.4.2.3 Cobalt

In addition to causing mechanical irritation to the respiratory tract, cobalt can be absorbed following inhalation exposure (Scansetti *et al.*, 1998; Tokar *et al.*, 2013). Cobalt can also be absorbed following dermal contact and ingestion (Linnainmaa and Kiilunen, 1997; Tokar *et al.*, 2013). Exposure to cobalt has been associated with increased erythrocytosis, skin sensitisation (allergic contact dermatitis), and, at high doses, cardiomyopathy (Jefferson *et al.*, 2002; Lidén *et al.*, 2006; Tokar *et al.*, 2013).

2.4.2.4 Molybdenum

In humans, 28-77% of ingested molybdenum is absorbed and distributed by the blood to various tissues, concentrating in the kidneys, liver, and bones. Ingestion of molybdenum can lead to impaired intestinal absorption of copper and sulphate. Following inhalation, molybdenum may lead to the development of pneumoconiosis (Tokar *et al.*, 2013). Dermal contact with molybdenum may cause contact hypersensitivity reactions (Thomas *et al.*, 2006). However, molybdenum is ultimately considered to be only mildly toxic (Tokar *et al.*, 2013).

The negative health effects associated with titanium and aluminium will be discussed in sections 2.6.2.1 and 2.6.2.2, respectively.

2.5 Stainless steel

Stainless steel is an iron-based alloy composed of several different elements. In addition to iron, stainless steel contains metals such as chromium, cobalt, manganese, molybdenum, and nickel. Each element is incorporated to add a specific quality to the steel. For example, chromium is added to provide resistance to corrosion, a characteristic that is enhanced by small amounts of molybdenum and nickel. Nickel also provides a smooth, polished surface and molybdenum increases rigidity. Carbon, one of the non-metallic elements added to stainless steel in small amounts, contributes to the strength of the alloy. Stainless steel is characterised by high specific strength, high resistance to corrosion, and a good degree of weldability (Baddoo, 2008; Lo *et al.*, 2009; Lever *et al.* 2010). As previously stated, the corrosion resistance of stainless steel is primarily attributed to chromium. Chromium is highly reactive and an inert layer of chromium oxide will readily form on the surface of stainless steel on contact with oxygen. This protects against the formation of rust (Tolosa *et al.*, 2010).

2.5.1 Uses

Stainless steel is very strong and resistant to corrosion making it an ideal and popular material for use in aerospace and biomedicine (Dewidar *et al.*, 2006; Baddoo, 2008; Lo *et al.*, 2009; Shaulov *et al.*, 2009). Biomedical applications of stainless steel include total hip arthroplasty, orthodontic brackets, and coronary stents (Dewidar *et al.*, 2006; Lo *et al.*, 2009; Shaulov *et al.*, 2009; Ortiz *et al.*, 2011). Stainless steel is also used in kitchenware, furniture, and construction, and as a raw material in AM (Dewidar *et al.*, 2006; Lo *et al.*, 2009). The extensive range of applications of this metal led Lo *et al.* (2009) to describe stainless steel as omnipresent in everyday life.

2.5.2 Adverse health effects

Stainless steel powders may be inhaled, come into contact with the skin, or be ingested. Like maraging steel, stainless steel powders may act as nuisance dusts causing irritation of mucous membranes and the respiratory tract (Afshar-Mohajer *et al.*, 2015). While stainless steel is not considered to be of particular threat to health, many of its component metals are associated with

certain toxicities. As stated previously, exposure to a powdered alloy may involve exposure to each of the individual elements of that alloy (Santos *et al.*, 2006; Gu *et al.*, 2012).

2.5.2.1 Chromium

The second most abundant metal in stainless steel (after iron) is chromium. The extent of chromium toxicity depends on its chemical form and the exposure route (Mäkinen and Linnainmaa, 2003; Day *et al.*, 2009; Tokar *et al.*, 2013). Stainless steel alloys are made with chromium metal, which has an oxidation number of zero. Oxidation, as occurs during the formation of the protective oxide layer, results in the formation of trivalent chromium, and heating processes such as melting chromium-containing alloys can cause further oxidation and the formation of hexavalent chromium (Mäkinen and Linnainmaa, 2003; OSHA, 2008). Hexavalent chromium is arguably the most harmful form. It is corrosive, able to cause local dermal and respiratory damage, it is carcinogenic (Group 1), and elicits allergic contact dermatitis (type IV allergic reaction) in those who have been sensitised to this metal; the prevalence of this allergy is less than 1% (Mäkinen and Linnainmaa, 2003; Day *et al.*, 2009; Tokar *et al.*, 2013). Hexavalent chromium is easily absorbed through the skin and lungs while other forms of the metal, such as trivalent chromium, are poorly absorbed (although still able to produce an allergic reaction in high enough concentrations) (Mäkinen and Linnainmaa, 2003; Tokar *et al.*, 2013). Erythema, pruritus, and oedema are among the physical manifestations of allergic contact dermatitis. Ingestion of large quantities of hexavalent chromium may cause acute renal failure (Tokar *et al.*, 2013).

2.5.2.2 Manganese

Approximately one to five percent of ingested manganese is absorbed (Tokar *et al.*, 2013). Dermal absorption of manganese is not considered to be significant thus dermal contact is not an important route of exposure (ATSDR, 2012). Inhalation of manganese particulates can result in localised inflammatory response and may cause irritation or damage to the lung tissue. Coughing, bronchitis, and pneumonitis are examples of the symptoms that arise from such irritation or damage. Once absorbed, manganese also affects cardiovascular function, resulting in conditions such as altered cardiac rhythm and hypotension, as well as neurological dysfunction (Tokar *et al.*, 2013). In the brain, manganese interferes with the release of dopamine from dopaminergic neurons giving rise to neurobehavioral changes and Parkinson's disease-like symptoms (Afridi *et al.*, 2009; Tokar *et al.*, 2013). Such neurotoxicity is the result of chronic exposure to manganese and is known as manganism. Manganism progresses with continued exposure and the initial symptoms which include headache, insomnia, and muscle cramps evolve into hypokinesia (reduced muscle movement), rigidity, tremors in the hand, and a 'cock-walk' gait. Manganism can result in increased levels of iron in the body causing oxidative stress (Fenton reaction), which

may contribute to the neuronal damage associated with manganism, and which may be augmented by simultaneous exposure to iron (Tokar *et al.*, 2013).

The negative health effects associated with iron, nickel, cobalt, and molybdenum can be found in sections 2.4.2.1, 2.4.2.2, 2.4.2.3, and 2.4.2.4, respectively.

2.6 Titanium-6aluminium-4vanadium

In metallic form, titanium possesses a specific set of physical and chemical properties, most notable of which are high specific strength, low density, and high resistance to corrosion, that make it greatly desirable for use in a number of fields ranging from aerospace and powder generation to biomedical implants (Kostov and Friedrich, 2006; Wen *et al.*, 2013). The resistance to corrosion is attributable to titanium's specific electron configuration which causes the metal to be highly reactive in the presence of oxygen. The high level of reactivity results in the ready formation of an inert layer of titanium dioxide on the surface of the metal (Prasad *et al.*, 2015). Pure titanium exhibits allotropism and can exist in two different elemental forms depending on temperature. At temperatures below 882 °C, titanium exists as a hexagonal, close-packed crystal known as the alpha (α) phase while at temperatures above 882 °C, it exists as a body centred cubic crystal known as the beta (β) phase (Hornby, 2005; Prasad *et al.*, 2015). Alloying titanium provides stability for the metal and enhances certain characteristics. Alpha stabilisers, such as aluminium, oxygen, and carbon, increase resistance to corrosion but may also reduce the strength of the titanium, whereas β stabilisers, such as molybdenum, vanadium, and nickel, increase strength. By creating a stable $\alpha+\beta$ alloy, such as Ti-6Al-4V, it is possible to provide both increased strength and increased corrosion resistance to the metal (Bhola *et al.*, 2011; Prasad *et al.*, 2015). Titanium alloys also possess varying degrees of weldability depending on the type of alloying elements (Kostov and Friedrich, 2006).

2.6.1 Uses

Literature highlights the importance of titanium alloys as materials in the aerospace, automobile, and biomedical sectors (Kostov and Friedrich, 2006; Cui *et al.*, 2010; Beese and Carroll, 2015). Their suitability in these industries lies in the physical and chemical properties of the metals. Titanium possesses a high degree of corrosion resistance to a wide pH range, providing biocompatibility and protection against weathering (Prasad *et al.*, 2015). Titanium possesses high specific strength and is durable and long-lasting; important characteristics when the metallic parts are to be subjected to harsh conditions and are not easily replaced (Prasad *et al.*, 2015). As stated previously, corrosion resistance and strength can be enhanced in alloys such as Ti-6Al-4V (Bhola *et al.*, 2011; Prasad *et al.*, 2015). In addition to these characteristics, titanium is

known for its low density (Wen *et al.*, 2013) and resistance to the effects of magnetic fields (Luo *et al.*, 2011). In biomedicine, titanium and Ti-6Al-4V are used in hard tissue replacements such as artificial hip joints and subperiosteal dental implants, in plates and screws used in reconstructive surgery, and in cardiovascular medicine as pacemaker casings and occlusion coils (Lui *et al.*, 2004; Fage *et al.*, 2016). Titanium and Ti-6Al-4V are also used in the production of certain consumer goods, including golf clubs and jewellery (Kostov and Friedrich, 2006; Cui *et al.*, 2010) and as raw materials in AM. The use of titanium and titanium alloys in AM of medical and dental implants and prostheses is gaining popularity. For example, in Egypt, Ti-6Al-4V has been used in the AM of nine different craniofacial implants and in South Africa, Ti-6Al-4V has been used in the AM of a maxilla prosthesis (Drstvensek *et al.*, 2008; Wohlers and Caffrey, 2015). The benefits of AM and powder metallurgy may help to overcome the expense involved in industrial use of titanium by reducing the cost of processing titanium and Ti-6Al-4V into parts (Cui *et al.*, 2010; Wen *et al.*, 2013).

2.6.2 Adverse health effects

Ti-6Al-4V powders may be inhaled, come into contact with the skin, or be ingested. In an occupational setting, such as in AM, titanium and Ti-6Al-4V powders may become airborne during any one of the processing phases (Schneider *et al.*, 1999). Regardless of what substance is involved, particulate matter can cause irritation of mucous membranes and the lungs leading to coughing, sneezing, and chest pains. Ti-6Al-4V powders may, therefore, act as nuisance dusts in addition to their element-specific adverse health effects, which become relevant as the alloy is used in its powdered form (Santos *et al.*, 2006; Gu *et al.*, 2012; Afshar-Mohajer *et al.*, 2015).

2.6.2.1 Titanium

There appear to be no studies on the ability of titanium metal to cause inhalation-related pathology. Examination of literature indicates that studies surrounding the adverse health effects of titanium were focused on two main areas: adverse health effects caused by exposure to titanium dioxide (Department of Labour, 1995; Nohynek *et al.* 2008; Fage *et al.*, 2016) and hypersensitivity to titanium and Ti-6Al-4V metals linked with internal exposure to medical and dental implants (Sicilia *et al.*, 2008; Vijayaraghavan *et al.*, 2012; Fage *et al.*, 2016).

2.6.2.1.1 Titanium dioxide

The adverse health effects associated with inhalation exposure to titanium dioxide have received more attention than those associated with the metallic form, reflecting, and likely resulting from,

the imbalance that exists in production of these two forms of titanium. In fact, there appear to be no studies on the ability of titanium metal to cause inhalation-related pathology. However, the degree of reactivity exhibited by titanium in the presence of oxygen (leading to the formation of titanium dioxide) (Prasad *et al.*, 2015) suggests that the toxicity associated with inhalation of titanium dioxide should not be disregarded when assessing the hazards and risks stemming from use of titanium metal and its alloys; unless the metal powders are only handled in a vacuum. Titanium dioxide is listed in Table two of the Hazardous Chemical Substances Regulations (Department of Labour, 1995). The table provides OEL-recommended limits for the listed substances, however, these OELs apply to inhalation exposure only. Skocaj *et al.* (2011) compiled a review on the toxicity of titanium dioxide as used in everyday life. The authors conclude that the health hazards associated with exposure to titanium dioxide primarily occur as a result of oxidative stress induction, which can precipitate cell damage, inflammatory responses, genotoxicity, and altered cell signalling. The adverse health effects that may develop following exposure depend on factors such as particle size and surface area, particle shape and crystal structure, particle charge, etc. (Skocaj *et al.*, 2011). Additionally, it is classified as a possible human carcinogen (Group 2B) by the International Agency for Research on Cancer (IARC), based on studies that focused on inhalation exposure (IARC, 2010).

However, titanium dioxide is found in many commercial products such as cosmetics and sunscreens, and it is commonly used as an additive in food and as a white pigment (Vijayaraghavan *et al.*, 2012; Fage *et al.*, 2016). Studies conducted by Nohynek *et al.* (2008) and Landsiedel *et al.* (2010) indicate that exposure to titanium dioxide through use of such commercial, everyday products is unlikely to pose a risk to health. This may be attributable, at least in part, to the reported inability of titanium dioxide to permeate the skin (Mavon *et al.*, 2007; Fage *et al.*, 2016). It should be noted, however, that research into the health effects associated with the use of sunscreens containing titanium dioxide nanoparticles under more realistic exposure conditions (long-term, repeated, and with concurrent ultraviolet exposure) is inadequate (Skocaj *et al.*, 2011).

2.6.2.1.2 Titanium hypersensitivity

Titanium metal (pure and alloyed) is highly biocompatible, a fact that led some researchers to believe that it was not capable of producing an allergic reaction. However, incidences of implant failure and symptoms of contact dermatitis have been reported in people who have medical and dental implants made from titanium or Ti-6Al-4V (Sicilia *et al.*, 2008; Vijayaraghavan *et al.*, 2012; Fage *et al.*, 2016). These reports have precipitated investigations into titanium hypersensitivity and have led researchers to make certain suggestions regarding titanium hypersensitivity. Firstly, they suggest that mucosal permeation by titanium is more likely than skin permeation (Sicilia *et*

al., 2008; Vijayaraghavan *et al.*, 2012; Fage *et al.*, 2016). Secondly, they suggest that titanium is a systemic sensitiser (sensitisation following internal exposure to the metal) as opposed to a dermal sensitiser (sensitisation following external dermal exposure to the metal) (Müller and Valentine-Thon, 2006). Thirdly, they suggest that the development of a titanium allergy is associated with internal exposure to the metal ions although the exact mechanism by which the ions produce sensitisation is unknown (Sicilia *et al.*, 2008; Vijayaraghavan *et al.*, 2012; Fage *et al.*, 2016). In 2016, Fage *et al.* published a review article on titanium as a potential sensitiser. Based on their search of the available literature, the authors proposed two main conclusions. The first is that people rarely become allergic to titanium, and the second conclusion is that, while the memory lymphocyte immunostimulation assay (MELISA®) and patch testing (Müller and Valentine-Thon, 2006; Sicilia *et al.*, 2008; Fage *et al.*, 2016) have been used in previous studies, there is no validated test for the detection of titanium hypersensitivity, which reduces the reliability of related prevalence studies.

Despite the inability of titanium to permeate through the skin (Mavon *et al.*, 2007; Fage *et al.*, 2016), this may still be an important occupational exposure route for titanium hypersensitivity as evidenced by three reported observations seen in literature. The first observation was that dermal contact with titanium can trigger an allergic reaction in sensitised individuals (Sicilia *et al.*, 2008). The second was that cutaneous and epicutaneous patch testing have been successfully used to determine the presence of a pre-existing titanium allergy (Sicilia *et al.*, 2008; Vijayaraghavan *et al.*, 2012). The third observation was that contact dermatitis-like symptoms (urticaria, eczema, oedema, erythema, and pruritus of the skin and mucosa, as well as localised granulomatous reactions) are associated with systemic sensitisation to this metal (Thomas *et al.*, 2006; Sicilia *et al.*, 2008; Vijayaraghavan *et al.*, 2012). In addition, titanium dioxide has been shown to accumulate in open infundibula, in which hair follicles grow, and in the outer layers of the stratum corneum (Mavon *et al.*, 2007).

2.6.2.2 Aluminium

Aluminium is poorly absorbed following inhalation and ingestion, however, it is a highly reactive metal with the potential to cause toxicity following chronic exposure (Tokar *et al.*, 2013; Stanfliet *et al.*, 2015). Inhalation of aluminium particulates can lead to fibrosis of the lungs through mechanical damage rather than absorption (Tokar *et al.*, 2013). Ingestion of aluminium can alter the gastrointestinal absorption of certain essential substances, such as calcium and phosphate, resulting in deficiencies. Such deficiencies can impair the motility of the gastrointestinal tract and cause dysfunction of the bone mineralisation-resorption process (Becaria *et al.*, 2002; Tokar *et al.*, 2013). In addition, there appears to be a connection between exposure to aluminium and the development of dementia and other neurodegenerative diseases implying that aluminium can

cross the blood-brain barrier (Becaria *et al.*, 2002; Tokar *et al.*, 2013). Metallic aluminium is reportedly not absorbed through the skin (Tokar *et al.*, 2013).

2.6.2.3 Vanadium

Following inhalation, vanadium can both cause mechanical irritation to, and be absorbed from, the respiratory tract. Bronchitis and bronchopneumonia are often associated with inhalation exposure to vanadium. Gastrointestinal absorption of vanadium is considered to be poor but exposure to greater amounts of this metal has been connected to the development of gastrointestinal symptoms, such as nausea and vomiting. Cardiac palpitations, tremors, and kidney damage are also seen in individuals following industrial exposure to vanadium. Absorption through the skin is also considered to be poor (Tokar *et al.*, 2013).

All of these metals may contaminate surfaces in the workplace resulting in the formation of reservoirs and secondary sources of exposure (Schneider *et al.*, 1999). Therefore, it is important to determine the nature and extent of this contamination during an occupational hygiene assessment, and surface sampling was developed as a means of obtaining this information.

2.7 Surface sampling

2.7.1 Purpose

Surface sampling serves two major purposes. First, it provides information about how contaminated surfaces can potentially contribute to overall exposure. Second, surface sampling serves to determine the effectiveness of housekeeping, cleaning, and controls. In addition, surface sampling can assist in identifying the boundaries of the exposure area, which can be used in the classification and demarcation of work areas (Badenhorst, 2007; ASTM, 2015).

2.7.2 Surfaces

Surface sampling can be carried out on a variety of different surfaces. The most obvious surfaces are those exposed directly to the source of the contaminant and those nearest to the source of contamination. These surfaces are not limited to the typically defined work surfaces such as table tops and machine panels, but also include tools, door handles, and PPE found or used in close proximity to the sources of contamination. Other surfaces that need to be monitored are those that may be considered to be clean but which may act as 'hidden' exposure points. These include surfaces such as those found in storage areas and administrative offices, as well as in break rooms and cafeterias where prevention of contamination is especially important due to the

increased possibility of ingestion of the contaminants in addition to dermal exposure (Badenhorst, 2007; Brouwers *et al.*, 2007).

Surface contamination is often overlooked but many surfaces can be contaminated and as a result, can contribute to exposure. It is, therefore, important to include surface sampling in an occupational hygiene monitoring survey (Wheeler and Stancliffe, 1998; Lundgren, 2006). However, because surface contamination is but one of the potential mechanisms that may lead to exposure in the workplace, surface sampling should not be used alone in assessment of the hazards and risks to health that exist in a workplace (Department of Labour, 1993; Badenhorst, 2007; ASTM, 2015).

2.7.3 Wipe sampling

Most surface sampling methods follow the same basic principle: a known area of surface is sampled to remove any contaminating materials and the sampling medium is then subjected to analysis (Badenhorst, 2007). Surface sampling methods include suction sampling, tape-stripping, and wipe sampling (Wheeler and Stancliffe, 1998; Byrne, 2000; Lundgren *et al.*, 2006; ASTM, 2015).

Wipe sampling is the most widely used method of surface sampling due to its ability to remove both solids and liquids, its use of inexpensive equipment and analysis techniques, and the simplicity of the method, which reduces the risk of errors (Wheeler and Stancliffe, 1998; Byrne, 2000). It involves drawing a suitable sampling medium over a predetermined area of the sampling surface following a predetermined pattern. This process can be done manually or with the use of semi-automatic rollers or sliders, but the manual method is preferred (Wheeler and Stancliffe, 1998). The wipes can be dry or wetted with an appropriate reagent. Wetted wipes are considered to be more effective as the mechanical forces applied to the wipe during collection of the sample are aided by chemical forces provided by the wetting reagent (Du Plessis *et al.*, 2008; ASTM, 2015).

Despite its simplicity, there are certain factors that may influence the effectiveness of the wipe sampling method; of particular importance is the selection of the sampling media. The sampling media must be appropriate for the nature, size distribution, and concentration of the contaminant of interest. To assess its appropriateness involves validation of the wipe for the contaminant, as well as consideration of the characteristics of the surfaces to be sampled—roughness, porosity, and sample area. Making use of the same number of wipes per sample and ensuring that the samples are taken by the same person, aids in eliminating certain errors or inconsistencies that might occur during sampling (Wheeler and Stancliffe, 1998; Badenhorst, 2007; ASTM, 2015).

Surface characteristics, such as sample area and surface texture, can influence the efficiency of wipe sampling. When selecting the size of the sample area, Badenhorst (2007) suggests that, while a minimum area of 5 cm² is recommended for evaluation of surface contamination, the most important factor to consider is representativeness. In other words, the ratio of area sampled to total surface area should be such that the information gained from the sample area is applicable to the total surface area. When sampling textured (rough and porous) surfaces, the presence of hollows or pits should be considered as this provides spaces in which contaminants may collect, potentially decreasing the fraction of contaminant that can be removed from the surface during wipe sampling (Badenhorst, 2007). Furthermore, the roughness of a surface can affect the integrity of the wipe itself, and should be considered when selecting the wipe to be used (Boeniger, 2006).

There are many different brands of wipes, each with advantages and limitations which should be considered when selecting the wipe medium to be used in a study. Whatman 540 ashless paper has been used to sample for soluble platinum (Badenhorst, 2007). Wash 'n Dri® wipes, Palintest, and Ghostwipes™ have been used to sample for lead; a study comparing the three wipes found Ghostwipes™ to be the most suitable (Boeniger, 2006). Nickel has been successfully sampled using Ghostwipes™ (Du Plessis *et al.*, 2010) and Jeyes 'Sticky Fingers' wet ones (Hughson *et al.*, 2010). Wash 'n Dri® wipes have also been used to sample for cobalt, chromium, and nickel (Day *et al.*, 2009). OSHA released a document in 2002 which contained a list of metals and metalloids for which Ghostwipes™ have been validated. The list contains antimony, beryllium, cadmium, chromium, cobalt, copper, iron, nickel, manganese, molybdenum, lead, vanadium, and zinc. With the exceptions of antimony and molybdenum, all the listed metals and metalloids were found to have removal efficiencies greater than 80%, and barring antimony, all were found to have recovery efficiencies greater than 90% (OSHA, 2002). This information indicates that Ghostwipes™ are potentially suitable for use in titanium and aluminium surface sampling.

In summary, the use of powdered maraging steel, stainless steel, and Ti-6Al-4V metals in AM may lead to surface contamination. Contaminated surfaces can act as secondary exposure sources and potentially lead to inhalation, dermal, and/or ingestion exposure. Evaluating contaminated surfaces is necessary to determine their possible contribution to overall exposure in the workplace, and to provide insight into the effectiveness of cleaning and control procedures. Exposure to powdered maraging steel, stainless steel, and Ti-6Al-4V may be associated with certain adverse health effects depending on the route of exposure, the physical form of the metal, and the chemical composition of the alloys. A reliable evaluation of surface contamination can be obtained through the use of validated surface sampling techniques and sampling media.

2.8 References

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Chapter 3: Article on surface contamination by maraging steel and stainless steel powders

Guidelines for authors

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- Annals of Work Exposures and Health publishes original research and development material that helps reduce risk of ill-health resulting from work, and welcomes submissions in these areas.
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- *Brevity.* The necessary length of a paper depends on the subject, but any submission must be as brief as possible consistent with clarity.
- *Title, abstract and keywords.* Titles should be constructed to succinctly describe the major issue or question examined by the paper and should not assert the research findings as a truth. Recognisable, searchable terms and keywords must be included to enable readers to more effectively find your paper. To optimise the visibility of your paper we advise you to make a list of the 10 most likely search terms that your intended readers will use to find your work, and to ensure that these appear in your title, the abstract and the keywords. The 'number one' search term from your list should appear somewhere in the paper's title. The 'top 5' search terms (including 'number one') should each appear at least once in the abstract, with the 'top 3' appearing more than once if possible. It is important that your abstract is written in a naturalistic and engaging style that will encourage readers to follow up by reading the full paper. The 'bottom 5' search terms can then be added as keywords.
- *Authorship.* Persons should only be named as authors if they have made substantial contributions to the conception or design of the work, or the acquisition, analysis or interpretation of data for the work AND have assisted with the drafting or revising of the paper for important intellectual content AND have final approval of the version to be published AND can take responsibility for the accuracy of the work.
- *Structure of paper.* Papers should generally conform to the pattern: Introduction, Methods, Results, Discussion, and Conclusions, unless these are clearly inappropriate. A paper must be prefaced by an abstract of the argument and findings, which may also be arranged under the same headings.
- *Units and symbols.* SI units must be used, though their equivalent in other systems may be given as well.
- *Figures.* The first submission should include good quality low resolution copies of Figures, and may be incorporated into the text or at the end of the manuscript.

- *Tables.* Tables should be numbered consecutively and given a suitable caption. As with Figures, it is helpful to incorporate them into the text of the first submission. Footnotes to tables should be provided below the table and should be referred to by superscript lowercase letters.
- *References.* References should only be included which are essential to the development of an argument or hypothesis, or which describe methods for which the original account is too long to be reproduced. References in the text should be in the form Jones (1995), or Jones and Brown (1995), or Jones et al. (1995) if there are more than two authors, and they should be incorporated naturally into the text. For example:

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

At the end of the paper, references should be listed in alphabetical order by name of first author, using the Vancouver Style of abbreviation and punctuation. ISBNs should be given for books and other publications where appropriate. Material unobtainable by readers should not be cited. Internet material can be referred to if it is likely to be permanently available; the date on which it was last accessed should be given. References will not be checked editorially, and their accuracy is the responsibility of authors. Examples:

- Simpson AT, Groves JA, Unwin J, Piney M. (2000) Mineral oil metal working fluids (MWFs)—Development of practical criteria for mist sampling. *Ann Occup Hyg*; 44: 165–72.
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Evaluation of surface contamination from maraging steel and stainless steel powders at two additive manufacturing facilities

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Surface sampling; occupational exposure; Ghostwipes™; metal powder; 3D printing.

Abstract

Background: Use of maraging steel (MS) and stainless steel (SS) powders in additive manufacturing (AM) introduces the possibility that metal powders, including three well known sensitising metals (nickel, chromium, and cobalt), may contaminate workplace surfaces. Contaminated surfaces may act as potential secondary sources of worker exposure, and subsequently may lead to adverse health effects such as sensitisation to metals or even cancer.

Objectives: To determine surface contamination from MS and SS powders during different processes at two AM facilities, using wipe sampling methodology.

Methods: Surface sampling, using Ghostwipes™, was conducted at two AM facilities during the use of MS and SS powders in printing and non-printing rooms. Where possible, samples were collected before and after pre-processing, processing, and post-processing activities. All samples were analysed using inductively coupled argon plasma atomic emission spectroscopy.

Results: Detectable levels of aluminium (below detection limit [BDL]-42.422 µg/cm²), cobalt (BDL-66.741 µg/cm²), chromium (BDL-132.727 µg/cm²), iron (BDL-1072.28 µg/cm²), and nickel (BDL-77.539 µg/cm²) metal powders were found to be present in the printing rooms and non-printing rooms at both facilities. For several surfaces at both facilities, samples collected prior to printing phases were found to contain higher concentrations of metal powders (overall metal contamination) than the samples collected after. Only the MS powder container was significantly more contaminated after the printing process compared to before. At both facilities, the concentrations of metals on printing room surfaces were significantly higher ($p \leq 0.05$) than those on surfaces in the non-printing areas, however, contamination of non-printing surfaces occurred.

Conclusions: Both powder bed fusion (PBF) with MS and directed energy deposition (DED) with SS resulted in quantifiable contamination of both printing and non-printing surfaces at AM facilities. This contamination and the presence of pre-existing contamination indicates that controls and cleaning procedures should be re-evaluated. These contaminated surfaces have the ability to increase the risk of occupational exposure to the metal powders through various exposure routes. Moreover, MS and SS contain metals that have the potential to cause adverse health effects such as allergic contact dermatitis and cancer.

Key words: Surface sampling; occupational exposure; Ghostwipes™; metal powder; 3D printing.

Introduction

Additive manufacturing (AM) uses computer-aided design (CAD) data to build three dimensional objects through successive layering of raw materials. This technology is becoming increasingly more popular, especially in the fields of aerospace and biomedicine (Wohlers and Caffrey, 2015; Ryan and Hubbard, 2016). Powdered metals are commonly used in the AM process categories of powder bed fusion (PBF), whereby powder layers are fused together in the powder bed using thermal energy; and directed energy deposition (DED), whereby powdered material is melted and fused together by thermal energy as the material is deposited (Wohlers and Caffrey, 2015).

Activities such as those occurring during PBF and DED may lead to the release of powdered metals into the workplace environment, contributing to potential worker exposure (Afshar-Mohajer *et al.*, 2015; Wohlers and Caffrey, 2015). In addition to primary sources of exposure, workplace surfaces, including the floor, may become contaminated and act as potential secondary exposure sources (Schneider *et al.*, 1999; Day *et al.*, 2007). These secondary sources can lead to additional worker exposure via inhalation (resuspension of settled particulates), dermal contact (touching contaminated surfaces), and ingestion (handling food and drink after touching contaminated surfaces, or storing or handling food and drink in areas where they may become directly contaminated) (Schneider *et al.*, 1999; Boeniger, 2006; Badenhorst, 2007).

AM can be divided into three printing phases: (1) pre-processing, which prepares the system for the print job, (2) processing, which involves operating the machines during printing, and (3) post-processing, which includes manually removing the part from the machine and separating it from unused feedstock. Activities during each phase could lead to possible surface contamination and subsequent worker exposure (Udroiu and Nedelcu, 2011; Beese and Carroll, 2015; Wohlers and Caffrey, 2015). In addition to contamination of surfaces directly involved in contamination-generating processes, poor containment protocols may result in contamination of surfaces in general areas, such as administrative offices, cafeterias, and change rooms. Such surfaces may be considered 'hidden' exposure points as workers may be unaware of the contamination (Badenhorst, 2007). Inner surfaces of personal protection equipment (PPE) and personal protection clothing may also become contaminated and continued use of this PPE and clothing can increase the risk of exposure (Rawson *et al.*, 2005).

The specific type of metal powder used in AM determines which exposure routes are of toxicological concern and what adverse health effects are associated with exposure (Lehman-Mckeeman, 2013). However, all powders may act as nuisance dusts, causing irritation of mucous membranes and the respiratory tract (Afshar-Mohajer *et al.*, 2015). As this article focuses on maraging steel (MS) and stainless steel (SS), these two metal alloys will be discussed briefly.

Maraging steel is an iron-nickel alloy. In addition to iron and nickel, the major component metals of MS include cobalt, molybdenum, titanium, and aluminium (EOS, 2011; Kempen *et al.*, 2011). Stainless steel, an iron-based alloy, commonly contains chromium, nickel, manganese, and molybdenum (Baddoo, 2008; Tolosa *et al.*, 2010). It typically exhibits biocompatibility due to the formation of an inert external layer of chromium oxide which prevents exposure to the other, potentially more toxic elements underneath and reduces leaching of metal ions (Baddoo, 2008; Lo *et al.*, 2009; Tolosa *et al.*, 2010; Prasad *et al.*, 2015). Powdered metal alloys, as used in AM, are formed by either powdering the individual metals and mixing them together, or by powdering the already alloyed metal. Powdering the already alloyed metal leads to the formation of particles that contain one or more, but not necessarily all, of the alloying elements. Regardless of which method is used, the result is that the workers may be exposed to the individual metals as well as different combinations of the metals (Santos *et al.*, 2006; Gu *et al.*, 2012). Thus, the potential exposure routes and toxicity associated with each of the component materials must be taken into consideration.

Aluminium is unable to permeate through the skin (Tokar *et al.*, 2013) and is poorly absorbed following inhalation and ingestion. Despite this, long term exposure may result in toxic responses such as impaired bone mineralisation and resorption, lung fibrosis, and possibly neurodegenerative diseases (Becaria *et al.*, 2002; Tokar *et al.*, 2013). Cobalt can be absorbed following inhalation, ingestion, and dermal contact exposure (Linnainmaa and Kiilunen, 1997; Scansetti *et al.*, 1998; Tokar *et al.*, 2013). Such exposure has been associated with increased erythrocytosis, allergic contact dermatitis, and cardiomyopathy with high doses (Jefferson *et al.*, 2002; Lidén *et al.*, 2006; Tokar *et al.*, 2013; Klasson *et al.*, 2017). Chromium metal (zero oxidation number) is readily oxidised to form trivalent chromium, which is poorly absorbed through the skin and respiratory tract. However, high concentrations can elicit an allergic reaction (Mäkinen and Linnainmaa, 2003; OSHA, 2008; Tokar *et al.*, 2013). Heat can induce further oxidation into hexavalent chromium (OSHA, 2008), which is readily absorbed following dermal contact and inhalation. Furthermore, hexavalent chromium acts as a carcinogen (Group 1) (IARC, 2012) and a sensitiser, and is also corrosive (Mäkinen and Linnainmaa, 2003; Day *et al.*, 2009; Tokar *et al.*, 2013). Iron absorbed from the gastrointestinal tract may cause nausea and vomiting, and increasing the body's overall iron levels may contribute to the development of cardiovascular disease (Tokar *et al.*, 2013). Iron particles smaller than 10 nm may permeate through the skin (Baroli *et al.*, 2007). Iron is relatively reactive and inhalation of iron oxide dust can cause fibrotic or non-fibrotic damage to the lungs (Tokar *et al.*, 2013). Nickel is carcinogenic when inhaled (Group 1) (IARC, 2012) and is the most common metal sensitiser following inhalation and dermal absorption (allergic contact dermatitis). Nickel elicits Type IV delayed hypersensitivity (ATSDR, 2005) and its potency is evidenced by the results of a study by Garg *et al.* (2013), which investigated the prevalence of nickel allergy in four European countries. The study found that

12.3-25.0% of the population tested positive for nickel allergy. Nickel can also be absorbed following ingestion. Once inside the body it may cause cardiovascular and respiratory system dysfunction (Denkhaus and Salnikow, 2001; Tokar *et al.*, 2013).

The importance of surface contamination as a secondary exposure source and the effectiveness of existing housekeeping programmes and controls can be evaluated using surface sampling (Schneider *et al.*, 1999; Boeniger, 2006; Badenhorst, 2007). Different types of wipes are available and should be selected according to the situation (Wheeler and Stancliffe, 1998; Byrne, 2000; OSHA, 2002). Additionally, the selected method and sampling media should be validated for the substances of interest. Wipe sampling with Ghostwipes™ has been validated for 13 metals, including chromium, cobalt, iron, manganese, molybdenum, nickel, and vanadium (OSHA, 2002).

The objective of this study was to determine surface contamination caused by use of MS and SS powders during different processes at two AM facilities, using the wipe sampling methodology.

Methods

The study involved surface sampling at two South African AM facilities. At one facility MS was used during PBF and at the other facility SS was used during DED. The selected sampling method was surface wipe sampling using Ghostwipes™ (SKC, Pennsylvania, USA). These wipes are individually packaged and pre-moistened (with distilled water) by the manufacturer (OSHA, 2002).

Workplace description

Where possible, the printing builds were divided into printing phases, namely pre-processing, processing, and post-processing. During PBF with MS, the operator wore gloves and used a spray bottle of ethanol and paper towelling to clean a baseplate and powder scoop. Then the operator installed the baseplate in the EOSINT M280 machine (EOS, Munich, Germany) and loaded the MS (specifically MS1) powder into the machine. This constituted the pre-processing phase. Thereafter, the operator closed the machine and, using the computer workstation next to the machine, began the print job. The print job took approximately 48 hours to complete, during which time the operator left the room, returning occasionally to make visual observations or minor computer-based adjustments. This constituted the processing phase. Once the print was complete, the operator opened the machine and removed the part from the supporting material. The excess powder was removed and sieved, after which the machine was cleaned of residual feedstock material. The equipment used included brushes, chisels, scoops, and a vacuum cleaner which was hung over the open machine door and used as local extraction ventilation. This constituted the post-processing phase. An air-conditioning unit, mounted onto the wall was present in the MS printing room. The operator working with MS wore nitrile gloves, a half-face

respirator, and a laboratory coat. The gloves were worn during pre- and post-processing but not during processing. The respirator was only worn during pre-processing and post-processing activities when the machine door was open.

A KUKA robot (KUKA Robotics Corporation, Augsburg, Germany) (DED) was used for the build with SS powder. The operator, who was not wearing gloves, set up the build and poured the metal powder into the powder input machine. This constituted the pre-processing phase. During the processing phase, the SS powder was simultaneously melted and deposited onto a rotating cylinder and the print was controlled using a control panel. Both the powder input machine and control panel were connected to the deposition machine. The post-processing phase included sweeping together the excess powder that was on the floor of the printing room using a broom, after which a paintbrush was used to collect the excess powder in a scoop. General extraction ventilation was installed in the printing room. The operator working with SS wore a half-face respirator but no gloves or other protective clothing throughout the printing process.

Non-printing rooms included in the study were the boardroom/tearoom and office at the facility where MS was used, and the kitchen and office at the facility where SS was used.

Surface wipe sampling

Surfaces on and around the AM machines, as well as in the offices and break rooms were selected for sampling. Where possible, samples were collected before and after each of the three printing phases. Sampling areas were marked with tape to ensure that the before and after samples were taken from the same area. For flat surfaces, 10 x 10 cm acetate templates were used to demarcate the sampling area. Each area was wiped using a single Ghostwipe and following an overlapping s-pattern. Each surface was wiped three times consecutively, folding the wipe, exposed side inward, after each time (NIOSH, 2003). The wipe was placed into a labelled vial, which was then sealed. Irregularly shaped surfaces were wiped three times consecutively folding the wipe as before, but a template was not used and the actual area wiped was measured and recorded. A new pair of powder-free, nitrile gloves and new acetate template were used for each sample. A field blank, not used to wipe a surface but otherwise handled and treated in the same manner as the surface samples, was collected on each day of sampling, and media blanks (unopened Ghostwipes™) were analysed in order to identify background concentrations of the metals in the wipes.

Laboratory analysis

The samples were sent to a South African National Accreditation System (SANAS)-accredited laboratory where they were subjected to inductively coupled argon plasma atomic emission spectroscopy analysis following the National Institute for Occupational Safety and Health (NIOSH)

method 7303 and the Occupational Safety and Health Administration (OSHA) method ID-125. All wipes were analysed for aluminium (Al), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), tin (Sn), titanium (Ti), and zinc (Zn). Additionally, the samples collected during the MS print were analysed for vanadium (V).

Data analysis

The results of all samples were blank corrected for each metal, that is the average mass of each metal found on the blanks was subtracted from the sample results for that metal, and reported in $\mu\text{g}/\text{cm}^2$. Samples that contained less than 0.5 μg were reported as below detection limit (BDL). All values that were negative after blank correction were also reported as BDL. For the purposes of statistical analysis, BDL values were assigned a value of detection limit/2 (Day *et al.*, 2007). Statistical analysis was carried out using Statistica Version 13 (Statsoft Inc., Palo Alto, California, USA). When tested for normality, the data was found to be skewed, even after being log transformed. Therefore, the data was subjected to non-parametric statistical analyses. Dependent groups were compared using the Wilcoxon signed-rank test and independent groups were compared using the Mann-Whitney U test. All results with a p-value ≤ 0.05 were considered to be statistically significant.

According to the risk level descriptors at the North-West University in health and health-related research, this study was classified as “no risk”. This is because only surface sampling took place with no contact with human participants. As such, ethical approval was not obtained.

Results

Surface contamination at two facilities

Detectable concentrations of metal powders were found to be present in both the printing and non-printing areas at both facilities as shown in Tables 1 and 2. The metals included in the results are those that were found in the highest concentrations and/or those that pose the greatest toxicological risk. As such, aluminium, cobalt, chromium, iron, and nickel were selected for presentation and the concentrations of each metal for the different surfaces are presented in Table 1 (MS) and Table 2 (SS). The metals that were not presented were: calcium (BDL-12.842 $\mu\text{g}/\text{cm}^2$), cadmium (BDL-0.051 $\mu\text{g}/\text{cm}^2$), copper (BDL-3.84 $\mu\text{g}/\text{cm}^2$), magnesium (BDL-0.109 $\mu\text{g}/\text{cm}^2$), manganese (BDL-3.625 $\mu\text{g}/\text{cm}^2$), molybdenum (BDL-22.943 $\mu\text{g}/\text{cm}^2$) lead (BDL-0.002 $\mu\text{g}/\text{cm}^2$), tin (BDL-0.139 $\mu\text{g}/\text{cm}^2$), titanium (BDL-8.0 $\mu\text{g}/\text{cm}^2$), vanadium (BDL-0.538 $\mu\text{g}/\text{cm}^2$), and zinc (BDL-1.175 $\mu\text{g}/\text{cm}^2$).

Table 1. Summary of surface contamination from metals during PBF with MS.

Sampling area	Printing phase	Surface	µg/cm²				
			Al	Co	Cr	Fe	Ni
Printing room	Pre-processing	Powder container*	1.832	42.904	0.841	335.442	92.277
		Machine workstation desk*	0.206	1.376	0.031	11.412	2.892
	Processing	Machine door handle*	0.174	0.801	0.007	6.462	1.708
		Entry door handle*	0.176	0.109	0.008	1.041	0.193
	Post-processing	Scoop handle*	1.083	5.13	0.05	39.74	11.157
		Vacuum hose*	0.954	17.132	0.356	143.619	39.138
		Machine door handle*	0.073	0.961	0.006	7.492	2.073
		Machine workstation mouse*	0.34	2.08	0.045	16.36	4.5
	N/A	Machine workstation handle [#]	0.079	0.275	0.006	2.217	0.592
		Top of entry door handle [#]	0.067	0.02	BDL	0.419	0.031
		Surface beside machine workstation [#]	0.144	2.222	0.039	11.411	3.134
		Corner table [#]	0.011	1.052	0.007	8.011	2.554
Office	N/A	Desk [#]	0.09	0.034	BDL	0.285	0.064
		Arm of desk chair [#]	0.172	0.027	BDL	0.324	0.047
Boardroom/tearoom	N/A	Door handle [#]	0.069	BDL	BDL	0.154	0.003
		Table [#]	0.035	0.017	BDL	0.127	0.028
Sum			5.503	74.14	1.397	584.496	160.391
GM			0.153	0.348	0.007	3.891	0.764

BDL = Below detection limit (detection limit was 0.5 μg); GM = Geometric mean; * indicates that values given equal the sum of the before and after concentrations for that surface; [#] indicates that values given are individual sample values.

Where MS was used, iron was found to be the most contaminating metal overall (sum of the iron concentrations on all surfaces) followed by nickel, cobalt, aluminium, and chromium. The geometric mean (GM) concentration of iron (averaged over all surfaces) was ± 2 times greater than that of nickel and ± 234.6 times greater than that of chromium.

Table 2. Summary of surface contamination from metals during DED with SS.

Sampling area	Printing phase	Surface	µg/cm ²				
			Al	Co	Cr	Fe	Ni
Printing room	Pre-processing	Powder container*	0.375	0.506	1.06	7.91	1.354
		Control panel*	14.94	31.707	84.604	510.81	33.06
		Powder input machine [#]	5.022	21.766	56.477	352.28	23.793
	Processing	Floor 1 m from machine*	50.344	21.307	102.822	168.31	25.621
		Floor directly below machine*	12.639	107.482	208.954	1524.56	95.486
		Entry door handle [#]	BDL	0.058	0.031	0.417	0.208
	Post-processing	Broom handle [#]	0.433	0.214	0.138	5.086	0.895
		Cleaning brush handle [#]	13.6	1.463	3.033	8.471	3.246
	N/A	Wooden shelves [#]	1.035	0.596	1.077	68.33	35.243
		Metal work surface [#]	0.482	0.084	0.705	3.58	2.743
		Wooden work bench [#]	42.422	0.441	6.152	32.03	11.793
Office	N/A	Desk [#]	0.016	BDL	BDL	0.2	0.019
Kitchen	N/A	Kitchen counter [#]	0.052	0.01	0.004	0.04	0.018
		Coffee tin [#]	BDL	BDL	BDL	BDL	BDL
Sum			140.715	184.636	465.058	2682.024	233.380
GM			0.522	0.384	0.633	6.117	1.425

BDL = Below detection limit (detection limit was 0.5 μg); GM = Geometric mean; * indicates that values given equal the sum of the before and after concentrations for that surface; [#] indicates that values given are individual sample values collected after the phase was completed.

Where SS was used, iron was also found to be the most contaminating metal (sum of the concentrations on all surfaces), followed by chromium, nickel, cobalt, and aluminium. However, the GM concentration of nickel was greater than that of chromium and the GM concentration of aluminium was greater than that of cobalt. This indicates that certain individual values for chromium and cobalt were high but overall, nickel and aluminium were more contaminating, respectively. The GM concentration of iron was ± 4.3 times higher than that of nickel and ± 15.9 times higher than that of cobalt.

Contamination before versus after printing process phases (individual metals)

While the printing activities were divided into phases, the aim of this study was not to compare these printing phases but to quantify the surface contamination that took place during each phase in various work areas, as well as to identify when and where the majority of contamination occurred. As such, samples were collected before and after pre-processing, processing, and post-processing, where possible. Figures 1 and 2, show that for some surfaces, contamination

mostly occurred before the printing phase and for other surfaces, it mostly occurred during the printing phase.

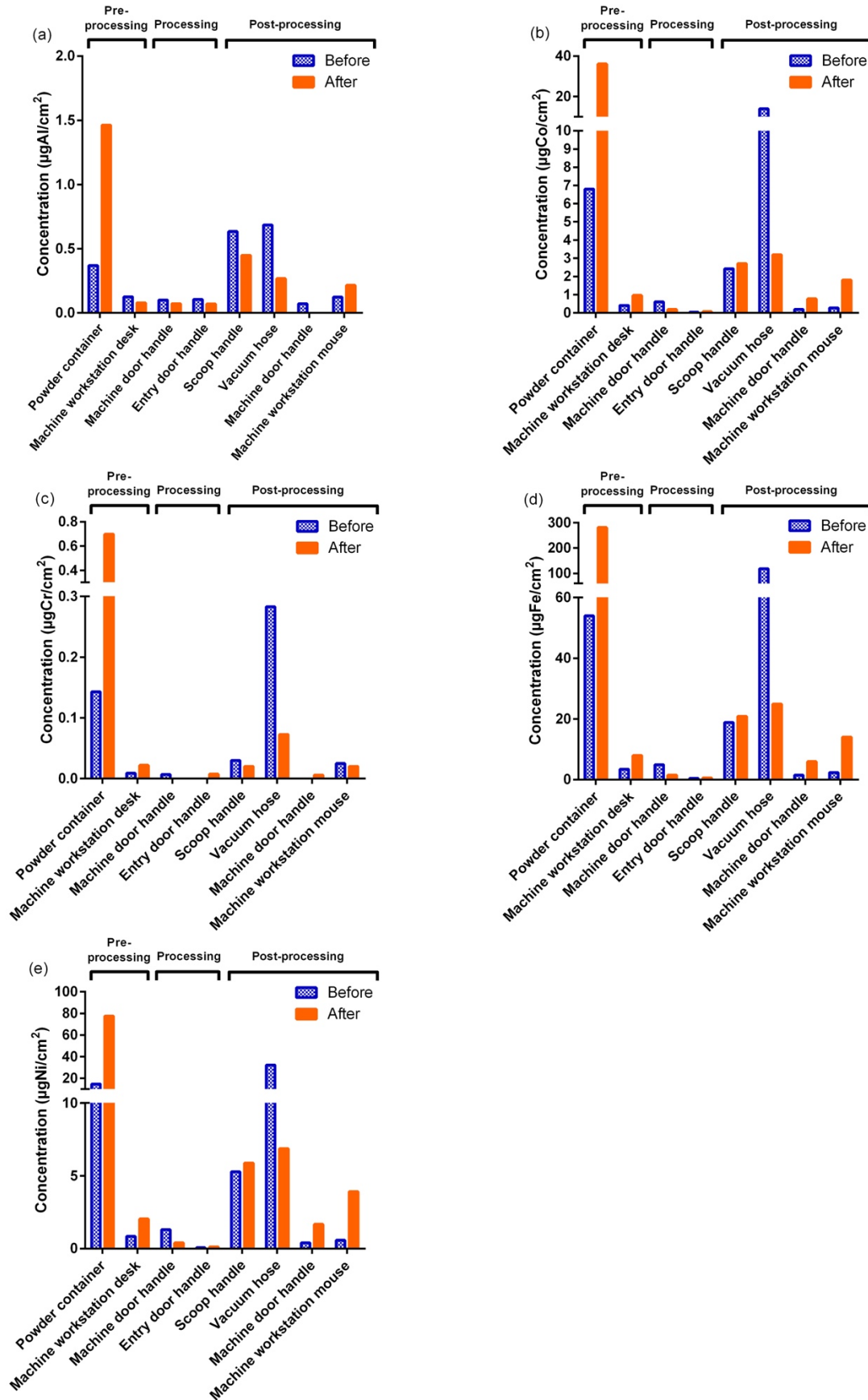


Fig. 1. Surface contamination from (a) Al, (b) Co, (c) Cr, (d) Fe, and (e) Ni before (single sample) and after (single sample) printing phases during PBF with MS.

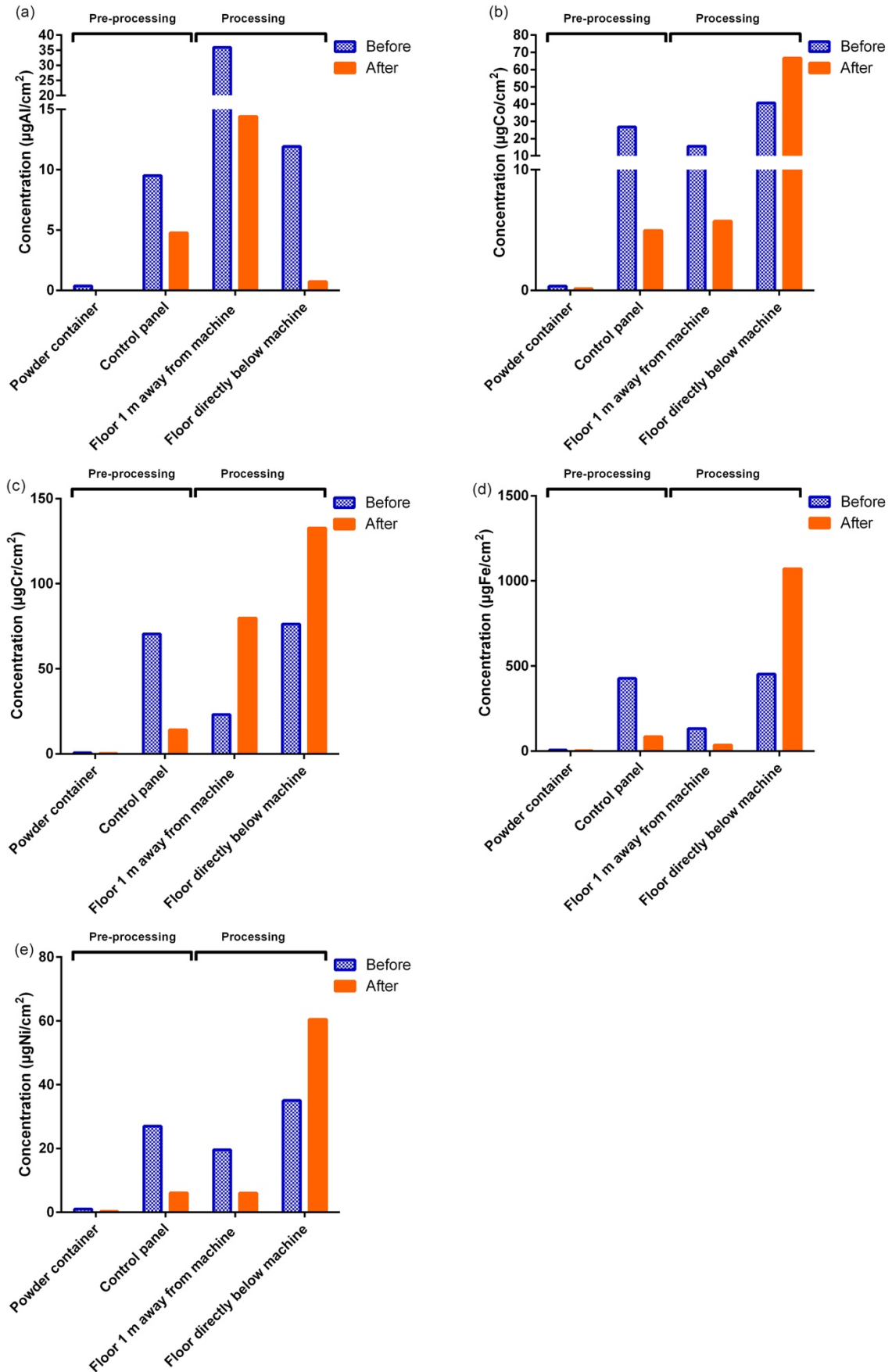


Fig. 2. Surface contamination from (a) Al, (b) Co, (c) Cr, (d) Fe, and (e) Ni before (single sample) and after (single sample) printing phases during DED with SS.

Total contamination before versus after printing process phases (all metals combined)

As significant differences could not be statistically determined for individual metals when comparing the before versus after printing phase contamination concentrations, total metal contamination (sum of all metals) was analysed. When comparing the total contamination found on the surfaces before pre-processing, processing, or post-processing, versus after these printing phases, significant differences were found at both facilities. Where MS was used, these differences were found to be present on the powder container (± 5.2 times more powder after pre-processing than before; $p = 0.043$), the machine door handle (± 3.2 times more powder before processing than after; $p = 0.043$), and the vacuum hose (± 4.7 times more powder before post-processing than after; $p = 0.043$). Where SS was used, significant differences were found on the powder container (± 2.6 times more powder before pre-processing than after; $p = 0.043$) and the control panel (± 4.9 times more powder before pre-processing than after; $p = 0.043$) (Figure. 3).

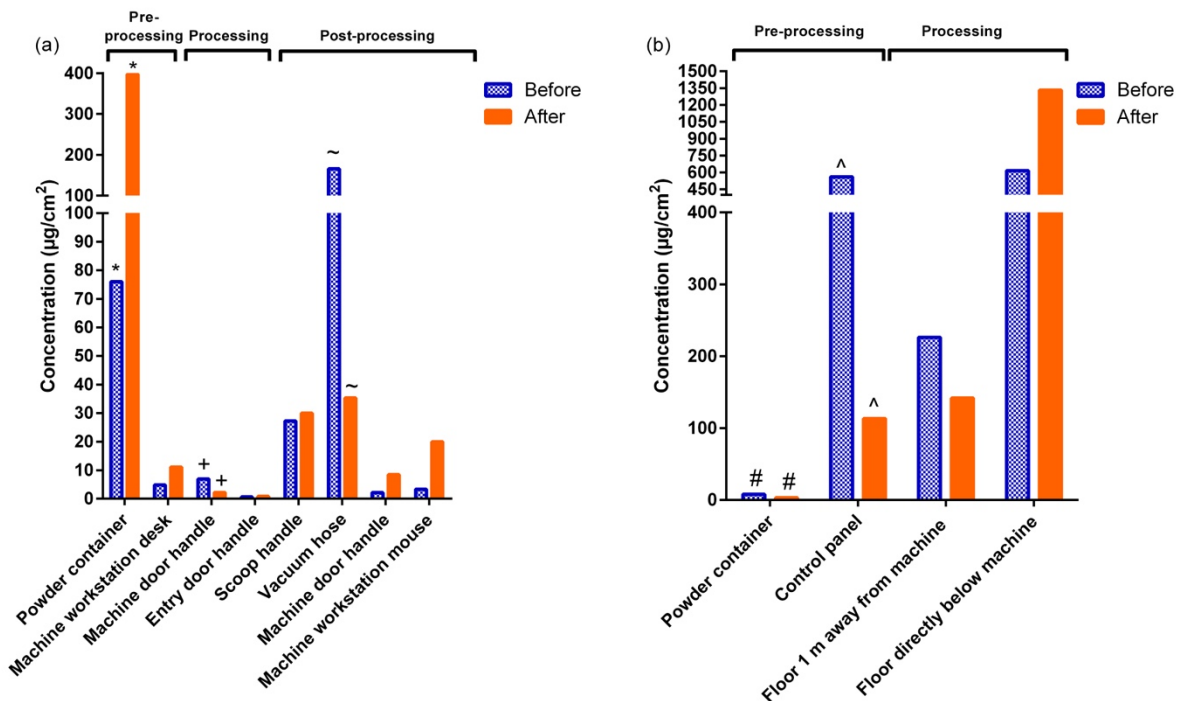


Fig. 3. Difference between total contamination (sum of all the metals for each surface) before printing phases and total contamination after printing phases with (a) MS and (b) SS. *, +, ~, #, and ^ indicate statistically significant differences between contamination measured before and after the printing phases ($p \leq 0.05$).

Printing room surfaces versus non-printing room surfaces

The concentration of metals in the printing rooms were compared to those in the non-printing rooms during the MS and SS printing builds (Table 3) in order to determine the extent of non-

printing room contamination, the results of which were used to assess the effectiveness of contaminant transfer prevention practices. Significant differences between printing room surfaces and non-printing room surfaces were determined using the relevant individual sample values as opposed to the mean values.

Table 3. Geometric mean concentrations of metals on surfaces in the printing rooms and surfaces in the non-printing rooms.

	$\mu\text{g}/\text{cm}^2$			
	Maraging steel		Stainless steel	
	Printing room surfaces	Non-printing room surfaces	Printing room surfaces	Non-printing room surfaces
Al	0.191	0.078	1.77 ^e	0.006 ^e
Co	1.227 ^a	0.008 ^a	1.690 ^f	0.002 ^f
Cr	0.019 ^b	0.000 ^b	4.168 ^g	0.001 ^g
Fe	10.36 ^c	0.206 ^c	33.049 ^h	0.013 ^h
Ni	2.471 ^d	0.023 ^d	6.890 ⁱ	0.004 ⁱ

^{a-i} indicate the significant differences found between printing room surfaces and non-printing room surfaces ($p \leq 0.05$).

At the facility where MS was used, significantly higher concentrations of cobalt, chromium, iron, and nickel were found on printing room surfaces compared to those found on non-printing room surfaces. At the facility where SS was used, significantly higher concentrations of aluminium, cobalt, chromium, iron, and nickel were found on printing room surfaces compared to those found on non-printing room surfaces.

Discussion

This study investigated contamination from the use of MS during PBF and from SS during DED. Analysis of the samples collected at the two AM facilities included in this study found quantifiable concentrations of metal powders (Al, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sn, Ti, V, and/or Zn) to be present on surfaces at the AM facilities (Tables 1 and 2). The metals that were present on surfaces at the AM facilities in the greatest quantities and/or those that posed the greatest toxicological risk to health were reported. These metals were aluminium, cobalt, chromium, iron, and nickel. Knowing that contamination from metal powders exists is of limited value without knowing how and when contamination occurred, the ways in which it may potentially contribute to exposure, and the possible adverse health effects associated with such exposure.

The presence of detectable concentrations of metal powders (Al, Co, Cr, Fe, and Ni) on surfaces at the AM facilities indicates that these surfaces may act as sources of potential worker exposure to these metals. This corresponds to Schneider *et al.* (1999), who proposed a model for the assessment of dermal exposure in which contaminated surfaces in the workplace were identified as potential secondary sources of exposure. The different methods by which surfaces at the AM facilities were potentially contaminated were also consistent with those presented by Schneider *et al.* (1999), namely emission, deposition, redistribution, and removal. Emission involves spilling of substances onto surfaces or ejection of substances into the air. Deposition occurs when airborne particulates settle onto surfaces. Redistribution involves the movement of substances from one contaminated surface to another surface which may or may not already be contaminated. Removal involves the movement of substances away from the worker and onto surfaces. Regardless of how contamination occurred, metal powders on surfaces at the AM facilities may lead to potential worker exposure via inhalation, dermal contact, and/or ingestion (Schneider *et al.*, 1999; Boeniger, 2006).

Contaminated surfaces have the potential to cause inhalation exposure if the metal powders become resuspended in the air due to either mechanical impacts associated with workplace and cleaning activities or air currents. Resuspended particulates may also subsequently be deposited onto skin or clothing from where they pose a risk via dermal exposure. Printing activities that involved direct contact between the operators and contaminated surfaces presented the risk of possible dermal contact exposure, especially when protective clothing was not used or was used incorrectly (Schneider *et al.*, 1999; Schneider *et al.*, 2000). Additionally, contact between the operator and contaminated surfaces presented a possible risk of inadvertent ingestion exposure as a result of subsequent hand- or object-to-mouth contact (Gorman Ng *et al.*, 2014). Tables 1 and 2 and Figure 3 indicate that the MS powder container and the floor directly below the DED machine were the most contaminated surfaces at the AM facilities. The MS powder container, which was most likely contaminated by emission, was handled while wearing gloves, controlling dermal exposure. However, handling the container might have caused the relatively high concentrations of settled powder on the container to become airborne again. The floor directly below the DED machine, which was contaminated through emission and deposition, was a potential source of inhalation exposure to SS as activities such as sweeping might have resulted in resuspension of metal powders. During the SS print, the operator did not wear gloves. This presented various opportunities for potential dermal exposure via contaminated surfaces such as the control panel (Table 2). The floor might have acted as a potential source of dermal exposure as the operator was observed to crouch down beside the machine during the print. Dermal exposure may occur should the operator need to steady himself with a hand on the floor. The cleaning brush handle and broom handle, which were found to be contaminated (deposition,

redistribution, and removal) (Table 2), were potential sources of dermal exposure when the operator used these tools. Although the parameters of this study did not extend to the sampling of clothing and PPE, machine operators working with MS were observed setting their respirators down onto contaminated surfaces beside the PBF machine (redistribution). Additionally, the proximity of the respirators to the machine itself introduced the possibility of the inner surfaces of PPE becoming contaminated (emission and deposition) and leading to exposure (Rawson *et al.*, 2005).

Identification of when contamination might have taken place could provide information that is useful to the assessment of existing controls and cleaning procedures as well as to the development of effective control strategies (Badenhorst, 2007). In this study, where possible, two samples were collected from each surface. One sample was collected prior to the printing phase and a second sample was collected after that printing phase. A significantly higher concentration of total metal contamination (sum of individual metal concentrations) was found to be present on the MS powder container after pre-processing when compared with the concentration before pre-processing (Figure 3). This indicates that most of the MS powder container surface contamination occurred while the containers were being handled during the pre-processing phase. A new or different powder container might have been used for each build thus eliminating the potential for cumulative contamination and this may provide a reason for its lower initial levels of contamination. Contrary to what was expected, only one surface (the MS powder container) became significantly more contaminated during the printing phase compared to before the printing phase. During the MS print, significantly higher concentrations of total metal contamination were found on the machine door handle before the processing phase, and on the vacuum hose before the post-processing phase, compared to after the respective phases. During the SS print, the concentrations of total metal contamination found on the powder container and control panel before the pre-processing phase were significantly higher when compared to the concentrations after pre-processing (Figure 3). Such contamination might have been the result of insufficient, ineffective, and/or infrequent workplace cleaning practices and/or ineffective extraction ventilation that allowed the metal powders to accumulate on workplace surfaces. Workers might have considered surfaces such as the machine door handle (MS print) and the control panel (SS print) to be 'clean' because they were not visibly dirty and/or they were not in direct contact with the primary sources of contaminants. As such, these surfaces might not have been cleaned as often as surfaces which were obviously contaminated, such as the floor in the SS printing room. The vacuum cleaner at the facility where MS powder was used might not have been cleaned often as it is itself a cleaning tool. This may have led to an oversight as to its potential to become contaminated. As the majority of surfaces showed this 'pre-existing' contamination, the accumulation of metal powders on surfaces over time presents a greater risk of exposure than that which arises from the individual printing build.

Tables 1 and 2 show that metal powders were not only found in the printing rooms but also in non-printing rooms, such as kitchens and offices. It is important to understand how this might have occurred and its implication in terms of potential worker exposure. As metal powders were not expected to be found in the non-printing rooms, 'hidden' sources of exposure exist at both facilities (Badenhorst, 2007). Such exposure points indicate that transfer between printing and non-printing areas was not controlled and the presence of toxic metals in these areas might not have been taken into account by the established cleaning protocols. It also indicates that individuals who do not work directly with the AM machines, such as administrative personnel, might be potentially be exposed to the metal powders as a result of transfer of contaminants from the printing areas to the non-printing areas. The existence of contaminated surfaces in rooms that are not involved in the printing process might have been the result of either contact transfer from contaminated hands or clothing, or airborne transfer. At the facility where MS was used, the printing rooms and the non-printing rooms where samples were collected, were not in close proximity to each other. There were also three doors, two of which were closed and the third which was closed intermittently, between the printing and non-printing rooms. This suggests that the metal powders found in the non-printing rooms were more likely to have been deposited by contact transfer as opposed to airborne transfer. While in the printing rooms, the operators were observed to wear laboratory coats, gloves, and respirators. However, the operators would also often leave the printing rooms while still wearing the laboratory coats and gloves, increasing risk of transfer. At the facility where SS was used, the printing room and the non-printing rooms opened up onto a shared hallway, making transfer of airborne particulates possible. However, the printing room was located on the opposite end of the hallway to the kitchen and office so the extent of airborne transfer is likely to be insignificant. The operators wore respirators but no other form of protective clothing thus, by crouching beside the machine, the operator increased the risk of personal clothing becoming contaminated and resulting in contact transfer of metal powders from printing areas to non-printing areas. While contamination did exist in the kitchen, boardroom/tearoom, and offices, the concentrations of metal powders were significantly lower than those in the printing rooms (Table 3). However, the presence of metal powders on surfaces in the boardroom/tearoom and the kitchen at the AM facilities increase the possibility of accidental ingestion occurring and contamination in these rooms needs to be eliminated.

MS and SS are not made up of equal quantities of their component metals (Baddoo, 2008; Tolosa *et al.*, 2010; EOS, 2011). This is reflected in the results as some metals were found at higher concentrations on the AM surfaces than others (Tables 1 and 2). Iron, the main component of both MS and SS, was found in the highest concentrations at both facilities, followed by nickel, cobalt, aluminium, and chromium at the facility where MS was used; and followed by chromium, nickel, cobalt, and aluminium at the facility where SS was used. Each of the five metals reported

in this study (aluminium, cobalt, chromium, iron, and nickel) are associated with certain toxicities. This toxicity as well as the specific route of exposure determine the nature of adverse health effects that may potentially occur as a result of worker exposure (Tokar *et al.*, 2013). Of particular concern was the presence of nickel, chromium, and cobalt, three potent sensitising metals (Day *et al.*, 2009). Nickel is the most sensitising of the three metals and even minor, non-occupational exposures such as contact with jewellery and zippers are able to cause sensitisation to nickel and subsequent occupational exposure may trigger an allergic reaction. Chromium and cobalt are less sensitising than nickel but they are still considered to be frequent causes of contact allergy, especially in occupational settings (Lidén *et al.*, 2008). It is also possible that simultaneous exposure to all three metals could compound the individual reactions (Day *et al.*, 2009). Nickel was found at concentrations up to a maximum of 92.277 $\mu\text{g}/\text{cm}^2$ (powder container) (GM = 0.764 $\mu\text{g}/\text{cm}^2$) on surfaces at the facility where MS was used and up to a maximum of 95.486 $\mu\text{g}/\text{cm}^2$ (floor directly below machine) (GM = 1.425 $\mu\text{g}/\text{cm}^2$) on surfaces at the facility where SS was used. Chromium was found at concentrations up to a maximum of 0.841 $\mu\text{g}/\text{cm}^2$ (powder container) (GM = 0.007 $\mu\text{g}/\text{cm}^2$) on surfaces at the facility where MS was used and up to a maximum of 208.954 $\mu\text{g}/\text{cm}^2$ (floor directly below machine) (GM = 0.633 $\mu\text{g}/\text{cm}^2$) on surfaces at the facility where SS was used. Cobalt was found at concentrations up to a maximum of 42.904 $\mu\text{g}/\text{cm}^2$ (powder container) (GM = 0.348 $\mu\text{g}/\text{cm}^2$) on surfaces at the facility where MS was used and up to a maximum of 107.482 $\mu\text{g}/\text{cm}^2$ (floor directly below machine) (GM = 0.384 $\mu\text{g}/\text{cm}^2$) on surfaces at the facility where SS was used. In comparison, a report on exposure in the electroplating industry reported a median surface nickel concentration of 1.5 $\mu\text{g}/\text{cm}^2$ and a median concentration for chromium of 0.6 $\mu\text{g}/\text{cm}^2$ (Beattie *et al.*, 2017). Furthermore, in a paper investigating surface metal contamination at three cemented tungsten carbide production plants, maximums of up to 40 $\mu\text{g}/\text{cm}^2$ of nickel, up to 9.6 $\mu\text{g}/\text{cm}^2$ of chromium, and up to 220 $\mu\text{g}/\text{cm}^2$ of cobalt were found on surfaces (Day *et al.*, 2009). These results indicate that the surfaces at the AM facilities where metal powders were utilised, were similarly or more contaminated than surfaces in these two industries.

Workers at the AM facilities were potentially at risk of exposure to metals via inhalation and/or dermal contact. Both of these exposure routes have been linked to the development of metal sensitisation (Fernández-Nieto *et al.*, 2006; Lidén *et al.*, 2008), suggesting that exposure during AM with MS and SS powders carries a risk of developing a metal allergy. In addition to contact allergy, inhalation exposure to nickel, chromium, and cobalt may result in the development of lung cancer as nickel is classified as a Group 1 metal (carcinogenic to humans) (IARC, 2012) and cobalt is classified as Group 2B (possibly carcinogenic to humans) (IARC, 2006). Additionally, heat, which was involved in both PBF and DED, might have led to the formation of hexavalent chromium, another Group 1 carcinogen (IARC, 2012). As these metals may cause adverse health effects following exposure, it is important to identify and control the ways in which AM processes

may lead to surface contamination thereby reducing secondary exposure.

As AM with MS and SS was shown to contaminate workplace surfaces, including those where such contamination was unexpected (non-printing areas), and because these contaminating metals are potentially associated with adverse health effects following exposure, it is necessary to eliminate or control surface contamination and subsequently potential worker exposure. Recommendations to minimise contamination of AM surfaces include installation or improvement of existing extraction ventilation and re-evaluation of the effectiveness and/or frequency of cleaning procedures. Recommendations to control worker exposure to contaminated surfaces in the printing areas and to eliminate transfer of contaminants to non-printing areas include the implementation and enforcement of proper PPE use, storage, and decontamination or disposal of dirty PPE, as well as providing information and training on the existence of potentially toxic contaminants in the workplace, and the proper use, donning, and doffing of PPE and protective clothing.

Further research into exposure to MS and SS powders at AM facilities as a result of surface contamination is required in order to fully understand the risk involved and the likelihood of exposure. As dermal exposure was observed to take place at the AM facilities included in this study, it would be beneficial to conduct dermal exposure sampling to determine the concentrations of metals present on the skin of workers at the AM facilities. Measurement of inhalation and dermal exposure at AM facilities may also contribute to an understanding of the relationship between surface contamination and the extent of personal exposure at AM facilities.

Conclusions

Metal powders, including aluminium, cobalt, chromium, iron, and nickel (the metals found in the highest concentrations and/or those which are highly toxic) were present at detectable concentrations on surfaces at AM facilities. Opportunities for possible worker exposure via inhalation, dermal contact, and even ingestion were observed at the AM facilities as a result of contaminated surfaces. Accumulated contamination from multiple builds existed in the AM printing rooms as evidenced by the fact that several surfaces showed significantly higher concentrations of metal powders before printing phases when compared with the concentrations after the printing phases. This suggests that cleaning procedures should be revised in order to properly control potential exposure. Surface contamination existed in both printing and non-printing areas creating risk of potential exposure to all workers at the AM facilities, not only those working directly with the AM machines. Additionally, the presence of metal powders on surfaces where they were not expected to be present, indicates a need for more effective control measures, including review and improvement of existing containment and cleaning measures and training employees on proper use of PPE and protective clothing, to prevent such transfer of metal

powders. The concentrations of metals present on AM surfaces were comparable to the concentrations reported in other industries.

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Chapter 4: Short communication on surface contamination by Ti-6Al-4V powder

Metal powder surface contamination during powder bed fusion with Ti-6Al-4V

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Surface sampling; Ghostwipes™; occupational exposure; 3D printing; additive manufacturing.

Abstract

Background: Surfaces at additive manufacturing (AM) facilities where metal powders such as titanium-6aluminium-4vanadium (Ti-6Al-4V) are used may become contaminated during processes such as powder bed fusion (PBF) and may become potential secondary sources of metal exposure.

Objectives: To make use of wipe sampling methodology to assess surface contamination caused by PBF with Ti-6Al-4V powder at two AM facilities.

Methods: At each of two AM facilities, Ghostwipes™ were used to conduct surface sampling for Ti-6Al-4V powder in printing and non-printing rooms. Where possible, samples were taken before and after each of three printing phases. All samples were subjected to inductively coupled argon plasma atomic emission spectroscopy analysis.

Results: Aluminium (below detection limit [BDL]-0.818 $\mu\text{g}/\text{cm}^2$), cobalt (BDL-3.282 $\mu\text{g}/\text{cm}^2$), chromium (BDL-0.429 $\mu\text{g}/\text{cm}^2$), iron (BDL-27.211 $\mu\text{g}/\text{cm}^2$), nickel (BDL-7.039 $\mu\text{g}/\text{cm}^2$), titanium (BDL-4.989 $\mu\text{g}/\text{cm}^2$), and vanadium (BDL-0.261 $\mu\text{g}/\text{cm}^2$) were found at detectable concentrations on printing and non-printing room surfaces at the AM facilities. The presence of metals other than titanium, aluminium, and vanadium indicated the possible occurrence of contamination from previous printing processes. Analysis of samples collected before and after printing phases showed that surfaces were contaminated before, and became contaminated during, the print process.

Conclusions:

PBF with Ti-6Al-4V led to detectable concentrations of aluminium, titanium, and vanadium being removed from surfaces at the AM facilities. Additionally, metals not found in Ti-6Al-4V, such as cobalt, chromium, iron, and nickel were removed from these surfaces indicating contamination from previous printing processes. Surface contamination by metal powders was present in printing and non-printing rooms.

Key words: Surface sampling; Ghostwipes™; occupational exposure; 3D printing; additive manufacturing.

Introduction

Additive manufacturing (AM), the layer by layer construction of three dimensional objects from raw materials, using computer-aided design data, affords customisation and geometric intricacies to printed parts thus garnering attention from various fields of application, including aerospace and biomedicine (Huang *et al.*, 2013; Wohlers and Caffrey, 2015; Ryan and Hubbard, 2016).

Metal powders, such as titanium-6aluminium-4vanadium (Ti-6Al-4V), are used in various categories of AM processes, including powder bed fusion (PBF) which involves fusing layers of powder together using thermal energy (Wohlers and Caffrey, 2015). Ti-6Al-4V is characterised by high strength and corrosion resistance, making it popular for use in aerospace and biomedicine where durability and biocompatibility or resistance to weathering are important (Kostov and Friedrich, 2006; Prasad *et al.*, 2015). While Ti-6Al-4V is biocompatible and unlikely to cause adverse health effects (Prasad *et al.*, 2015), workers are potentially exposed to the individual alloying metals while working with the powdered form (Santos *et al.*, 2006; Gu *et al.*, 2012). Titanium, aluminium, and vanadium are poorly absorbed from the gastrointestinal tract and are unable to permeate through skin (Mavon *et al.*, 2007; Tokar *et al.*, 2013). Aluminium is poorly absorbed from the respiratory tract, although chronic exposure may be associated with lung fibrosis and neurodegenerative diseases, and inhalation of titanium dioxide (relevant because titanium is highly oxidative) is associated with the development of cancer (Group 2B) (IARC, 2010; Prasad *et al.*, 2015) and inhalation of vanadium may cause bronchitis and bronchopneumonia (Tokar *et al.*, 2013).

AM activities, assigned to pre-processing, processing, or post-processing phases, present opportunities for metal powders to contaminate printing room surfaces (Udroiu and Nedelcu, 2011) forming new sources of inhalation, dermal contact, and/or ingestion exposure (Schneider *et al.*, 1999; Boeniger, 2006). Non-process exposure points, such as kitchen or office surfaces, can be created through transfer of contaminants, and inner surfaces of personal protection equipment (PPE) may also become contaminated. Such contamination would be neither expected nor controlled (Rawson *et al.*, 2005; Badenhorst, 2007). Although often overlooked, surface contamination monitoring can provide useful information regarding potential worker exposure and may provide an indication of the effectiveness of existing workplace housekeeping protocols and controls (Boeniger, 2006; Badenhorst, 2007).

The objective of this study was to make use of wipe sampling methodology to assess surface contamination caused by PBF with Ti-6Al-4V powder at two AM facilities.

Methods

Wipe sampling using Ghostwipes™ (SKC, Pennsylvania, USA) was carried out during PBF at two

South African AM facilities, hereafter referred to as printing room one (PR1) and printing room two (PR2). The AM workplace layout is indicated in Figure 1. PR1-associated non-printing rooms were office 1 and the boardroom/tearoom. PR2-associated non-printing rooms were the kitchen and office 2.

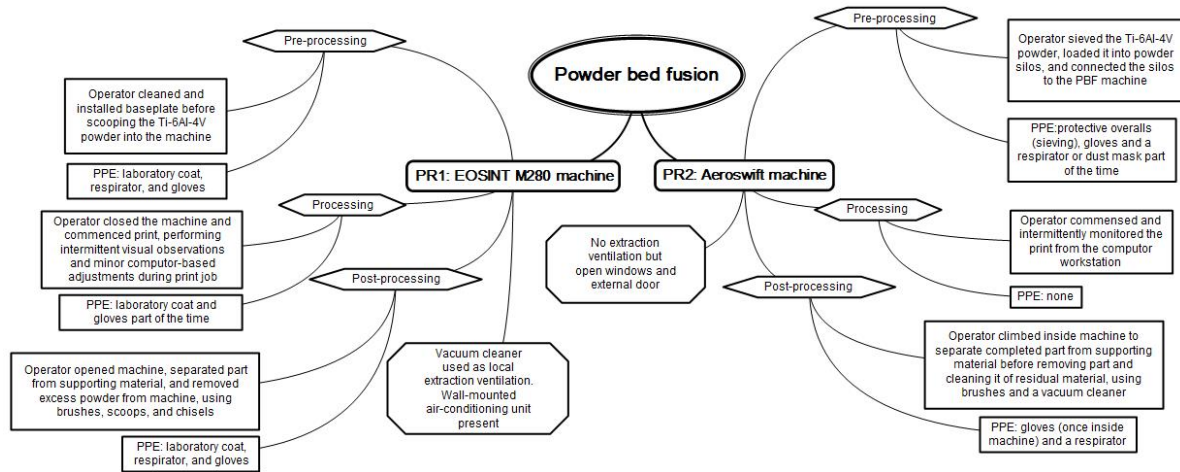


Fig. 1. Description of printing phases in PR1, in which an EOSINT M280 PBF machine (EOS, Munich, Germany) was used; and PR2, in which an Aeroswift PBF machine (Aerosud, Pretoria, South Africa) was used. PR1 = printing room one; PR2 = printing room two; Ti-6Al-4V = titanium-6aluminium-4vanadium; PPE = personal protective equipment.

Surfaces in printing and non-printing rooms were sampled. Where possible, samples were collected before and after each printing phase. Samples were analysed by a SANAS-accredited laboratory for metals using inductively coupled argon plasma atomic emission spectroscopy. Data were statistically analysed using Statistica Version 13 (Statsoft Inc., Palo Alto, California, USA). See article on *Evaluation of surface contamination from maraging steel and stainless steel powders at two additive manufacturing facilities* (Chapter 3) for further details on the surface sampling methodology, laboratory analysis, and data analysis procedures.

Results

Detectable concentrations of aluminium (Al), calcium (Ca), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), tin (Sn), titanium (Ti), vanadium (V), and zinc (Zn) were removed from surfaces during PBF with Ti-6Al-4V. In addition to Ti-6Al-4V component metals, detailed results of cobalt, chromium, iron, and nickel are provided due to their toxic potential. The contamination ranges of the metals not reported are: calcium (below detection limit [BDL]-22.553 $\mu\text{g}/\text{cm}^2$), cadmium (BDL), copper (BDL-0.644 $\mu\text{g}/\text{cm}^2$), magnesium (BDL-0.351 $\mu\text{g}/\text{cm}^2$), manganese (BDL-0.126 $\mu\text{g}/\text{cm}^2$), molybdenum (BDL-2.148 $\mu\text{g}/\text{cm}^2$) lead (BDL-0.311 $\mu\text{g}/\text{cm}^2$), tin (BDL-0.217 $\mu\text{g}/\text{cm}^2$), and zinc (BDL-0.55 $\mu\text{g}/\text{cm}^2$).

Table 1 shows that, of the Ti-6Al-4V component metals, titanium was found in the highest concentrations in PR1 (geometric mean [GM] = 0.274 $\mu\text{g}/\text{cm}^2$) and PR2 (GM = 0.179 $\mu\text{g}/\text{cm}^2$) followed by aluminium (GM = 0.075 $\mu\text{g}/\text{cm}^2$) and vanadium (GM = 0.003 $\mu\text{g}/\text{cm}^2$) in PR1; and followed by vanadium (GM = 0.035 $\mu\text{g}/\text{cm}^2$) and aluminium (GM = 0.004 $\mu\text{g}/\text{cm}^2$) in PR2.

Table 1. Summary of surface contamination from metals in printing rooms during PBF with Ti-6Al-4V.

Phase	Surface	$\mu\text{g}/\text{cm}^2$						
		Al	Ti	V	Co	Cr	Fe	Ni
Pre-processing	Metal work bench* [§]	0.481	1.363	0.039	0.145	0.036	1.387	0.317
	Sieve rim* [‡]	0.01	3.864	0.225	0.014	0.056	1.815	0.033
	Top of sieve* [‡]	0.006	2.802	0.149	0.006	0.026	0.513	0.01
	Powder container lid* [‡]	0.013	2.338	0.143	0.012	0.059	3.376	0.025
	Brush/scoop container lid* [‡]	0.016	0.479	0.049	BDL	0.076	2.21	0.032
	Silo rim* [‡]	0.025	0.764	0.087	BDL	0.109	2.714	0.056
	Silo loading station* [‡]	0.015	0.986	0.075	BDL	0.035	1.18	0.018
	Loading station ramp* [‡]	0.006	3.426	0.197	0.021	0.126	5.051	0.063
Processing	Entry door handle 1* [§]	BDL	0.006	BDL	0.031	0.012	0.575	0.051
	Machine workstation mouse* [§]	0.53	0.535	BDL	0.21	BDL	2.683	0.413
	Control panel* [‡]	BDL	BDL	BDL	BDL	0.017	0.432	0.007
	Control station railing* [‡]	BDL	BDL	0.007	BDL	0.035	0.153	0.004
Post-processing	Ethanol bottle* [§]	0.126	0.136	BDL	0.223	0.01	1.897	0.454
	Vacuum hose 1* [§]	0.122	1.58	0.077	1.689	0.03	13.467	3.631
	Machine workstation mouse* [§]	0.107	0.133	BDL	0.13	0.038	2.325	0.16
	Machine door handle 1* [§]	BDL	0.369	BDL	0.086	0.006	1.107	0.144
	Machine workstation desk* [§]	0.172	0.104	BDL	0.049	0.013	0.506	0.085
	Ledge inside machine* [‡]	BDL	6.558	0.351	0.044	0.185	2.803	0.072
	Vacuum hose 2* [‡]	0.012	0.406	0.079	0.005	0.058	1.07	0.032
	Back platform railing* [‡]	0.015	0.48	0.051	0.008	0.04	1.121	0.01
	Machine back panel* [‡]	0.014	0.442	0.038	BDL	0.013	BDL	0.001
N/A	Wooden work bench* [§]	0.376	0.691	0.012	0.3	0.017	2.766	0.624
	Top of machine* [§]	0.818	0.681	0.062	3.282	0.053	27.211	7.039
	Machine door handle 2* [‡]	0.015	0.023	0.033	0.15	0.429	7.896	0.177
	Entry door handle 2* [‡]	BDL	BDL	BDL	BDL	0.027	0.358	0.002
	Powder storage shelves* [‡]	BDL	0.074	0.019	BDL	0.039	4.88	0.016
Sum (both printing rooms)		2.88	28.241	1.698	6.272	1.546	89.495	6.272
GM (both printing rooms)		0.012	0.204	0.013	0.012	0.031	1.3	0.012
Sum (PR1)		2.732	5.58	0.193	6.145	0.216	53.924	6.145
GM (PR1)		0.075	0.274	0.003	0.213	0.013	2.36	0.213
Sum (PR2)		0.148	22.643	1.505	0.127	1.33	35.572	0.127
GM (PR2)		0.004	0.179	0.035	0.002	0.054	0.896	0.002

BDL = Below detection limit (detection limit was 0.5 μg); GM = Geometric mean; * indicates values equal to the sum of the before and after concentrations for that surface; # indicates individual sample values collected after the phases were completed; § indicates PR1 surfaces; ‡ indicates PR2 surfaces.

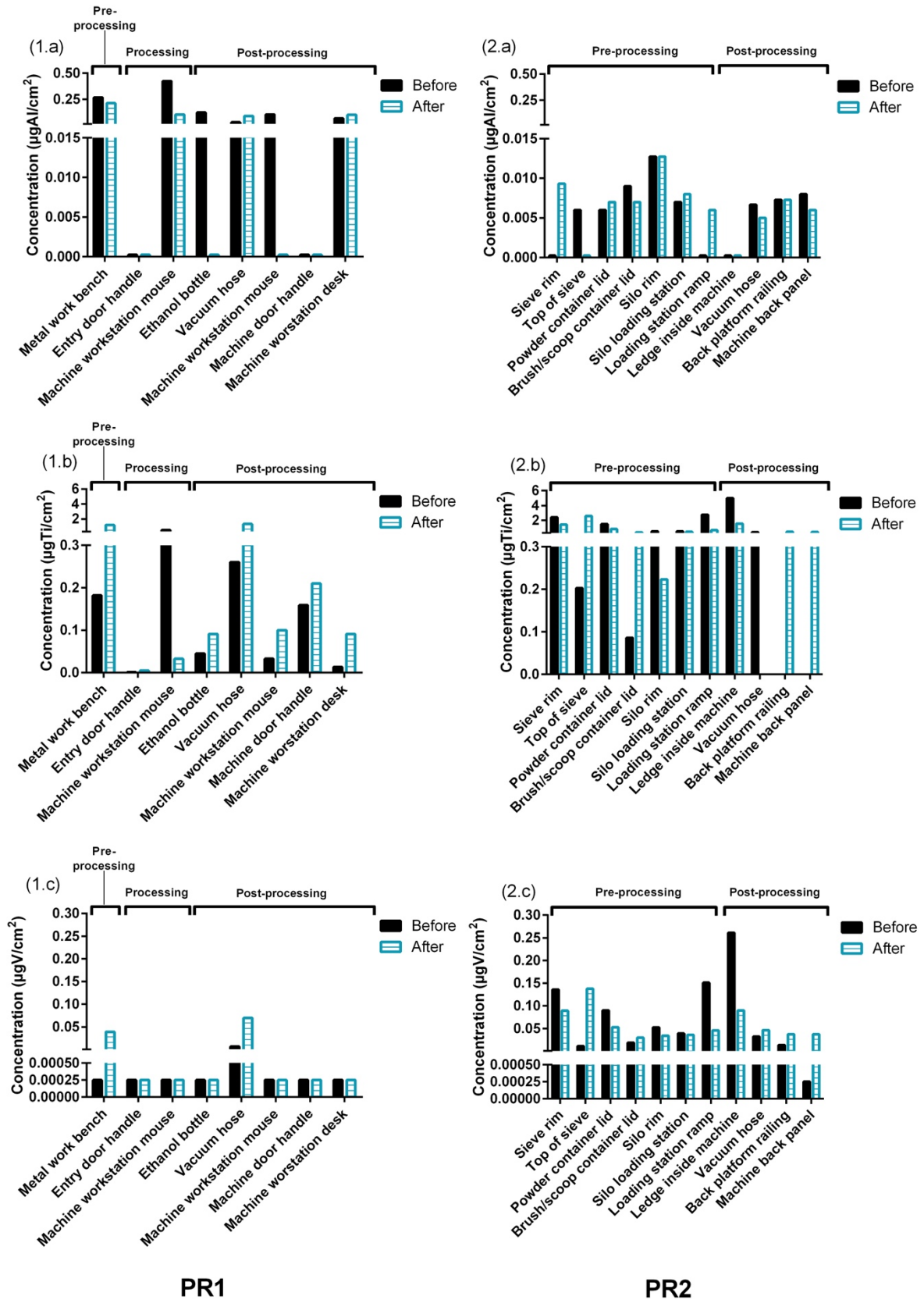


Fig. 2. Surface contamination from (a) aluminium, (b) titanium, and (c) vanadium before (single sample) and after (single sample) printing phases in (1) PR1 and (2) PR2 during PBF with Ti-6Al-4V.

Figure 2 shows that, for surfaces such as the workstation mouse (processing) in PR1 and the ledge inside the machine (post-processing) in PR2, contamination both existed before the printing phases began and occurred during these phases. Furthermore, Figure 3 shows that, when comparing the surface samples (sum of all reported metals) collected before specific printing phases with those collected after, significant differences were found on nine surfaces. Only two of these (22%), the vacuum hose and machine workstation desk in PR1, were found to be significantly more contaminated after post-processing than before; while seven surfaces (78%) all showed significantly more contamination prior to the relevant printing phases compared to after these phases.

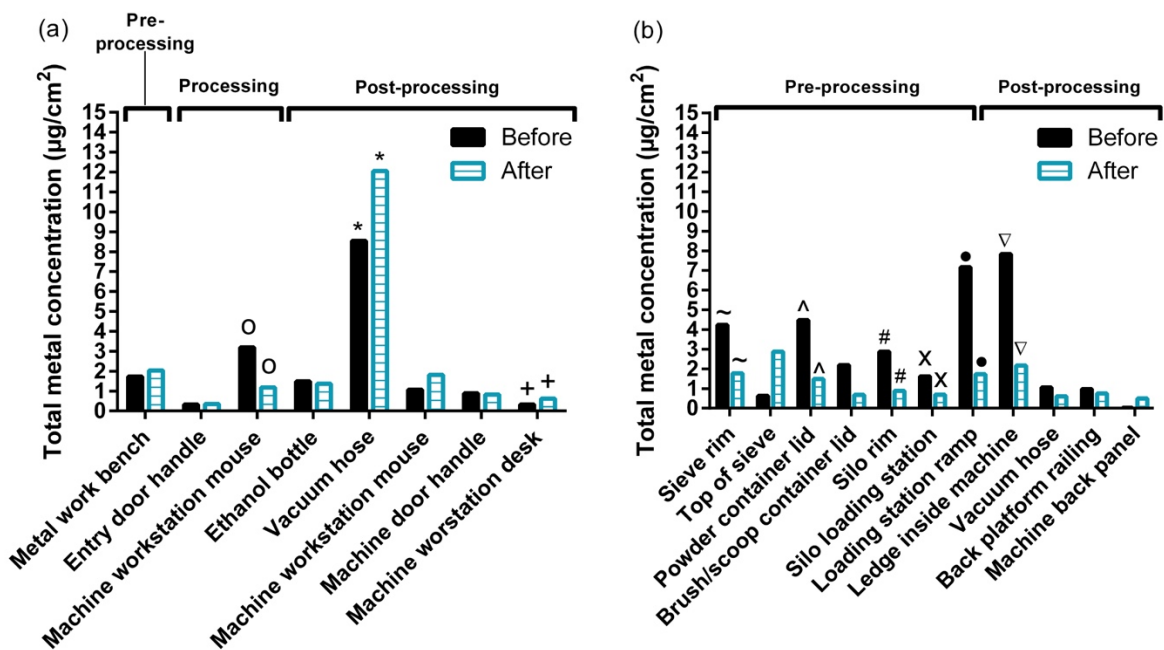


Fig. 3. Difference between total contamination (sum of all the metals for each surface) before printing phases and total contamination after printing phases from PBF with Ti-6Al-4V in (a) PR1 and (b) PR2. °, *, +, ~, ^, #, x, •, and ∇ indicate statistically significant differences ($p \leq 0.05$).

Surface contamination with metals was also found in non-printing areas: aluminium (BDL-0.172 µg/cm²), cobalt (BDL-0.034 µg/cm²), chromium (BDL-0.004 µg/cm²), iron (BDL-0.824 µg/cm²), nickel (BDL-0.064 µg/cm²), titanium (BDL-0.032 µg/cm²), and vanadium (BDL). Surface concentrations of cobalt, chromium, iron, nickel, titanium, and vanadium were significantly higher ($p \leq 0.05$) in PR1 compared to associated non-printing rooms, and surface concentrations of chromium, iron, and titanium were significantly higher in PR2 compared to associated non-printing rooms.

Discussion

During PBF with Ti-6Al-4V, AM surfaces were found to be contaminated with metal powders as

indicated in Table 1. In PR1, aluminium was found in the highest concentrations on top of the machine while titanium and vanadium were found in the highest concentrations on the vacuum hose. Such contamination is likely the result of deposition of suspended particulates. In PR2, aluminium was found in the highest concentrations on the silo rim, while titanium and vanadium were found in the highest concentrations on the ledge inside the machine. This contamination might have been caused by emission from the powder container (spillage) and deposition of suspended particles.

Surface contamination by aluminium, titanium, and vanadium was anticipated, however, the results indicate that an additional 12 metals (of which cobalt, chromium, iron, and nickel were reported) were present at detectable concentrations on AM surfaces. The presence of these non-Ti-6Al-4V metals indicates contamination by other workplace activities. Moreover, Figure 3 shows that significant contamination existed prior to the different printing phases and was likely the result of previous builds. The extent to which other workplace activities and previous builds contribute to overall surface contamination during PBF with Ti-6Al-4V is highlighted by the fact that iron, chromium, nickel, and titanium were on average (GM) found in the highest concentrations in the printing rooms (Table 1). As a consequence of this pre-existing and cumulative contamination, workers might have been at greater risk of exposure than was anticipated, indicating a need to re-evaluate existing cleaning procedures, especially those pertaining to cleaning after each build. PR1 was used for builds with either Ti-6Al-4V or maraging steel, an iron-nickel based metal alloy that also contains cobalt, molybdenum, titanium, aluminium, chromium, copper, and manganese. Without effective or sufficient cleaning protocols, the use of maraging steel in the same machine that is used for Ti-6Al-4V would account for the high concentrations of cobalt, chromium, iron, and nickel found on surfaces during AM with Ti-6Al-4V (EOS, 2011). Additionally, while titanium, aluminium, and vanadium have limited health effects and existing control measures may be sufficient to prevent or mitigate adverse health effects resulting from exposure to these metals, contamination from previous printing processes indicates the possibility of potential exposure to more toxic metals such as nickel, chromium, and cobalt, three potent dermal sensitizers (Day *et al.*, 2009). Only Ti-6Al-4V was used in PR2, however, indicating that the presence of non-Ti-6Al-4V metals in this room as shown in the results, would not be expected and would place workers at risk of exposure-related health effects, such as hypersensitivity reactions. The source of these non-Ti-6Al-4V component metals was unclear. Nickel, chromium, and cobalt are also respiratory sensitizers (Fernández-Nieto *et al.*, 2006) and are classified as Group 1 human carcinogens (nickel and hexavalent chromium) (IARC, 2012) and Group 2B, possible human carcinogens (cobalt) (IARC, 2006).

In addition to primary exposure in the workplace, contaminated surfaces may become secondary sources of potential worker exposure through inhalation, dermal contact, and ingestion.

Inhalation exposure may follow resuspension of settled particulates (Boeniger, 2006). Opening and closing the machine door in PR1 might have caused particulate resuspension from the top of the machine, which was contaminated. In PR2, the open external door and windows might have allowed uncontrolled air flow through the room and might have caused resuspension of surface contaminants. The operator in PR1 wore a respirator during AM activities but was observed placing the respirator onto the contaminated wooden work bench, potentially resulting in unknown contamination of the respirator's inner surfaces (Rawson *et al.*, 2005). During post-processing in PR2, only the primary operator wore a respirator. Two other workers were present in PR2; one wore a dust mask intermittently and the second wore no respiratory protection. Deposition of resuspended particulates onto skin and clothing, and contact with contaminated surfaces while not wearing protective clothing would have the potential to cause dermal exposure (Schneider *et al.*, 1999). Processing activities in PR1 involved contact with the contaminated workstation mouse, and in PR2 involved contact with the contaminated control panel, and in both instances the operators did not wear gloves. The operator in PR2 climbed into the PBF machine without gloves, bracing his hands on the contaminated ledge inside the machine. Furthermore, operators in both PR1 and PR2, handled personal cellular phones after handling contaminated equipment. This might have led to contamination of these devices which might have subsequently resulted in dermal contact exposure when the operators were no longer wearing gloves. Activities that presented risk of dermal contact exposure may also have increased the risk of incidental ingestion exposure through hand- or object-to-mouth worker behaviour (Gorman Ng *et al.*, 2014).

The presence of metal powders on surfaces in non-printing rooms, confirms the existence of 'hidden' exposure points as described in Badenhorst (2007). This contamination might have resulted from contact transfer with contaminated skin, clothing, and/or personal items.

The results of this study indicate a need for re-evaluation of cleaning and containment protocols. Surface contamination associated with PBF may be reduced through improvement of existing extraction ventilation or installation of more effective ventilation. Additionally, implementation of new or improved cleaning and containment protocols could help reduce surface contamination. Contaminated surfaces not included in cleaning schedules, for example, the top of the machine in PR1, should be included and surfaces likely to become contaminated during a single printing process should be cleaned after every build. Furthermore, surfaces cleaned with dry methods (sweeping or dusting) should be cleaned with liquid agents to aid in removal of metal powders and to minimise resuspension and redistribution of particles. Potential exposure can also be reduced by improving worker behaviour through information and training/retraining on: proper use, donning, and doffing of PPE, the potential for surfaces and PPE to become contaminated, the importance of minimising contaminant transfer, and potential adverse health effects that may arise from exposure to metal powders.

Conclusions

At AM facilities, PBF with Ti-6Al-4V led to contamination of printing and non-printing rooms with titanium, aluminium, and vanadium. Furthermore, contamination with metals, including sensitising metals, from previous activities and builds or from other sources, was found to have occurred. Surface contamination can lead to potential inhalation, dermal, and ingestion exposure. Overall, the existence of surface contamination at the AM facilities indicates a need to re-evaluate and improve the current methods of mitigation or control of contamination with metal powders, especially considering the potential adverse health effects, such as sensitisation and cancer, associated with exposure to the selected metals.

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Chapter 5: Conclusion

5.1 Background

Until recently, additive manufacturing (AM) with metal powders was mostly used for research purposes although it found application in specialised fields such as aerospace and biomedicine (Wohlers and Caffrey, 2015). The use of metal powders with AM enables the production of parts with a unique set of characteristics. AM processes, such as powder bed fusion (PBF) and directed energy deposition (DED) allow for more intricate designs and customisation of parts than traditional manufacturing (Gong *et al.*, 2014), and metal alloy powders, such as maraging steel, stainless steel, and titanium-6aluminium-4vanadium (Ti-6Al-4V), are used for their strength, resistance to corrosion, and durability, among other beneficial properties (Kostov and Friedrich, 2006; Baddoo, 2008; Kempen *et al.*, 2011; Prasad *et al.*, 2015). In occupational hygiene, it is important to thoroughly assess the workplace to determine the extent of potential worker exposure to a variety of health hazards as a result of the workers' activities, or even just their presence, in that workplace (Department of Labour, 1993). Contaminated surfaces may contribute to overall worker exposure by producing secondary exposure possibilities. There are various ways in which surfaces can become contaminated, including emission from the source, deposition from the air, and contact transfer (redistribution from other contaminated surfaces and removal from contaminated skin or clothing). Additionally, there are numerous ways in which contaminated surfaces may lead to exposure including, but not limited to, resuspension of settled contaminants (inhalation), direct contact with contaminated surfaces (dermal), and contaminated object-to-mouth actions (ingestion) (Schneider *et al.*, 1999; Badenhorst, 2007). While surface contamination from metals has been investigated in other industries, such as the cemented tungsten carbide industry (Day *et al.*, 2009), this study is the first to investigate surface contamination from use of maraging steel, stainless steel, and Ti-6Al-4V powders in AM.

5.2 Main findings

The results of this study show that detectable concentrations of 16 powdered metals were found to be present on surfaces in printing rooms and also in non-printing rooms at the AM facilities. These metal powders were aluminium (Al) (below detection limit [BDL]-42.422 $\mu\text{g}/\text{cm}^2$), calcium (Ca) (BDL-22.553 $\mu\text{g}/\text{cm}^2$), cadmium (Cd) (BDL-0.051 $\mu\text{g}/\text{cm}^2$), cobalt (Co) (BDL-66.741 $\mu\text{g}/\text{cm}^2$), chromium (Cr) (BDL-132.727 $\mu\text{g}/\text{cm}^2$), copper (Cu) (BDL-3.84 $\mu\text{g}/\text{cm}^2$), iron (Fe) (BDL-1072.28 $\mu\text{g}/\text{cm}^2$), magnesium (Mg) (BDL-0.351 $\mu\text{g}/\text{cm}^2$), manganese (Mn) (BDL-3.625 $\mu\text{g}/\text{cm}^2$), molybdenum (Mo) (BDL-22.943 $\mu\text{g}/\text{cm}^2$), nickel (Ni) (BDL-77.539 $\mu\text{g}/\text{cm}^2$), lead (Pb) (BDL-0.311 $\mu\text{g}/\text{cm}^2$), tin (Sn) (BDL-0.217 $\mu\text{g}/\text{cm}^2$), titanium (Ti) (BDL-8.0 $\mu\text{g}/\text{cm}^2$), vanadium (V) (BDL-0.538 $\mu\text{g}/\text{cm}^2$), and zinc (BDL-1.175 $\mu\text{g}/\text{cm}^2$). It should be noted that this list of detected metals includes the potent sensitisers nickel, chromium, and cobalt (Day *et al.*, 2009). This study reported the results for the major maraging steel and stainless steel component metals (Al, Co, Cr, Fe, and

Ni) (Chapter 3), as well as the component metals in the Ti-6Al-4V alloy (Chapter 4). Selected surfaces in the printing rooms were sampled before and after each of the three printing phases: pre-processing, processing, and post-processing. On 14 of the surfaces for which these two samples were collected, significant differences were found between the surface concentrations of metal powders before the printing phases and the surface concentrations after the printing phases. Of these 14 surfaces, 21% became significantly more contaminated during the printing phases compared to before. For the remaining 79%, significantly more contamination existed prior to the printing phases than that which occurred during these phases. Quantifiable concentrations of metal powders were also found on surfaces in general or non-printing areas of the AM facilities, including offices, kitchens, and breakrooms. This surface contamination was significantly lower than that found in printing rooms (see Table 3 of Chapter 3 and results of Chapter 4). The presence of metal powders on AM surfaces indicates that existing controls for minimising contamination of these surfaces during AM activities are insufficient. The presence of metal powders on surfaces prior to printing phases indicates that the existing cleaning procedures are insufficient. The presence of metal powders on non-printing room surfaces indicates that existing containment protocols are insufficient. Thus, reassessment of existing control measures, cleaning procedures, and containment protocols is necessary at the AM facilities.

The hypothesis of this study stated that detectable concentrations of metal powder, such as aluminium, chromium, cobalt, iron, manganese, molybdenum, nickel, titanium, and vanadium are present on surfaces which workers come into contact with at the AM facilities. This hypothesis is accepted based on the results indicating detectable concentrations of the metal powders on surfaces in both printing and non-printing rooms at the AM facilities.

5.3 Further discussion

As discussed in previous chapters, there were several methods (described by Schneider *et al.*, 2000) through which surfaces at the AM facilities became contaminated: source emission, airborne particulate deposition, redistribution from contaminated surfaces, and removal from contaminated skin and clothing. The highest risk of contamination occurred during loading of the AM machines with metal powders (pre-processing) and separating the printed part from the surrounding material (post-processing). However, the results indicate that surface contamination was present during all three printing phases (Tables 1 and 2 of Chapter 3 and Table 1 of Chapter 4), demonstrating that surface contamination presents the potential risk of exposure throughout the entire build procedure. Additionally, the presence of pre-existing surface contamination (before the start of printing phases) (Figures 1, 2, and 3 of Chapter 3 and Figures 2 and 3 of Chapter 4) and the presence of non-Ti-6Al-4V component metals in printing room one (PR1) and printing room two (PR2) (Table 1 of Chapter 4) indicate cumulative contamination. This

contamination may be from non-build-related activities and/or previous builds and suggests that current cleaning practices are insufficient. In PR1, this contamination with non-Ti-6Al-4V component metals might have been the result of previous builds as maraging steel is also used in this printing room. In PR2, Ti-6Al-4V was the only metal alloy used. Thus, any contamination with other metals may be the result of airborne or contact transfer contamination from other printing rooms where different metals are used. Contamination of surfaces in PR2 with non-Ti-6Al-4V component metals might not have been anticipated during the planning and implementation of controls thus existing control measures may be insufficient to protect against these metals.

5.3.1 Surface contamination with metal powders and potential worker exposure

In occupational hygiene, the significance of contaminated surfaces, as found during AM with metal alloy powders, lies in their ability to act as sources of inhalation, dermal, and ingestion exposure (Schneider *et al.*, 1999) and potential for such worker exposure was observed at each AM facility as discussed below.

5.3.1.1 Inhalation exposure

At the AM facilities, operators only wore respiratory protective equipment intermittently while in printing rooms, typically only during pre-processing and post-processing when the risk of primary inhalation exposure (direct emissions from the source into the air) was the greatest. However, air currents caused by opening and closing of entry doors, the presence of open external doors and windows (PR2), and the use of vacuum cleaners might have caused settled metal powders to become resuspended. Mechanical resuspension of settled particulates from activities such as opening and closing the machine doors, and from the oscillating action of the sieve in PR2 might have also occurred. The accumulation of surface contamination, as was found at the AM facilities, increased the quantity of contaminants that were available to become airborne and the occurrence of particulate resuspension was not necessarily limited to during pre- and post-processing when respiratory protective equipment was worn. Thus, surface contamination created the risk of potential inhalation exposure at the AM facilities throughout the entire printing process. Moreover, reducing the extent of surface contamination would reduce the potential for inhalation exposure.

5.3.1.2 Dermal exposure

In the printing room where stainless steel (an alloy containing dermal sensitisers) was used, the operator did not wear gloves during any of the three printing phases and in the printing rooms where maraging steel (an alloy containing dermal sensitisers) and/or Ti-6Al-4V were used, operators wore gloves intermittently during pre- and post-processing but did not wear gloves during processing. The fact that processing typically excludes direct or obvious contact with primary sources of contaminants may explain the lack of protective clothing used during processing. The results, however, indicate that surface contamination was found during all three printing phases and cumulative contamination from previous processes or other activities may not be considered when handling objects or touching surfaces not directly involved in the printing process. Thus, surface contamination created opportunities of potential dermal exposure, which also increases the risk of ingestion exposure (hand-to-mouth actions) (Gorman Ng *et al.*, 2014). Therefore, a reduction in surface contamination would reduce the risk of potential dermal and ingestion exposure.

5.3.2 Health implications should exposure to surface contaminants occur

The implications of possible exposure depend on the type of metal and its associated exposure routes and toxicities (Tokar *et al.*, 2013). The risk of exposure to maraging steel and stainless steel powders has been discussed in previous chapters (in sections 2.4 and 2.5 of Chapter 2 and in Chapter 3). It is noteworthy that, despite AM being a mostly research-based technology, the concentrations of nickel, chromium, and cobalt found during PBF with maraging steel and DED with stainless steel (Chapter 3) were comparable to those reported in the cemented tungsten carbide industry (Day *et al.*, 2009). This suggests that the workers at the AM facilities are potentially exposed to industrial levels of metal powders which have been associated with a number of toxicities. Based on the toxicokinetics of aluminium, titanium, and vanadium (discussed in detail in section 2.6 of Chapter 2 and in Chapter 4), inhalation would appear to be the exposure route of most concern during PBF with Ti-6Al-4V. However, the results indicate that other metals, including the dermal and respiratory sensitisers nickel, chromium, and cobalt, were also found on surfaces during the Ti-6Al-4V builds.

Surface wipe sampling at the AM facilities showed that the presence of surface contamination in this industry has the potential to influence overall worker exposure. Additionally, the results of this study provided enough information to make recommendations which may limit the amount of surface contamination and minimise potential worker exposure.

5.4 Recommendations

There are two main approaches to minimising the risk of exposure associated with surface contamination: (1) to reduce contamination of surfaces by means of elimination, substitution, and engineering controls and (2) to reduce the chance of exposure at the level of the worker with the use of administrative controls and PPE. Based on the hierarchy of controls, elimination should be implemented first, followed by substitution, engineering controls, administrative controls, and finally PPE (HSE, 2013). Engineering controls are often costly, therefore, before they are implemented, a thorough cost-benefit analysis should be carried out. This analysis should take into account the effectiveness of these controls in each particular workplace as not all workplaces are designed in a way that would allow optimal benefit from installation of engineering controls. Additionally, although administrative controls and PPE may require a lower initial investment, the employer should consider the cost over time as PPE will need to be supplied per employee as opposed to per workplace, and will also need to be replaced at regular intervals. Another factor that should be taken into account by the employer is that the effectiveness of administrative controls and PPE are dependent on proper use and worker cooperation which cannot always be ensured. However, should the results of the cost-benefit analysis indicate that improved administrative controls and PPE would provide the same benefit as engineering controls, then these administrative controls and PPE may be the more appropriate option. Additionally, as cleaning protocols and PPE are already implemented at the AM facilities, improving such controls would be less disruptive to work than, for example, the installation of new local extraction ventilation (LEV) systems.

5.4.1 Elimination and substitution

Since it is not possible to eliminate the use of metal powders, the number of surfaces which may become contaminated during AM processes could be reduced through the removal of all non-essential tools, furniture, and other items from the printing rooms, and the removal of portable equipment from the room when it is not in use. In addition, items that need to be stored should be stored in separate rooms so as to limit their contamination and reduce the possibility of the storage shelves and tables becoming contaminated. However, it is important that separation of printing and storage rooms does not break containment protocols and cause transfer of contaminants to ingress and egress areas between the printing and storage rooms, such as hallways. To reduce the number of contaminated surfaces the operator may come into contact with during the AM activities, method substitutions could be employed. This includes pouring the metal powders (that do not require sieving) directly into the machine from the powder containers (using funnels to reduce airborne emissions) so as to eliminate the need for the powder scoops during pre-processing, and using suction methods, as opposed to brush and scoop methods, to remove powder from the machines after use.

5.4.2 Engineering controls

Isolation or enclosure of printing processes or workers would limit the area vulnerable to contamination and the number of people exposed to the metal powders during AM activities. LEV would reduce the amount of metal powders released into the work environment and therefore the amount of powder available to cause surface contamination. Printing room-specific engineering control recommendations are given below.

5.4.2.1 The printing room where maraging steel was used (Chapter 3)

- Install LEV. While the operators employ vacuum cleaners in the role of LEV, this is not ideal. The operator has to touch the vacuum hose during the printing phases, increasing the risk of transfer between the operator's hands and the vacuum hose. Additionally, the vacuum nozzle has a relatively small circumference and lacks a hood to increase the capture area. Movable LEV with an appropriate hood could be installed (Figure 1). This would then also allow the LEV to be moved around the room and used during other processes, such as handling the powder container.
- If LEV is not feasible, a non-spark vacuum cleaner could be used. The vacuum hose should have as few and as shallow grooves as possible so as to minimise collection of metal powders.
- General extraction ventilation that creates a negative pressure inside the printing room would prevent the flow of air, and therefore airborne particulates, out of the printing room.

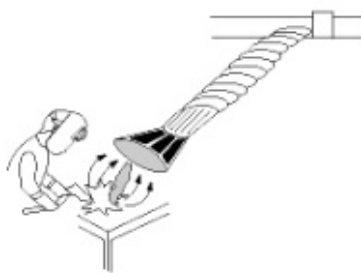


Fig. 1. Illustration of movable LEV (CCOHS, 2017).

5.4.2.2 The printing room where stainless steel was used (Chapter 3)

- Enclosure. The DED machine is controlled by a separate control panel. As such, the robotic arm and machine onto which the metal powder is deposited could be enclosed within the room to minimise the area that may be affected by the contaminants, especially airborne particulate deposition. An added benefit of enclosure will be to eliminate the

need for laser-protective eyewear as the enclosure can be fitted with specialised panels to prevent the laser from causing eye damage. However, the implications of such enclosure should be considered with regards to the required movement of the machine during operation as well as the cooling and extraction ventilation with which the enclosure may need to be provided.

- LEV. One of the most visible problems observed during DED with stainless steel was the large quantities of powder released onto the floor. LEV with a capturing hood should be installed below the machine onto which the stainless steel is deposited in order to minimise deposition contamination of the floor. This will, in turn, eliminate the potential of the particulates being 'walked' to other areas at the AM facility and will eliminate the need for sweeping which causes resuspension and potential dermal exposure as the broom handle was shown to be contaminated.
- General extraction ventilation as described in point five of section 5.4.2.1 could be installed.

5.4.2.3 PR1 in which Ti-6Al-4V was used (Chapter 4)

The PBF machine in PR1 is the same model as that used for maraging steel. Additionally, the layout of these two printing rooms is the same, except that there was no adjoining storage room in PR1. As such, the same local and general extraction ventilation engineering control recommendations apply as discussed in points three, four, and five of section 5.4.2.1.

5.4.2.4 PR2 in which Ti-6Al-4V was used (Chapter 4)

- The sieving station could be moved into a separate room in order to reduce the number of workers exposed during sieving.
- Enclosure. As the activities involved in processing in PR2 are, to a large extent, separate from pre- and post-processing activities, enclosure of the control station would minimise the amount of deposition contamination of the control panel and stool at the control station during pre- and post-processing.
- LEV with capture hoods could be installed next to the sieve and beside or below the silo loading station.
- Additionally, movable LEV with a capture hood (Figure 1) could be installed at the opening of the PBF machine so that it can be moved inside the machine during post-processing (operator works inside machine) but could be moved back out so that it would not interfere with closing the machine.

- General extraction ventilation should be installed so as to eliminate the need for natural ventilation as uncontrolled airflow created by the open external doors and windows causes resuspension of surface contaminants.

5.4.3 Administrative controls

5.4.3.1 Cleaning and containment

At the AM facilities, not all surfaces or areas were cleaned, and surfaces that were cleaned were not necessarily cleaned after every build. Improvement of cleaning protocols and containment procedures would eliminate or mitigate cumulative contamination and would decrease the chance of worker exposure from contaminated surfaces.

- Surfaces such as the top of the AM machines and AM machine panels should be included in regular cleaning schedules.
- The entire printing room should be thoroughly cleaned after each printing process, not just the surfaces directly involved with the AM activities or those which were obviously contaminated.
- Wet methods should be used over dry methods to improve removal of metal powders through chemical action as well as to minimise resuspension of contaminants. Wet methods include wiping surfaces with wetted cloths as opposed to dry cloths and wetting the floor before cleaning it, preferably using a vacuum cleaner rather than a broom. Furthermore, using a vacuum with a water filtration system will minimise resuspension of particles while emptying the vacuum cleaner.
- Dirty PPE should not be carried or worn to other areas at the AM facilities. Hooks should be provided outside the printing rooms on which operators may hang their dirty PPE. These hooks should not be placed inside the printing rooms as this could lead to contamination of inner surfaces of PPE.
- Proper changing facilities should be provided where the workers can remove dirty PPE without contaminating other areas of the AM facilities.
- The employer must provide supervision to ensure that workers adhere to protocols.

5.4.3.2 Information and training

It is important, and indeed legally required as per the Hazardous Chemical Substances (HCSs) Regulations (Department of Labour, 1995), for workers to be informed regarding the nature of their potential risk and the methods by which they are protected. Information and training sessions should be provided, according to the HCSs Regulations, at the start of employment and

henceforth at regular intervals, as defined by the health and safety committee, and should cover the following:

- The potential sources of exposure, including contaminated surfaces.
- The potential adverse health effects associated with the metal powders to which AM operators are potentially exposed.
- The available control measures, such as LEV, and the proper use and maintenance thereof.
- The purpose of the provided PPE.
- The proper use, donning, and doffing of PPE.
- The potential for inner surfaces of PPE to become contaminated and how this may occur (placing PPE onto contaminated surfaces).
- Proper storage of PPE (facilities should be provided by employer).
- The risk of contamination of personal items brought into the printing rooms.
- Proper cleaning and personal hygiene protocols.

5.4.4 PPE

5.4.4.1 The printing rooms where maraging and stainless steel are used (Chapter 3)

Maraging steel and stainless steel contain dermal and respiratory sensitising metals. As such, it is important that the following PPE should be provided for all persons working in the printing rooms:

- A full-face P3 particulate respirator should be supplied as per the material safety data sheet (MSDS) for maraging steel (SDS, 2016b) and the MSDS for stainless steel (SDS, 2016a).
 - This is recommended for the operators working with maraging steel as the machine door opens at a height in line with the operator's upper body and head, and the operator often leans towards the opening of the machine. Thus, the operator requires dermal and respiratory face protection.
 - This respirator is recommended for the operator working with stainless steel as the operator crouches down near the machine during processing. Thus, the operator requires dermal and respiratory face protection.
- Alternatively, if the full-face respirator is not feasible, a half-face FFP3 particulate respirator may be used (SDS, 2016a), although this would provide less protection, especially against the dermal hazards associated with maraging and stainless steel.
- A face shield or safety goggles (SDS, 2016a; SDS, 2016b) should be used with the half-face respirator if the full-face respirator is not feasible.

- Protective full-length overalls. The safety data sheets for maraging and stainless steel (SDS, 2016a; SDS, 2016b) recommend fire-resistant cotton or an equivalent material. The overalls should have cinched cuffs, high collars (buttoned or otherwise closed up), and cinched hoods. This is recommended for the same reasons as given for the full-face respirator.
- Work boots to be worn instead of personal shoes.
- Nitrile rubber gloves (SDS, 2016a; SDS, 2016b) worn so that the cuffs of the gloves cover the cuffs of the protective coat.

5.4.4.2 PR1 in which Ti-6Al-4V is used (Chapter 4)

The PPE recommended in section 5.4.4.1 should also be provided for persons working in PR1 until such a time as the contamination caused by previous builds with maraging steel can be controlled sufficiently to ensure that no metals from the maraging steel build can be found on surfaces when printing with Ti-6Al-4V. Once this contamination from previous print jobs has been eliminated, the following PPE should be provided:

- Dust masks or apparatus with a filtering face-piece (FFP) of at least one (FFP1) are recommended (SDS, 2015).
- Tightly sealed safety glasses or chemical goggles (SDS, 2015).
- Nitrile gloves (SDS, 2015) to prevent transfer of contaminants to non-printing areas. Gloves should be removed before leaving the printing room.
- Laboratory coats or working overalls.

5.4.4.3 PR2 in which Ti-6Al-4V is used (Chapter 4)

The PPE listed in section 5.4.5.1 should also be used by persons working in PR2 until such a time as the source of metals other than aluminium, titanium, and vanadium can be identified and eliminated. Once the source of these non-Ti-6Al-4V component metals has been eliminated, the following PPE should be provided for operators while working inside the machine:

- Quarter- or half-face P3 particulate respirators.
- Nitrile gloves (SDS, 2015) to limit transfer of contaminants to other areas. To be effective in this regard, gloves should be changed when moving from activities that involve direct contact with metal powders, such as sieving the powder, to those which involve indirect contact with metal powder, such as operating the machine from the control panel. Additionally, gloves should be removed completely before leaving the printing room.
- Tightly sealed safety glasses or chemical goggles (SDS, 2015).

- Working overalls, the safety data sheet (SDS) (2015) recommends antistatic material to limit contamination of personal clothing.
- Work boots to be worn instead of personal shoes to prevent contamination of personal shoes.

And the following should be provided for operators while not working inside the machine (during pre-processing and processing):

- Dust masks or apparatus of at least FFP1 (SDS, 2015).
- Nitrile gloves (SDS, 2015).
- Laboratory coats or working overalls (SDS, 2015).

5.5 Limitations

This study is limited by the number of samples collected. This prevented the determination of significant differences in concentrations of individual metal powders between samples collected before printing phases and samples collected after those phases. The fact that only some of the surfaces were sampled prior to and following printing phases limits the comparisons that can be made between surfaces that were sampled once and those that were sampled twice.

5.6 Future studies

- This study was designed to determine if detectable amounts of metal powders were present on surfaces at AM facilities. As such contamination was found, surface sampling for metal powders at AM facilities should be performed on a larger scale (greater number of samples) in order to reinforce the conclusions drawn in this study. Additionally, results from larger scale studies may be more applicable to the specific AM process or AM as a whole.
- Additionally, further research may provide insight into the relationship between surface contamination and worker exposure. This is important because workers are not necessarily exposed to contaminants that are on surfaces and the extent of exposure will not necessarily correlate to the amount of contamination found on surfaces.
- As this study indicated that surface concentration from metal powders was comparable with that of other, non-research-based industries, further investigations into surface contamination at AM facilities will allow comparisons to be made regarding exposure in AM and exposure in other industries.
- As dermal exposure to metal powders was observed, determination of the types and concentration of metals on the skin of AM workers may provide useful information regarding the risk associated with dermal exposure. Although not all metals found to be

present on surfaces at the AM facilities are able to permeate through the skin, dermal exposure sampling is still recommended as known dermal sensitisers were found to be present on AM surfaces.

- Additionally, as operators at AM facilities were potentially exposed to sensitising metals, it would be beneficial if future studies could investigate the prevalence of AM-related metal hypersensitivity.
- Further investigation would be required to identify the source of contamination by calcium, chromium, cobalt, copper, iron, lead, nickel, magnesium, manganese, molybdenum, tin, and zinc during PBF with Ti-6Al-4V in PR2 (Chapter 4).
- Once the recommended control measures are implemented, surface contamination at the AM facilities should be reassessed in order to determine the effectiveness of these new controls.

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Annexure

Table 1. Blank corrected concentrations for each of 16 metals per sample for all samples collected during this study.

		$\mu\text{g}/\text{cm}^2$															
Surface		Al	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Mo	Ni	Pb	Sn	Ti	V	Zn
PRINTING ROOM WHERE MARAGING STEEL WAS USED																	
Powder container	Before	0.3695	1.598	BDL	6.802	0.143	0.121	53.961	BDL	0.049	4.458	14.739	BDL	0.015	0.441	0.066	0.525
	After	1.4625	2.853	0.011	36.102	0.698	0.411	281.46	BDL	0.219	22.943	77.539	BDL	0.035	2.386	0.503	1.175
Machine workstation desk	Before	0.1265	0.523	BDL	0.414	0.009	0.049	3.451	BDL	0.015	0.293	0.8435	BDL	0.012	0.449	BDL	BDL
	After	0.0795	0.788	BDL	0.962	0.022	0.041	7.961	BDL	0.015	0.623	2.0485	BDL	BDL	0.065	BDL	0.34
Machine door handle	Before	0.1015	3.0525	BDL	0.612	0.007	0.012	4.931	BDL	0.007	0.407	1.3085	BDL	0.004	0.062	BDL	BDL
	After	0.0725	2.6525	BDL	0.189	BDL	0	1.531	BDL	BDL	0.116	0.3995	BDL	0.007	0.025	BDL	BDL
Entry door handle	Before	0.1056	2.8781	BDL	0.035	BDL	BDL	0.4525	BDL	BDL	0.02	0.0656	BDL	0	0.045	BDL	BDL
	After	0.0706	1.7219	BDL	0.0738	0.0075	BDL	0.5888	BDL	0.0075	0.0525	0.1269	BDL	0.0113	0.0138	BDL	BDL
Scoop handle	Before	0.635	12.841	BDL	2.4233	0.03	0.2067	18.87	BDL	0.0233	1.5467	5.2783	BDL	0.02	0.1467	BDL	0.6167
	After	0.4483	12.008	BDL	2.7067	0.02	0.0733	20.87	BDL	0.0233	1.7267	5.8783	BDL	0.0033	0.3367	0.0333	0.7667
Vacuum hose	Before	0.6857	2.318	0.0044	13.935	0.2831	0.1316	118.72	BDL	0.0949	9.2963	32.271	BDL	0.0279	1.2654	0.1735	0.4853
	After	0.268	1.7298	BDL	3.1963	0.0728	0.1265	24.898	0.0022	0.0279	2.3037	6.8665	BDL	0.0096	0.9309	0.0713	0.4301
Machine door handle	Before	0.0725	2.6525	BDL	0.189	BDL	0	1.531	BDL	BDL	0.116	0.3995	BDL	0.007	0.025	BDL	BDL
	After	BDL	7.1525	BDL	0.772	0.006	0.022	5.961	BDL	0.008	0.467	1.6735	BDL	BDL	0.092	0.005	0.35
Machine workstation mouse	Before	0.1238	4.5063	BDL	0.275	0.025	BDL	2.3525	BDL	BDL	0.18	0.5788	BDL	BDL	0.025	BDL	0.525
	After	0.2163	7.0063	BDL	1.805	0.02	0.035	14.028	BDL	0.0175	1.1625	3.9213	BDL	0.015	0.12	BDL	0.7167
Machine workstation handle		0.0788	0.906	BDL	0.2748	0.0057	0.0319	2.2171	BDL	0.0081	0.2633	0.5921	BDL	0.0062	0.06	BDL	0.0071
Top of entry door handle		0.0669	1.7781	BDL	0.02	BDL	BDL	0.4188	BDL	0.0438	0.0025	0.0306	BDL	BDL	0.005	BDL	BDL
Surface beside machine workstation		0.1435	BDL	BDL	2.222	0.039	0.136	11.411	BDL	0.04	1.468	3.1335	BDL	0	0.0275	0.207	BDL
Corner table		0.0105	BDL	BDL	1.052	0.007	0.044	8.011	BDL	0.01	1.213	2.5535	0.002	BDL	0.087	0.538	BDL
PRINTING ROOM ONE (PR1) WHERE TI-6AL-4V WAS USED																	
Metal work bench	Before	0.2675	1.0725	BDL	0.109	0.036	0	0.896	BDL	0.034	0.064	0.2435	BDL	0.007	0.182	BDL	BDL
	After	0.2135	1.4525	BDL	0.036	BDL	BDL	0.491	BDL	0.009	0.022	0.0735	0	0.006	1.181	0.039	BDL
Entry door handle	Before	BDL	6.6281	BDL	0.01	0.0113	0.0163	0.2813	0.0813	0.0088	0.0088	0.0194	BDL	0.005	0.0013	BDL	0.7938
	After	BDL	5.5656	BDL	0.0213	BDL	BDL	0.2938	0.0625	0.0075	0.005	0.0319	BDL	0.005	0.005	BDL	0.2313
Machine workstation mouse	Before	0.4238	4.2563	BDL	0.16	BDL	0.0675	1.7775	0.275	0.0225	0.145	0.3263	BDL	0.02	0.5025	BDL	0.55
	After	0.1063	4.8813	BDL	0.05	BDL	BDL	0.905	BDL	BDL	0.0375	0.0863	BDL	0.025	0.0325	BDL	0.3375
Ethanol bottle	Before	0.1255	1.6525	BDL	0.111	0.01	0.023	0.971	0.185	0.007	0.08	0.2245	0	0.011	0.045	BDL	0.265
	After	BDL	3.8525	BDL	0.112	BDL	0.004	0.926	BDL	BDL	0.081	0.2295	BDL	0.011	0.091	BDL	0.13
Vacuum hose	Before	0.0315	4.7435	BDL	0.7345	0.0138	0.0612	5.9147	0.1207	0.0147	0.4638	1.5806	BDL	0.0233	0.2603	0.0069	0.306
	After	0.0909	4.097	BDL	0.9543	0.0164	0.0647	7.5526	0.1164	0.0155	0.5931	2.0504	BDL	0.0164	1.3198	0.0698	0.4612

		$\mu\text{g}/\text{cm}^2$															
Surface		Al	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Mo	Ni	Pb	Sn	Ti	V	Zn
Machine workstation mouse	Before	0.1063	4.8812	BDL	005	BDL	BDL	0.7975	BDL	BDL	0.0375	0.0863	BDL	0.025	0.0325	BDL	0.3375
	After	BDL	11.756	BDL	0.08	0.0375	BDL	1.5275	BDL	0.0375	0.035	0.0738	BDL	BDL	0.1	BDL	0.1625
Machine door handle	Before	BDL	7.1025	BDL	0.048	BDL	0.051	0.611	BDL	0.0138	0.022	0.0675	BDL	0.013	0.159	BDL	0.255
	After	BDL	6.8525	BDL	0.038	0.006	0.022	0.496	BDL	0.0113	0.016	0.0765	BDL	0.002	0.21	BDL	0.27
Machine workstation desk	Before	0.0685	2.4025	BDL	0.02	BDL	BDL	0.182	0.13	BDL	0005	0.0345	BDL	0	0.013	BDL	0.29
	After	0.1035	3.8525	BDL	0.029	0.013	BDL	0.324	0.03	BDL	0.013	0.0505	BDL	0	0.091	BDL	0.365
Wooden work bench		0.3755	0.9925	BDL	0.3	0.017	0.025	2.766	BDL	0.03	0.19	0.6235	BDL	0.008	0.691	0.012	BDL
Top of machine		0.8175	22.553	BDL	3.282	0.053	0.644	27.211	0.34	0.098	2.148	7.0385	BDL	0.012	0.681	0.062	0.415
NON-PRINTING ROOM SURFACES ASSOCIATED WITH THE PRINTING ROOM WHERE MARAGING STEEL WAS USED AND PR1																	
Office desk (by mouse)		0.0895	2.3025	BDL	0.034	BDL	BDL	0.285	BDL	BDL	0.02	0.0635	BDL	BDL	0.031	BDL	0.295
Arm of desk chair		0.1722	3.6960	BDL	0.0273	BDL	0	0.3239	BDL	BDL	0.0193	0.0472	0	0.0125	0.0295	BDL	0.3182
Boardroom/tearoom entry door handle		0.0694	1.9531	BDL	BDL	BDL	BDL	0.1538	BDL	0.0375	BDL	0.0031	BDL	0.005	0.0013	BDL	BDL
Boardroom/tearoom table		0.0345	0.2875	BDL	0.017	BDL	BDL	0.127	BDL	BDL	0.007	0.0275	BDL	0.007	0.032	BDL	BDL
PRINTING ROOM WHERE STAINLESS STEEL WAS USED																	
Powder container	Before	0.375	1.2	BDL	0.354	0.705	0.01	5.58	BDL	0.033	0.089	0.993	BDL	BDL	0.006	-	BDL
	After	BDL	3.625	BDL	0.152	0.355	0.003	2.33	0.013	0.015	0079	0.261	BDL	BDL	0.009	-	BDL
Control panel	Before	9.522	1.825	0.027	26.741	70.477	0.289	427.28	BDL	2.203	15.275	26.993	BDL	0.113	1.755	-	0.357
	After	4.772	0.575	0.006	4.966	14.127	0.072	83.53	BDL	0.475	2.725	6.068	BDL	0.025	1.455	-	BDL
Floor 1 m away from machine	Before	35.922	4.7	0.012	15.566	23.052	0.647	132.28	0.038	0.72	3.83	19.578	BDL	0.04	8	-	BDL
	After	14.422	1.05	0.007	5.741	79.77	0.193	36.03	BDL	0.224	1.085	6.043	BDL	0.01	2.975	-	BDL
Floor directly below machine	Before	11.922	1.425	0.045	40.741	76.227	3.484	452.28	BDL	2.25	15.4	34.993	BDL	0.115	3.625	-	0.162
	After	0.717	BDL	0.051	66.741	132.73	0.357	1072.3	BDL	3.625	16.55	60.493	BDL	0.139	0.048	-	BDL
Powder input machine		5.022	2.675	0.021	21.766	56.477	0.204	352.28	0.003	1.475	12.1	23.793	BDL	0.092	0.603	-	0.237
Broom handle		0.4328	6.4063	BDL	0.214	0.138	0.1516	5.0859	0.1094	0.088	0.027	0.895	BDL	0.011	0.027	-	0.4953
Cleaning brush handle		13.6	8.269	BDL	1.463	3.033	0.0288	8.4712	BDL	0.048	0.058	3.246	BDL	BDL	0.933	-	BDL
Entry door handle		BDL	4.7917	BDL	0.058	0.031	0.0056	0.4167	BDL	0.017	0.017	0.208	BDL	BDL	BDL	-	BDL
Wooden shelves		1.035	1.025	BDL	0.596	1.077	0.424	68.33	0.02	0.187	0.138	35.243	BDL	0.042	0.049	-	0.282
Metal work surface		0.482	BDL	BDL	0.084	0.705	0.054	3.58	BDL	0.056	0.161	2.743	BDL	BDL	0.023	-	BDL
Wooden work bench		42.422	0.85	BDL	0.441	6.152	0.144	32.03	BDL	0.171	0.097	11.793	BDL	0.006	1.973	-	BDL
PRINTING ROOM TWO (PR2) WHERE TI-6AL-4V WAS USED																	
Sieve rim	Before	BDL	2.396	BDL	0.0133	0.0413	0.0106	1.6004	0.068	0.034	BDL	0.0307	BDL	BDL	2.412	0.136	0.1427
	After	0.0093	0.436	BDL	BDL	0.0147	BDL	0.2151	BDL	BDL	BDL	0.0027	BDL	BDL	1.452	0.0893	BDL

		µg/cm ²															
Surface		Al	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Mo	Ni	Pb	Sn	Ti	V	Zn
Top of sieve	Before	0.006	1.327	BDL	BDL	0.015	BDL	0.3963	BDL	0.0015	BDL	0.008	BDL	BDL	0.203	0.011	BDL
	After	BDL	1.127	BDL	0.006	0.011	BDL	0.1263	BDL	0.0225	0.002	0.002	BDL	0.001	2.599	0.138	BDL
Powder container lid	Before	0.006	2.087	BDL	0.006	0.045	0.003	2.8003	0.101	0.0645	BDL	0.021	BDL	0.217	1.509	0.09	0.073
	After	0.007	2.007	BDL	0.006	0.014	BDL	0.5753	BDL	0.0005	BDL	0.004	BDL	0.142	0.829	0.053	0.019
Brush/scoop container lid	Before	0.009	1.517	BDL	BDL	0.065	0.008	1.9803	0.351	0.0475	BDL	0.029	BDL	BDL	0.086	0.019	0.142
	After	0.007	1.117	BDL	BDL	0.011	BDL	0.2293	BDL	BDL	BDL	0.003	BDL	BDL	0.393	0.03	BDL
Silo rim	Before	0.0127	2.2855	BDL	BDL	0.0782	BDL	2.146	BDL	0.0464	BDL	0.0418	BDL	BDL	0.54	0.0527	BDL
	After	0.0127	3.7581	BDL	BDL	0.0309	BDL	0.5678	BDL	BDL	BDL	0.0146	BDL	BDL	0.2236	0.0345	BDL
Silo loading station	Before	0.007	2.467	BDL	BDL	0.027	0	1.0103	0.181	0.0195	0.013	0.014	BDL	BDL	0.524	0.039	0.341
	After	0.008	1.507	BDL	BDL	0.008	BDL	0.1693	BDL	BDL	0.001	0.004	BDL	BDL	0.462	0.036	0.008
Loading station ramp	Before	BDL	3.477	BDL	0.013	0.099	0.01	4.1003	0.211	0.0775	BDL	0.054	BDL	BDL	2.749	0.151	0.084
	After	0.006	1.107	BDL	0.008	0.027	BDL	0.9503	BDL	0.0065	BDL	0.009	BDL	BDL	0.677	0.046	BDL
Vacuum hose	Before	0.0067	2.0141	BDL	BDL	0.0333	BDL	0.5603	BDL	0.0071	BDL	0.0158	0.0125	BDL	0.4058	0.0325	0.0233
	After	0.005	0.1808	BDL	0.005	0.025	0.0008	0.5094	BDL	0.0013	0	0.0158	BDL	0.0275	BDL	0.0467	BDL
Back platform railing	Before	0.0073	4.2573	BDL	0.0073	0.0292	BDL	0.9055	BDL	0.0162	BDL	0.0104	0.3115	BDL	BDL	0.0135	BDL
	After	0.0073	BDL	BDL	BDL	0.0104	BDL	0.2159	BDL	BDL	BDL	BDL	0.0198	BDL	0.4802	0.0375	BDL
Machine back panel	Before	0.008	0.757	BDL	BDL	0.005	BDL	BDL	0.031	BDL	0.002	0	BDL	BDL	BDL	BDL	BDL
	After	0.006	BDL	BDL	BDL	0.008	BDL	BDL	BDL	BDL	BDL	0.001	BDL	BDL	0.442	0.034	BDL
Ledge inside machine	Before	BDL	BDL	BDL	0.031	0.155	0.022	2.3403	0.091	0.0185	BDL	0.063	BDL	BDL	4.989	0.261	0.028
	After	BDL	BDL	BDL	0.013	0.03	BDL	0.4623	0.031	BDL	0.007	0.009	BDL	BDL	1.569	0.09	BDL
Control panel railing		BDL	3.424	BDL	BDL	0.0354	BDL	0.1534	BDL	BDL	BDL	0.0042	0.0615	BDL	BDL	0.0073	BDL
Control panel		BDL	1.537	BDL	BDL	0.017	BDL	0.4323	0.001	0.0355	BDL	0.007	BDL	BDL	BDL	BDL	BDL
Entry door handle		BDL	5.1018	BDL	BDL	0.0268	0	0.3577	0.1268	BDL	BDL	0.0018	BDL	BDL	BDL	BDL	0.05
Powder storage shelves		BDL	3.467	BDL	BDL	0.039	0.02	4.8803	0.301	0.0625	BDL	0.016	BDL	0.014	BDL	0.019	0.077
Machine door handle		0.0146	6.9729	BDL	0.0146	0.4292	0.1146	7.8965	0.2521	0.126	BDL	0.1771	0.1417	0.075	0.0229	0.0333	0.2167
NON-PRINTING ROOM SURFACES ASSOCIATED WITH THE PRINTING ROOM WHERE STAINLESS STEEL WAS USED AND PR2																	
Kitchen counter		0.052	BDL	BDL	0.01	0.004	BDL	0.04	BDL	0.009	BDL	0.018	BDL	BDL	BDL	-	BDL
Coffee tin		BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	-	BDL
Office desk		0.016	0.9	BDL	0.002	BDL	0	0.2	BDL	0.012	0.006	0.019	BDL	BDL	BDL	-	BDL