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october 2022

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UMinho | 2022

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Doctoral Thesis
Doctoral Program in Industrial and Systems Engineering
Industrial and Systems Engineering

Work carried out under the supervision of
Prof. Dr. Pedro Miguel Ferreira Martins Arezes
Dr. Francisco António Coelho da Silva

October 2022

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ACKNOWLEDGEMENTS

I could not have undertaken this journey without Pedro Arezes and Francisco Silva. I am very grateful for their crucial support, valuable advice and for sharing their knowledge.

I would like to express my gratitude to CATIM (Technological Centre for the Metalworking Industry) for encouraging me to study and to learn more, and for supporting me throughout this process. I would like to extend my sincere thanks to my department colleagues (and friends) from AHS, for their help and encouragement.

A special thanks to Matilde Rodrigues and Paul Swuste, with whom I had my first talk about this PhD in Prague, in 2017.

I am also thankful to CTCV (Technological Centre for Ceramics and Glass) for providing the necessary equipment for the monitoring campaigns, and to all the organizations that participated in the case studies.

I would also like to express my deepest appreciation to the Ergonomics & Human Factors Research Group, from ALGORITMI Research Centre, for their help and support.

I am also grateful to Fátima Magalhães, for helping me through and for making this experience easier and more pleasant.

Lastly, words cannot express my gratitude to my family, from Portugal and Ukraine. A special acknowledgment to my parents, Paulo and Fátima, and my sister Sofia, for their endless support and motivation. And finally, to my husband, Dmytro Maslov, for believing in me, encouraging me and inspiring me every day.

STATEMENT OF INTEGRITY

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RESUMO

A manufatura aditiva, também chamada impressão 3D, de metais deixou de ser um processo de prototipagem e está agora integrada em diversas indústrias, com trabalhadores alocados a estes postos de trabalho. Esta tecnologia emergente apresenta diversos riscos ocupacionais, nomeadamente a exposição dos trabalhadores a nanomateriais incidentais libertados durante este processo de manufatura. Estudos recentes evidenciam a libertação de nano-objetos e muitas têm sido as abordagens utilizadas para estudar a exposição aos mesmos. Alguns autores optam por uma abordagem quantitativa, que inclui a utilização de equipamentos de leitura direta, análise laboratoriais às características físico-químicas das emissões e/ou indicadores biológicos. Foram ainda publicados alguns estudos com uma abordagem qualitativa, nomeadamente a aplicação de métodos baseados na abordagem por bandas de controlo. Independentemente do tipo de abordagem, tem havido lugar a descobertas relevantes neste campo ainda pouco explorado. No entanto, estes estudos revelam também algumas limitações e pouco se sabe ainda acerca do controlo adequado deste risco.

Motivada pela necessidade e importância de gerir o risco nestes postos de trabalho e de proteger os trabalhadores envolvidos, esta tese debruçou-se sobre o estado-da-arte e teve como principal questão de investigação qual a abordagem a adotar para gerir o risco ocupacional de exposição a nanomateriais incidentais na impressão 3D de metais. Para esse efeito, foram testadas diferentes abordagens em casos de estudo, culminando na criação de um método de gestão do risco ocupacional de exposição a nanomateriais incidentais na impressão 3D de metal, intitulado IN Nanotool. Esta ferramenta, baseada no CB, permite alcançar um nível de risco, com base na pontuação atribuída a diferentes fatores de risco quer na banda de perigo, quer na de exposição. A IN Nanotool fornece ainda recomendações para o controlo do risco, propondo assim uma solução para a abordagem a ter na gestão deste risco ocupacional. Esta ferramenta foi testada num caso de estudo concreto, apresentando resultados coerentes com o estado-da-arte e mostrando-se promissora. Não obstante, este método carece de mais aplicações práticas e de validação, apresentando algumas limitações também exploradas no decorrer da presente tese.

Palavras-chave: exposição ocupacional; gestão do risco; manufatura aditiva de metais; nanomateriais incidentais

ABSTRACT

Additive manufacturing, also known as 3D printing, of metals is no longer a prototyping process and is now integrated in several industries, with workers allocated to these workplaces. This emerging technology presents various occupational hazards, namely the exposure of workers to incidental nanomaterials (INM) released during this manufacturing process. Recent studies show this release of nano-objects and many approaches have been used to study exposure to these INM. Some authors prefer quantitative approaches, including the use of direct reading equipment, laboratory analysis of the physicochemical characteristics of emissions and/or biological indicators. Other studies provided a qualitative approach, namely the application of methods based on control banding. Regardless of the type of approach, relevant discoveries have been made in this still unexplored field. However, these studies also reveal some limitations, and little is known about the adequate control of this risk.

Motivated by the need and the importance of managing risk in these workplaces and protecting the workers involved, this thesis focused on the state-of-the-art and had as main research question what approach to adopt to manage the occupational risk exposure to incidental nanomaterials in 3D printing of metals. For this purpose, different methodologies were tested in case studies, culminating in the design of a method for occupational risk management of exposure to incidental nanomaterials in metal 3D printing, entitled IN Nanotool. This CB-based tool allows reaching a risk level, based on the score assigned to different risk factors, either in the hazard band and the exposure band. IN Nanotool also provides recommendations for risk control, thus proposing a solution for the approach to be taken in the management of this occupational risk. This tool was tested in a specific case study, presenting promising results, consistent with the state-of-the-art. However, this method requires more practical applications and validation, presenting some limitations also explored in the course of this thesis.

Keywords: occupational exposure; risk management; additive manufacturing of metals; incidental nanomaterials

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LIST OF ABBREVIATIONS AND ACRONYMS

3D	Three-dimensional
ABS	Acrylonitrile-butadiene-styrene
AFM	Atomic Force Microscopy
AM	Additive Manufacturing
ANSES	French Agency for Food, Environmental and Occupational Health & Safety
BJ	Blinder Jetting
CB	Control Banding
CFC	Closed-face Cassette
CLP	Classification, Labelling and Packaging
CPC	Condensation Particle Counter
DC	Diffusion Charger
DED	Directed Energy Deposition
DLS	Dynamic Light Scattering
DMD	Direct Metal Deposition
DMLM	Direct Metal Laser Melting
DMLS	Direct Metal Laser Sintering
DNA	Deoxyribonucleic Acid
DNEL	Derived No Effect Level
EBFFF	Electron Beam Free Form Fabrication
EBM	Electron Beam Melting
EDS	Energy Dispersive Spectrometry

ELPI	Electrical Low-Pressure Impactor
ENM	Engineered Nanomaterials
ENP	Engineered Nanoparticles
EPFL	Ecole Polytechnique Fédérale de Lausann
GSD	Geometric Standard Deviation
HAZOP	Hazard and Operability Study
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
IN	Incidental
INM	Incidental Nanomaterials
ISO	International Standard Organization
LC	Laser Cladding
LC-MS	Liquid Chromatography-Mass Spectrometry
LENS	Laser Engineered Net Shaping
LIBS	Laser-Induced Breakdown Spectroscopy
MJ	Material Jetting
MNM	Manufactured Nanomaterial
MSDS	Material Safety Data Sheet
MWCNT	Multi-Walled Carbon Nanotubes
NM	Nanomaterial
NSAM	Nanoparticle Surface Area Monitor
NTA	Nanoparticle Tracking Analysis

OECD	Organization for Economic Co-operation and Development
OEL	Occupational Exposure Limit
OPC	Optical Particle Counter
OPS	Optical Particle Sizer
OSH	Occupational Safety and Health
PBF	Powder Bed Fusion
PLA	Polylactic Acid
PM	Parent Material
PM_{10}	Particulate Matter with diameter ≤10 µm
$PM_{2.5}$	Particulate Matter with diameter ≤2.5 µm
PM_{1}	Particulate Matter with diameter ≤1 µm
PPE	Personal Protective Equipment
RL	Risk Level
SEM	Scanning Electron Microscopy
SLM	Selective Laser Melting
SMPS	Scanning Mobility Particle Sizer
STM	Scanning Tunneling Microscopy
SYDAPP	Systematic Design Analysis Approach
TEM	Transmission Electron Microscopy
UFP	Ultrafine Particles
WHO	World Health Organization

CHAPTER 1. INTRODUCTION

1.1 Framework and Motivation

Additive Manufacturing (AM), also known as three-dimensional (3D) printing, is a manufacturing process of joining feedstock materials such as wire, powder or sheets, based on 3D model data, aiming to build parts by the successive addition of material, typically layer upon layer (DebRoy et al., 2018). It has various applications, such as architecture, automotive industry, aerospace industry, military services, medical and dental purposes, construction, transportation, consumer products, and electronics (Vafadar et al., 2021). The feedstock materials include polymers, ceramics, composites, and metals. These last ones are nowadays under the watchful eye of the industry and researchers, positioning metal 3D printing as the fastest growing segment of AM (DebRoy et al., 2021).

There are numerous bibliographic references on the advantages of metal 3D Printing. Unlike the conventional manufacturing processes, this technology allows the production of metal parts with complex structural shapes, without time-consuming additional manufacturing steps. Many parts that required assembly processes can now be printed as a single component. Additionally, it usually produces less waste than conventional technologies and it allows higher freedom of design (Ngo et al., 2018). Other significant benefits are the reduction of energy consumption and of manufacturing time (Duda & Raghavan, 2016). These advantages are crucial for industry. For example, aerospace and biomedical industries use expensive materials, such as titanium and its alloys, and need to produce very complex parts. Therefore, for these organizations, using metal AM represents a major advantage, since it allows to print high quality parts with unusual geometries while reducing waste and energy consumption (Ngo et al., 2018).

According to Lewandowski and Seifi (2016), it is possible to divide metal AM in two main groups: powder bed fusion (PBF) and directed energy deposition (DED). These groups can be further classified in other categories, according to the type of heat source used: laser, electron beam, plasma arc or gas metal arc. In PBF based technologies (the most common ones), the heat source fuses regions of powder bed. Examples of these technologies are Direct Metal Laser Sintering (DMLS), Selective Laser Melting (SLM), Electron Beam Melting (EBM), and Direct Metal Laser Melting (DMLM) (Vafadar et al., 2021). On the other hand, in DED based technologies, the head source melts a metal powder or a wire as it is being deposited. Laser Engineered Net Shaping (LENS), Direct Metal Deposition (DMD) and Electron Beam Free Form Fabrication (EBFFF) are some examples of DED technologies (Duda & Raghavan, 2016). Recently, some authors refer other metal AM technologies besides PBF and DED, such as Material Jetting (MJ) and Blinder Jetting (BJ) (DebRoy et al., 2021; Stefaniak et al., 2021; Vafadar et al., 2021).

As any other emerging technology, metal 3D printing faces some limitations and demands. For instance, mass production is still challenging, given that material costs are higher than for conventional processes, there are limited available alloys, and equipment requires high investment. Also, components with large dimensions are difficult to print in commercially available equipment (DebRoy et al., 2018), since the printing process typically occurs in a closed chamber of the printer, isolated from the working atmosphere and that limits the space for the printing part. There are also limitations regarding quality of the final parts, since some mechanical properties may vary during printing, leading to material behavior changes. This has a significant impact on metrology and quality control (Vafadar et al., 2021). Additionally, post processing is usually required after each printing process, increasing production time and costs (Ngo et al., 2018). There are also computational and simulation limitations (Vaneker et al., 2020), lack of standards and difficulty in compliance (DebRoy et al., 2021) and challenges regarding training and skills of workforce, due to the scarcity of effective training programs and of public awareness (Vafadar et al., 2021).

When balancing the pros and cons of this innovative technology, it is essential to consider not only economic, efficiency and environmental criteria, but also implications on occupational safety and health. Roth et al. (2019) recently published an article focused on the potential occupational hazards of additive manufacturing, while simultaneously calling attention to the lack of investigation on this field. In this study, some specific hazards for metal AM are highlighted, including inhalation and dermal exposure to powder/fume, explosion, laser/radiation exposure, electrical shock, and ergonomic hazards. It is known that metals and alloys used in metal 3D printing often include chromium, nickel, and cobalt, which are associated with carcinogenicity, neurotoxicity, and respiratory/skin sensitization upon human exposure. Therefore, the fact that AM workers may be exposed to these materials via dermal contact and/or inhalation, rises significant concerns on occupational health conditions (Vallabani et al., 2022).

Furthermore, during metal AM, condensate powders are generated from evaporation and sublimation of metal alloy powders, frequently with nano-scale size (Sutton et al., 2020). When inhaled, matter with higher dimensions than 0.1 μm typically deposit in the upper respiratory tract, but ultrafine particles (UFP) (particles with aerodynamic diameter less than 100 nm) can penetrate the lung tissues and can interact with different cells, causing, for example, inflammatory responses or genotoxicity (Vallabani et al., 2022). Moreover, nanosized matter can reach the bloodstream, penetrate biological membranes and accumulate in organs (Dugheri et al., 2022). The health effects of UFP have been studied for decades, highly driven by the exposure of industry workers, but still there is a need for further investigation to prevent negative impacts on human health (Madl & Pinkerton, 2009).

Stefaniak et. al. (2021) highlighted some research gaps and needs on occupational hygiene in AM processes. These included, among others, improving the knowledge on factors that influence emissions in real-world settings, perform more field assessments to study which tasks contribute most to exposure during AM processes (pre-printing, printing, post-printing, and post-processing) and develop standardized methods for occupational assessments of exposures.

According to the state-of-the-art, explored subsequently on in this thesis, most studies focus on the evaluation and characterization of emissions from thermoplastic filament AM and do not mention risk treatment (Kwon et al., 2017). Although knowledge on hazards is of high importance, it is essential to implement adequate risk control measures to protect workers' health (Roth et al., 2019). Therefore, to ensure the safety and health conditions of workers exposed in these workstations, a complete risk management approach is required and not only risk assessments. According to Warheit et al. (2008), risk management is based on the identification of the nanomaterial hazards, assessment of the exposure potentials, and implementation of control measures for risk reduction. These authors state that the hierarchy of control measures should be respected, including: elimination, substitution, confinement, engineering control, procedural control and Personal Protective Equipment (PPE).

This thesis was motivated by the need and the challenge to create a risk management method for exposure to incidental nanomaterials released during metal additive manufacturing processes, respecting the knowledge provided by the current state-of-the-art and the principles of occupational risk management.

1.2 Objectives and research questions

As the literature shows, metal 3D printing is an emergent manufacturing technology which entails a series of risks to the safety and health of workers, including the risk of exposure to airborne nano-objects. However, the main problem addressed in this research project is not the exposure itself or its consequences on human health, but the lack of proposals and solutions to manage this risk in workplaces. The scarcity of studies in this field creates an opportunity to explore and improve occupational risk management methods, to collect new relevant data to the scientific community and to give a contribution to the protection of workers that are working with this recent technology in the metalworking field.

The main research question of this thesis was: which approach should be considered to manage the occupational risk of exposure to incidental nanomaterials during metal AM? Therefore, other important questions were raised:

- Is there a significant occupational risk associated with airborne nanomaterials in metal 3D printing processes?
- Based on the state-of-the-art, is there a suitable approach to assess (or manage) the risk of exposure to incidental nanomaterials in metal AM processes?
- Which type of approach is more reliable to assess this risk: quantitative, qualitative or a combination of both?
- Which factors should be considered when developing a risk management framework suitable for metal incidental nanomaterials from AM of metals?
- Which control measures should be explored to eliminate or, if not possible, to reduce workers' occupational exposure to this risk?

1.3 Thesis overview

The present thesis provides a compilation of scientific papers produced during this research project, to accomplish and share the established research objectives. Most papers are already published, except the one present in Chapter 5, which at the time of submission of this thesis was already submitted for publication but yet not published. The complete reference and current status of each paper is indicated at the beginning of each chapter.

The thesis starts with an introduction, the present chapter, which intends to clarify the research scope and to explain the significance of this investigation. In this chapter, essential aspects are shared, such as framework, motivation, objectives, and research questions.

Chapter 2 presents a literature review regarding risk management of occupational exposure to nanomaterials during metal additive manufacturing. It intends to explore the real need for this research and to emphasize that lack of investigation in this field. As this paper was published in 2019 (and submitted for publication in 2018), there was a need to update some information on subsection 1.4, enriching the literature review with recent studies published in the meantime to date.

Chapter 3 consists in a literature review on the application of control banding (CB) based methods to manage the risk of exposure to incidental nanomaterials (INM). This paper, published in 2021, shows the lack of standardized methods to assess this occupational risk and the potential to apply CB approach to INM.

Considering the assumptions of the previous chapter, chapter 4 presents the application of a CB method to a metal AM case study. In fact, this paper intended to be a pilot study on the application of different methodologies to manage the occupational risk of exposure to INM, using qualitative and quantitative approaches that have been used to study exposure to ENM. It finishes with a critical analysis regarding the application of these approaches to manage the occupational risk of exposure to INM, raising the potential of combining both.

Chapter 5 is an extension of the investigation proposed in chapter 4, exploring the application of qualitative and quantitative risk assessment methods to another metal AM case study. The use of these approaches shows again significant limitations, which is why in this chapter a method of risk management for INM in metal 3D printing is designed and proposed. IN Nanotool is presented as a risk management method for INM from metal AM, designed to overcome the limitations of other existing approaches and to allow non-experts to manage this risk and act preventively to guarantee the health and safety conditions of exposed workers.

Finally, chapter 6 describes the conclusion of the research, highlighting not only the main contributions of this project but also its limitations. Recommendations for future work are also stated in this chapter.

1.4 Background

All chapters of this thesis, mostly Chapter 2 and 3, present relevant literature review. Regardless, since further relevant information has been published within the scope of this investigation, it is relevant to update this topic. Therefore, the aim of this subsection is to give a brief overview of the background of this research and share some updates on literature review.

As previously stated, metal additive manufacturing is a relatively recent technology, therefore the available studies regarding its occupational risks are not vast, especially the ones focused on nano-scale airborne matter. In this thesis, the literature review on this topic was narrowed to peer-reviewed articles and other available online published documents, written in English, focused on studying the occupational risk in real workstations of metal AM. In July 2018, when the first literature review of this thesis was conducted, only two articles were considered eligible considered the mentioned criteria. The outcome of these review is shown in Chapter 2, which consists of a published article on nanomaterials exposure as an occupational risk in metal AM. Summarizing, it cites two articles focused on SLM emissions. The first one, published in 2016, used scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) to confirm the emission of nano-sized by-products in metal AM, with similar chemical composition to the primary alloy (Mellin et al., 2016). One year later, Graff et al. (2017) used direct reading equipment and traditional filter-based analysis to reach similar conclusions. Both mentioned studies provide recommendations on how to control the risk of exposure to these particles, including the use of personal protective equipment (PPE), good ventilation conditions, improving powder handling systems, biomonitoring for metals and workforce training. These studies also have in common a quantitative approach to study the risk of exposure to nanomaterials.

In the beginning of 2019, an article on potential occupational hazards of additive manufacturing was published, identifying the inhalation and dermal exposures to fine powders and fumes as an occupational risk during metal AM and post-processing (Roth et al., 2019). This article also called attention to the sensitizing and/or toxic properties of metals used during these processes. In the same year, three case studies focused on quantitative assessments of airborne nano-sized matter released during metal 3D printing were published (Gomes et al., 2019; Lewinski et al., 2019; Ljunggren et al., 2019). Different approaches were used, which included gravimetric analysis, transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), biomonitoring for dermal exposure and metals in urine, in vitro experiment with human lung cells, and direct reading equipment (scanning mobility particle sizer (SMPS), optical particle sizer (OPS), nanoparticle surface area monitor (NSAM) and other particle counters). The results of these three case studies led to similar conclusions, showing the risk of exposure to nanomaterials exists in these workplaces and emphasizing the need for future investigation in these field.

Besides a literature review aiming to provide general knowledge of particle release during metal 3D printing (Chen et al., 2020), in 2020 two case studies were published on this topic (Jensen et al., 2020; Noskov et al., 2020). Jensen et al. (2020) performed *in situ* measurements in an SLM Danish facility, using diverse equipment and quantitative techniques. The monitoring campaign included the use of a diffusion size classifier miniature (DiscMini), an OPS, a condensation particle counter (CPC), a NanoScan SMPS, a DustTrak (to measure the mass fractions of the aerosol divided into total mass, PM_{10}, respirable, $PM_{2.5}$, and PM_1), and an electrical low-pressure impactor (ELPI) (to measure the aerodynamic particle size distributions). Additionally, SEM and EDS analysis were performed to airborne samples collected during 3D printing. This study brought important insights on the characterization of emissions during metal AM, inclusively during cleaning and post-processing tasks. Noskov et al. (2020) also performed measurements to characterize UFP emitted during metal AM, however using a different approach and analyzing three different AM techniques: PBF, DED and laser cladding (LC). This case study showed the results of high-resolution electron microscopy analysis to the particle matter collected during these three AM processes and studied the particle growth and oxidation by numerically modelling a gas flow and temperature fields accompanying the processes. This research also concluded that nanomaterials are emitted during the laser AM and gave insights on their physical and chemical characteristics.

In 2021, more case studies were published on this field, presenting quantitative multimetric approaches to characterize the emissions resulting from different metal AM techniques, focused on physicochemical characteristics, particle number or mass concentration, particle size distribution and/or shape of airborne matter (Azzougagh et al., 2021; Ding & Ng, 2021). At the same time, other perspective to study this exposure to airborne matter emitted by metal AM arises, with the publication of studies focused on biological monitoring. Ljunggren et al. (2021) investigated this exposure though clinical markers (which included metal analysis in blood, clinical analysis in blood and urine and spirometry), and Assenhöj et al. (2021) studied the effect of this exposure on the nasal lavage fluid proteome.

This same year, the first case study providing a qualitative approach attempt to assess the risk of exposure to UFP during metal AM was published (Sousa et al., 2021b). This paper is provided in Chapter 4 of the present thesis. Still in 2021, three reviews were published regarding occupational risks in 3D printing processes, yet not limited to metal AM (Leso et al., 2021; Mohammadian & Nasirzadeh, 2021; Stefaniak et al., 2021). Mohammadian & Nasirzadeh (2021) review was centered on toxicity risks due to occupational exposure to pollutants in the 3D printing and bioprinting industries. Regarding metal AM it highlights that the density for UFP increases during printing. Stefaniak et al. (2021) provided a comprehensive review on AM processes, emissions and exposures, not focusing on the occupational risk of exposure in metal AM. On the other hand, the review of Leso et al. (2021) addressed risk assessment and management in occupational AM settings, however not only for metals. This review gives a valuable insight on risk management and draws attention to the lack of information regarding exposure, which is essential to develop adequate risk management approaches. On its conclusions, it mentions the need for more workplace measurements that include pre- and post-processing activities, for more toxicological investigation on this field, and also to the importance of following the hierarchy of controls to mitigate occupational exposure.

In 2022, present year, quantitative approaches continue to be common practice to study UFP on metal AM (Dugheri et al., 2022; Noskov et al., 2022; Vallabani et al., 2022), unable to respond fully to the need to manage this risk in workplaces. Additionally, another publication presented a qualitative risk assessment regarding exposure to nanomaterials during metal AM, contributing to confirm the potential of this approach in these workplaces (Dugheri et al., 2022).

The research findings, assumptions and limitations provided by the state-of-the-art mentioned in this subsection 1.4 and in chapters 2 and 3 of the present thesis, contributed strongly to this thesis and to its outcomes.

CHAPTER 2. NANOMATERIALS EXPOSURE AS AN OCCUPATIONAL RISK IN METAL ADDITIVE MANUFACTURING

Paper published in 2019:

Sousa, M., Arezes, P., Silva, F. (2019). Nanomaterials exposure as an occupational risk in metal additive manufacturing. Journal of Physics: Conference Series, 1323, 012013. https://doi.org/10.1088/1742-6596/1323/1/012013.

Abstract

Metal Additive Manufacturing (AM) is a process of joining metallic materials based on 3D model data, aiming the manufacture of three-dimensional parts by the successive addition of material, usually layer upon layer. This technology is nowadays seen as an emerging one, showing exceptional perspectives of growth, being able to produce parts in various materials such as precious metals (for example gold, silver, and platinum) and several metal alloys, such as aluminium, titanium, nickel, cobalt, and magnesium-based alloys, among others. However, as the range of feedstock materials, technologies and applications increases, so do the concerns about its impact on health and safety of those who are exposed to the particles emitted during these processes, particularly when AM uses metal powder. Regarding emissions, studies thus far show that nanomaterials are emitted during AM processes, a fact that rises the concern about its impacts and enhances the complexity of risk management on these processes. When risk management aims nanoscale, it becomes a true challenge as it deals with several different nanomaterials and the lack of systematic and standardized risk assessment methodologies. At this scale, risk management raises many doubts regarding the selection of quantitative or qualitative approaches, the identification, characterization and quantification of nanomaterials, the definition of occupational exposure limits and the outlining of control measures. Having this conscience, a review was developed to summarize some of the recent developments in the field of risk management of occupational exposure to nanomaterials during metal additive manufacturing. Additionally, this review emphasizes the need for more investigation about risks regarding nanomaterials in workplaces, which is essential to ensure workers' safety conditions and preserve their health, as well as to make conscious decisions on risk

assessment, public health, medical monitoring, and control measures, namely the adoption of personal protective equipment.

2.1 Introduction

Technology evolution made possible the manufacturing of three-dimensional parts from 3D model data by using the concept of printing. This process is known by Additive Manufacturing (AM) and consists in joining feedstock materials such as powder, wire or sheets, typically layer upon layer, to create 3D parts by the successive addition of material (DebRoy et al., 2018). Reducing material costs and simplifying processes are two of the many advantages of AM over conventional manufacturing, so this technology is now seen as an emerging one (Kwon et al., 2017).

AM has various applications in different fields, for example, medicine, aerospace industry, energy, jewelry, cosmetic, automotive sector and architecture, having also domestic applications nowadays (Ngo et al., 2018). There are different AM process categories, such as vat photopolymerization, material jetting, binder jetting, powder bed fusion, material extrusion, direct energy deposition and sheet lamination, as described in the Standard ISO 17296-2:2015, each one of them with particular characteristics (International Standard Organization, 2015b). Nevertheless, these processes are permanently being updated and improved, so they cannot be listed exhaustively and strictly. As for materials, AM processes use a large type of materials, including metals, ceramics, polymers and composites (Ngo et al., 2018).

Regarding metal additive manufacturing, significant advances were achieved in the last twenty years, allowing the fabrication of components in complex structural shapes, that are difficult or even impossible to fabricate by subtractive manufacturing methods (DebRoy et al., 2018).

The fact that metal 3D printing is a growing technology, capable of using a wide-range of metallic materials, counting nickel, chromium, aluminium and titanium alloys, and different technological processes, poses a challenge in terms of assessing health and safety impacts on workers, which will require tailored approaches (Baumers et al., 2017). Investigation regarding metal AM impact on health and safety has a large scope, particularly when it comes to its emissions, being necessary to develop studies about toxicology of emitted particles, approaches for exposure assessment, exposure control measures, potential health impacts of exposure to ultrafine particles, among others (Baumers et al., 2017). A deeper look to ultrafine particle can lead to nanoscale, as this scale designates the length interval approximately from 1 to 100 nanometers (nm) (Azimi et al., 2017). In accordance with Standard ISO

80004-2:2015, most nanoparticles, defined by their geometrical dimensions, are ultrafine particles when measured (International Standard Organization, 2015a).

Studies thus far show that during 3D printing processes nanomaterials are emitted, with diverse emission rates, depending on the experimental design, modelling, temperature applied, and materials used (Kwon et al., 2017). Judging from studies carried out previously, concerning possible impacts of human exposure to metal nanomaterials, for example during welding, it becomes clear that it is of extreme relevance to study deeply the risk of occupational exposure to nanomaterials during metal 3D printing, including both incidental and engineered nanomaterials.

This paper provides a comprehensive review of literature on occupational risk management of exposure to nanomaterials, when emitted during metal additive manufacturing processes, emphasizing the need of deeper research in this field.

2.2 Methods

Given their size, surface area and other characteristics (mainly electronic, optical, mechanical and chemical) nanomaterials have exceptional properties, that make them as useful as harmful for the environment and human health (López-Serrano et al., 2014). Due to a greater awareness of researchers and regulators regarding environmental, health and safety impact of nanomaterials, the number of studies in this field has been increasing in the last fourteen years, although the majority of them have focused on nanotoxicology (Erbis et al., 2016). Therefore, more research on risks including the monitoring and characterization of nanomaterials is essential to ensure workers' safety conditions and preserve their health, as well as to make conscious decisions on risk assessment, public health, medical monitoring and use of appropriate personal protective equipment (Duarte et al., 2014). Thus, the challenges in risk management begins when dealing with the diversity of nanomaterials and the lack of systematic and standardized risk assessment methodologies (Erbis et al., 2016).

To assess the risk of exposure to nanomaterials there are many possible approaches that can be classified into two main groups: qualitative and quantitative methods (Silva et al., 2013), although some authors begin to propose semi-quantitative approaches as well (Dimou & Emond, 2017).

2.2.1. Risk management regarding occupational exposure to nanomaterials – An overview on quantitative approaches

Nanomaterials can be characterized and quantified using different approaches, which allow a quantitative approach to risk management. The quantitative methods commonly used in occupational safety field are based on the measurement of the concentration of particles (or other chemical agents) in the atmosphere, collecting samples of air in the workers' breathing zone, considering the duration of the exposure. Usually, after the sampling and measurement procedures, the level of exposition obtained is compared to the corresponding exposure limit value set for that agent to assess the risk of exposure, considering the concentration and exposure time. However, when it comes to nanoscale, even in assessments that involve well-known nanomaterials, there are many uncertainties when choosing the most appropriate quantitative method (Silva et al., 2013). On the other hand, occupational exposure limits (OELs) are not defined for all nanomaterials. For engineered nanomaterials with sufficient data, OELs where defined based on quantitative risk assessment; for others the base point were the qualitative methods, although nowadays quantitative data is available so there is a risk that this OELs are not the most proper; and additionally, there are other nanomaterials, engineered and incidental, with no OEL yet defined (Schulte et al., 2018).

Due to this lack of established and accurate OELs for nanomaterials, as well as to the fact that nanomaterials have distinct characteristics and have often unstable behavior; it is still a challenge to define which characteristics of nanomaterials and which methods of characterization and quantification are relevant for hazard identification and risk assessment.

If considered that particle size is important for risk assessment, analytical techniques can be useful to characterize nanomaterials. For instance, microscopic techniques are frequently used to characterize nanoparticles, such as: Atomic Force Microscopy (AFM) that provides information on size, morphology, surface texture and roughness; Scanning Tunneling Microscopy (STM) which gives chemical characterization; Scanning and Transmission Electron Microscopy (SEM and TEM) analyzing surface, crystal structure, elemental composition, size, shape and other properties; among others (López-Serrano et al., 2014). All the same, quantitative approaches can be based on other techniques, for example: light scattering for particle size characterization, such as Dynamic Light Scattering (DLS); X-ray which provides information on surface properties and coatings, crystallographic structure or elemental composition; Spectroscopic for details on size, aggregation, structure, stabilization and surface chemistry; Nanoparticle Tracking Analysis (NTA) that sizes particles from the range of 30 to 1000 nm; or Hyperspectral Imaging that delivers information on spatial distribution and spectral characteristics (López-Serrano et al., 2014).

On the other hand, if the baseline for risk assessment is defined to be the quantification of particles, other approaches must be taken into consideration, mostly based on plasma techniques, such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Optical Emission

Spectroscopy (ICP-OES), Liquid Chromatography-Mass Spectrometry (LC-MS), Laser-Induced Breakdown Spectroscopy (LIBS), among others (López-Serrano et al., 2014).

Although there is a variety of existing quantitative approaches, nonetheless there is no ideal method to characterize nanomaterials and there are no standardized methods and sampling strategies, which represents a barrier to further studies in this area.

Currently, it is also possible to use direct-reading methods, which provide a fast and real-time response. These methods are capable of measuring a single compound or a wide range of them, and can be applied to area, process and personal monitoring (Duarte et al., 2014). They also provide on-site measurement, identifying short-term exposures, estimating long-term exposures, and be used to produce, for example, an evacuation alarm. One of their great advantages is that they allow immediate results on-site, sparing unnecessary steps as collecting, storing, and shipping samples (Duarte et al., 2014). The most common direct-reading devices that have been used for monitoring nanomaterials in workplaces' air are (Duarte et al., 2014):

- the Condensation Particle Counter (CPC);
- the Scanning Mobility Particle Sizer (SMPS);
- the Diffusion Charger (DC);
- the Electrical Low-Pressure Impactor (ELPI).

Nevertheless, although the use of these devices allows the identification, characterization, and quantification of some nanomaterials, assessing the occupational risk based only in quantitative methods is still difficult since for many nanomaterials no OELs are defined and there is not enough knowledge about their potential effects. Additionally, most studies focus on manufactured nanoparticles (Mellin et al., 2016), even if they only constitute a portion of the existing nanomaterials on the working atmosphere. The presence of nanomaterials that have not been produced with a certain purpose can make estimating and modelling exposure a real challenge (European Commission, 2017). For that reason, other methods are required to properly study the risks associated with the occupational exposure to nanomaterials, namely incidental ones.

2.2.2. Risk management regarding occupational exposure to nanomaterials – An overview on semi-quantitative and qualitative approaches

As mentioned previously, even though the importance to assess the risk associated with exposure to nanomaterials is clear, the quantification of it is full of uncertainties. For instance, the unknown contribution of a nanoparticle's physical structure to its overall toxicity, the lack of agreement on the relevant indices of exposure (for example, particle size and surface area are pointed as being more significant than mass), the little information on exposure scenarios and populations at risk (Zalk et al., 2009) and the absence of toxicological data to establish OELs (Zalk & Nelson, 2008). Facing these and other difficulties, the application of traditional risk assessment methods withdrawn, and qualitative risk assessment methods became more suitable and frequently used (Zalk & Nelson, 2008).

In the qualitative methods group, Control Banding (CB) is considered by several authors as an appropriate approach for assessing the exposure risk to nanomaterials (Brouwer, 2012) and is the one applied more frequently (Silva et al., 2013). This methodology consists of a strategy for identification and recommendation of exposure control measures for potentially hazardous chemicals for which reliable toxicological and exposure information are limited (World Health Organization, 2017), as it is the case of the exposure to nanomaterials. The designation Control Banding comes from the classification of these chemicals into "bands" (each one correspondent to a risk control strategy) that separate them into groups considering the hazard level of known chemicals similar to those being studied, subsequently assessing the risk and determining if there is a need for action (Dimou & Emond, 2017).

In 2017, Dimou and Emond presented a literature review regarding control banding and proposed a semi-quantitative method for hazard assessment of nanomaterials to occupational health and safety. This review offered some examples of Control Banding methods applied by some authors to assess nanomaterials' exposure risk namely: Control Banding Nanotool (developed in the United States); Stoffenmanager Nano (The Netherlands); French Agency for Food, Environmental and Occupational Health & Safety CB Tool (France); NanoSafer (Denmark); The Guidance (The Netherlands); and Precautionary Matrix for Synthetic Nanomaterials (Switzerland).

These authors state that each of them has a particular scope and specific purpose. For example, NanoSafer and Stoffenmanager Nano focus on the assessment of occupational risk during the synthesis and downstream use of engineered nanomaterials in laboratories, CB Nanotool is very focused on nanotechnology researchers' protection and Precautionary Matrix for Synthetic Nanomaterials focuses on workers and consumers' protection.

After analyzing these methods strengths and weaknesses, Dimou and Emond (2017) proposed a semi-quantitative methodology of CB based on physicochemical and biological characteristics of engineered nanomaterials and claim that this tool will protect workers that deal with manufactured nanomaterials and hazardous chemicals.

Apart from Control Banding, other risk analysis methods can be used to evaluate the risk regarding nanomaterials, as shown by Erbis et al. (2016), in their review regarding research trends and methods in nano environmental, health and safety risk analysis. Besides control banding, these authors highlight Monte Carlo Simulation Model, Decision tree analysis, Multicriteria decision analysis and Bayesian analysis.

Yet concerning risk management regarding exposure to nanomaterials, different concepts continue to emerge, such as safety by design approaches. For instance, Silva, Arezes and Swuste (2015) claim that a Systematic Design Analysis Approach (SYDAPP) allows taking a step forward in risk management, as it highlights risk control, rather than achieving only the results of a regular risk assessment. According to these authors, merging design analysis with the identification of the different exposure scenarios, makes it possible to percept how the diverse processes will affect the level of exposure. In addition, the authors state that, in the case of nanoparticles, it is relevant to be aware of the hazards from previous stages of the processes that involve their emission and exposure, and therefore achieve more efficient ways to control occupational risk.

First of all, the authors suggest applying the design analysis to a production process identifying production functions (that splits the process into its core activities); production principles (recognizes the general process, motive power, and operational control methods to reach the production function); and production forms (that specifies the detailed design to achieve the production principle). After that, emission and exposure scenarios shall be identified during regular operations, process disturbances, cleaning, and maintenance activities, using Hazard and Operability Study (HAZOP) or an equivalent method. The third step consists in the identification of possible emission and exposure reduction barriers, followed by risk assessment for each operation (for example, using a control banding tool), assembling different production process alternatives based on the design analysis and finally repeating stages 2, 3, 5 and eventually 1, for alternative production processes.

As the design analysis approach focuses in risk control rather than in risk evaluation, it is suitable when dealing with nanotechnology occupational risks, being able to eliminate risks, prevent exposure and/or protect the workers (Silva et al., 2015b).

Other more complex models for nanomaterials exposure have been developed, such as the conceptual model proposed by Schneider et al. (2011), which considers the main processes tangled in the transport of nanoparticles emitted from a source to a receptor (Schneider et al., 2011).

As presented here, similar to quantitative approaches, qualitative and semi-quantitative methods for nanomaterials' exposure risk assessment are varied but not yet standardized and systematized.

2.2.3. Risk management regarding occupational exposure to nanomaterials during metal additive manufacturing – A literature review

To understand and study metal AM occupational risks, it is first of all essential to be conscious of the variety of feedstock materials and technologies that can be involved, and the particularities of all of them, keeping in mind that it is evolving and improving rapidly. Essentially, AM metal processing consists of using an energy source (laser or electron beam mainly) to melt metallic feedstock.

Afterwards this melted material is transformed layer by layer making a solid part. DebRoy et al. (2018) state that the two main processes of AM processes for metallic components are directed energy deposition (DED) and powder bed fusion (PBF), as supported by Ngo et al. (2018), although this last publication refers other emerging techniques, such as binder jetting, cold spraying, friction stir welding, direct metal writing and diode-based processes. As for metallic feedstock in 3D metal printing, it is possible to use stainless steel, precious metals (for example gold, silver, and platinum), several metal alloys, such as aluminium, titanium, nickel, cobalt, and magnesium-based alloys, among other metal materials. Ngo et al. (2018) also refer engineered nanomaterials as emerging feedstock materials for 3D printing, as they can drop sintering temperatures and improve electrical and mechanical properties. Nevertheless, it is believed that the exposure to nanomaterials during 3D printing processes is not exclusive to processes that add nanomaterials as a feedstock, being also relevant to study exposure to incidental nanomaterials during metal AM.

The present literature review took into consideration peer reviewed publications regarding nanomaterial emissions during metal AM, using two databases: ISI Web of Knowledge, from Thomson Reuters, and Scopus, from Elsevier. The keywords used in this research included "Metal Additive Manufacturing" or "Metal 3D Printing", "Exposure to Nanomaterials" or "Exposure to Nano-objects" or "Exposure to Nanoparticles", and "Risk Assessment" or "Risk Management". Considering the fact that additive manufacturing was established in the late 1980s, the time period considered in the current article was between January 1990 and July 2018. The search was limited to peer-reviewed journals, thesis, and other available online published documents, written in English. Another important criterion was that only studies performed in real occupational environments were considered, excluding simulations in possible controlled environments.

The searches resulted in a total of 18 registries to analyze. Studies that merely referred the risk of exposure but did not assess it were not considered, as well as those who did not assess the risk of occupational exposure to metal nanomaterials. Takin into account the inclusion criteria previously set and the scope of this literature review, two articles were considered eligible.

2.3 Results

During additive manufacturing procedures, nano-objects are released as shown in a considerable number of published studies. So far most of them have been focused on evaluating and characterizing the emitted pollutants emissions of 3D printers that use polymers, mainly acrylonitrile-butadiene-styrene (ABS) and polylactic acid (PLA) (Kwon et al., 2017). Nonetheless metal AM should also be emphasized in these studies, as metal nano-objects health effects are recognized in other metal manufacturing operations such as welding, namely long-term pulmonary effects (Andujar et al., 2014).

Having that conscious, Mellin et al. (2016) published a study regarding emission of nano-sized by-products in metal AM, specifically in selective laser melting (SLM) technology, and also in composite manufacturing and fabric production. Using Scanning Electron Microscopy (SEM), the authors found micron-sized particles in samples of recycled powder of a nickel base superalloy (Inconel 939) emitted by SLM process, that were within the respirable range, raising health and safety concerns, as the metal particles released contain sensitizing constituents (some elements, as Cobalt, are known carcinogens).

Even though this study focused only in SLM, the authors refer that evaporation is a problem in Electron Beam Melting (EBM) technology, that can hence the chance of occupational exposure to nano-sized particles, but no studies have been published in this field so far. As for control measures, this study suggests good ventilation equipment (with filters), personal breathing masks and the handling of the powder in a confined space. The authors suggest additional to add information in the safety data sheet for powder intended to be used in metal 3D printing.

One year later, Graff et al. (2017) published a related study, focused on the assessment of particle emission during additive manufacturing of metals, including nanoparticles. The AM technology studied was also SLM with metal powder, involving mostly chromium, nickel, and cobalt. The assessment was carried out taking into account the number, mass, size, and identities of particles, using Nanotracer (10 to 300 nanometres), Lighthouse Handheld Particle Counter (Handheld 3016 IAQ) (300 nanometres to 10 micrometers) and traditional filter-based particle mass estimation followed by inductively coupled plasma mass spectrometry. Apart from clearing the existence of risk to particle exposure in certain AM operations, namely exposure to nanosized particles in handling the metal powder, one of the interesting conclusions of this study was that the size of particles tended to be smaller in recycled metal powder compared to new. According to the authors, it would be imperative to improve powder handling systems and measurement techniques for nanosized particles, allowing the future development of work environment regulations. To this point, the recommendations were the use of personal protective equipment, improvement in powder handling systems, regular metal analyses of urine and regular analyses of the presence of metal in urine (biomonitoring for metals).

A compilation of both studies' relevant outputs regarding exposure to nanomaterials during metal AM can be found in Table 2.1.

Table 2.1. Outputs of the literature review on occupational risk management of exposure to nanomaterials during metal AM.

	Graff et al. (2017)	**Mellin et al. (2016)**
Aim of the study	Study generated nano-sized by-products during production in metal 3D printing, composite manufacturing and fabric production	Use measuring techniques optimized for different particle sizes while analyzing numbers, sizes, masses, and identities of metal particle emissions
Metal material	Nickel-base Inconel 939 (both virgin and used powder)	Chromium, nickel, and cobalt alloy (both virgin and used powder)
AM technique	Selective laser melting (SLM)	Selective laser melting (SLM)
Methods performed	• Scanning electron microscopy (SEM); • Energy Dispersive Spectrometer (EDS).	• Nanotracer (10 to 300 nm); • Lighthouse (300 nm to 10 μm); • Traditional filter-based particle mass estimation and inductively coupled plasma mass spectrometry.
Main results	• Nanosized particles were generated during metal AM; • Presence of nanosized particles in samples with recycled powder.	• Nanosized particles were generated during metal AM; • Operators were exposed mainly while handling powder; • Particle sizes tended to be smaller in recycled powder.
Control measures and other recommendations for risk management	• Powder handling in a confined space; • Personal protective equipment; • Good ventilation with HEPA filters; • Inclusion of information in the safety data sheet for powder intended to be used in metal 3D printing; • Educate workers.	• Improve powder handling systems; • Measurement techniques for nanosized particles; • Work environment regulations; • Personal protective equipment; • Regular metal analyses of urine.

2.4 Conclusions

Metal Additive Manufacturing is an emerging technology that is becoming more common in occupational environments, having still many unknown and unstudied risks. Nowadays workers are already working side-by-side with machines that print 3D metal parts, using diverse technologies and various metal feedstock materials. Their routine may involve feeding metal powder to machines, brushing parts after printing, ensuring maintenance operations, among other tasks that might have a serious impact on their safety and health conditions. One of the root causes for concern is the unintentionally generated nano-objects during metal AM processes, as their impact on health and the environment is not yet sufficiently clear. Studies developed recently show emission of nanomaterials during metal 3D printing, even when no engineered nanomaterials are involved, rising concern, and emphasizing the need for more investigation in this field. Studies reviewed in the current article focus on recognizing the presence of nanomaterials in these work environments, though no deep risk assessment is performed, and no risk management methodology is even mentioned. It is important not only to be aware of the risk, but also to be able to assess and manage it, even though nowadays no risk management methodologies are proven to be totally credible and reliable.

Many doubts may occur when it comes to choosing the best approach for risk assessment of exposure to nanomaterials during metal AM, and particularly for risk management, but the importance of more investigation in this field in not called into question.

CHAPTER 3. OCCUPATIONAL EXPOSURE TO INCIDENTAL NANOPARTICLES: A REVIEW ON CONTROL BANDING

Paper published in 2021:

Sousa, M., Arezes, P., Silva, F. (2021). Occupational exposure to incidental nanoparticles: a review on control banding. Journal of Physics: Conference Series, 1953, 012008. https://doi.org/10.1088/1742-6596/1953/1/012008.

Abstract

As the integration of nanomaterials in our lives evolves, these materials become more noticeable and so do the concerns about the associated risks. Handling engineered nanomaterials (ENM) increases these concerns and has been leading to multiple studies about how to assess the risk of exposure to these materials. In the meanwhile, many workers are not conscious that they are exposed to nanomaterials, since some are unintentionally released in workplaces, during industrial activities, for example. The exact approach to be taken to study this exposure risk is far from being fully established and unanimously accepted. Choosing a quantitative approach can lead to more consistent results, but it requires expert's knowledge and proper equipment. A qualitative methodology may be less expensive and time consuming. Control Banding (CB) is an example of a qualitative approach, frequently used to manage the risk of exposure to engineered nanomaterials. But while numerous authors and organizations are focused on risk management of ENM, is the exposure to incidental nanomaterials being neglected? If not, how is this being managed? The purpose of this work was to review different CB approaches for occupational risk management of nanomaterials and to highlight its application for the specific case of incidental nanoparticles. Using two databases for the literature review and after some data analysis, the results of this work allowed to clarify the tendency to apply CB methodologies to ENM risk management research and also the opportunity of applying such approach to incidental nanomaterials.

3.1 Introduction

In 2011, a definition of nanomaterial (NM) was published in the Official Journal of the European Union, stating that it is "a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm-100 nm" (European Commission, 2011).

Natural nanomaterials have been present in our planet for billions of years, playing important roles in the Earth's system and evolution. Meanwhile humankind emerged and evolved and so did the anthropogenic nanomaterials, both incidental and manufactured. The first ones have been produced unintentionally by humans over the years since the beginning of humanity. On the other hand, manufactured nanomaterials (MNM) are not even a century old, since the first products started been made in the 40s of the 20th century. Even nowadays incidental NM are in fact more abundant than engineered ones (Hochella et al., 2019).

This notion that nanomaterials are so diverse, are practically everywhere and cannot be seen, rises concerns about safety. Deliberately working with engineered nanomaterials, increases this conscience and has been leading to multiple studies about assessing and managing the associated risk factors. However, many workers are not aware of the presence and much less of the risks associated with unintentional NM including nanoparticles produced, for example, during industrial activities. Many questions are yet to be answered regarding the best occupational risk management frameworks for nanomaterials. It is known that using the traditional industrial hygiene approach is still not an adequate option, since most information required is unknown or not available. Quantitative methodologies may be a good option, although they may require using highly specialized measurement techniques and equipment, which is usually expensive, and also expert knowledge. Therefore, a qualitative approach may nowadays be more suitable for occupational risk management, as these usually require less investment and can be also used by non-experts. Control Banding (CB) is an example of these qualitative approaches. In 2016, Erbis et al. published a review regarding the emerging research trends and methods to study the risk of nanomaterials related to safety, health and the environment (Erbis et al., 2016). In this publication, strengths, and limitations of five risk analysis methodologies are highlighted: Monte Carlo Simulation Models, Bayesian Methods, Multicriteria Decision Making, Decision Tree Analysis and Control Banding. Although Monte Carlo Simulation can be used in occupational environments to determine the mean value concentration and Decision trees can help study the possible hazard scenarios in workstations, Control Banding is pointed out as the approach that can deliver better endorsement for work-related safety measures. Besides, this article mentions strong and weak points of CB, such as being useful for small to medium-sized enterprises and being able to suggest ways to reduce exposure in workplaces; and, on the other hand, requiring expert opinion, accurate exposure data and providing static control instead of dynamic control measures (Erbis et al., 2016). With its advantages and disadvantages, Control Banding has been frequently used for studying the risk of exposure to NM, particularly to engineered nanomaterials (Wu et al., 2014). And regardless its limitations, at first sight, it is adequate for studies in occupational environments and may even be suitable for incidental nanomaterials. The purpose of this paper was to review the different CB approaches for occupational risk management of nanomaterials and to highlight its application for incidental nanomaterials, namely nanoparticles.

3.2 Methods

3.2.1. Literature review

Aiming to review the pertinence of Control Banding approaches to manage the occupational risk of exposure to nanomaterials, especially incidental ones, a literature review was conducted on scientific articles using the following databases: Scopus, from Elsevier, and Web of Science, produced by the Institute for Scientific Information and currently maintained by Clarivate Analytics. The research was conducted in order to find documents covering the terms "control banding", “risk assessment" or “risk management”, "occupational exposure" and “nanomaterials” or “nanoparticles”. As a result, 59 records were identified in the database search. Studies were then selected based on exclusion criteria. Firstly, book chapters, notes and technical reports were excluded, as well as documents not written in English. Then, articles were excluded if the complete document was not available online. Also, duplicate articles were excluded and considered as only one document. The fourth and last criterion was the exclusion of studies not focused on nanomaterial’s occupational exposure and Control Banding approaches. There was no search limitation regarding publication period, so the results included papers published between 2008 and 2020. After applying the inclusion criteria, 35 articles were considered eligible.

3.2.2. Literature analysis

Apart from the title, author(s) and Journal, the following data were gathered from each selected reference: 1) publication year; 2) keywords; 3) objective of the study; 4) type of document (scientific article, review or conference paper); 5) type of nanomaterials under study (engineered nanomaterials, incidental nanomaterials or both); 6) type of approach (qualitative or qualitative and quantitative); 7) Method used for risk assessment/management (documents using more than one method were considered more than once). All these data were analyzed, and a critical literature review was conducted.

3.3 Results and discussion

The results of the current review consisted of a compilation and analysis of 35 eligible publications regarding CB approaches to manage the occupational risk of exposure to nanomaterials, in the last 12 years, as presented in Figure 3.1. The publications include 20 scientific articles, 8 literature reviews and 7 conference papers.

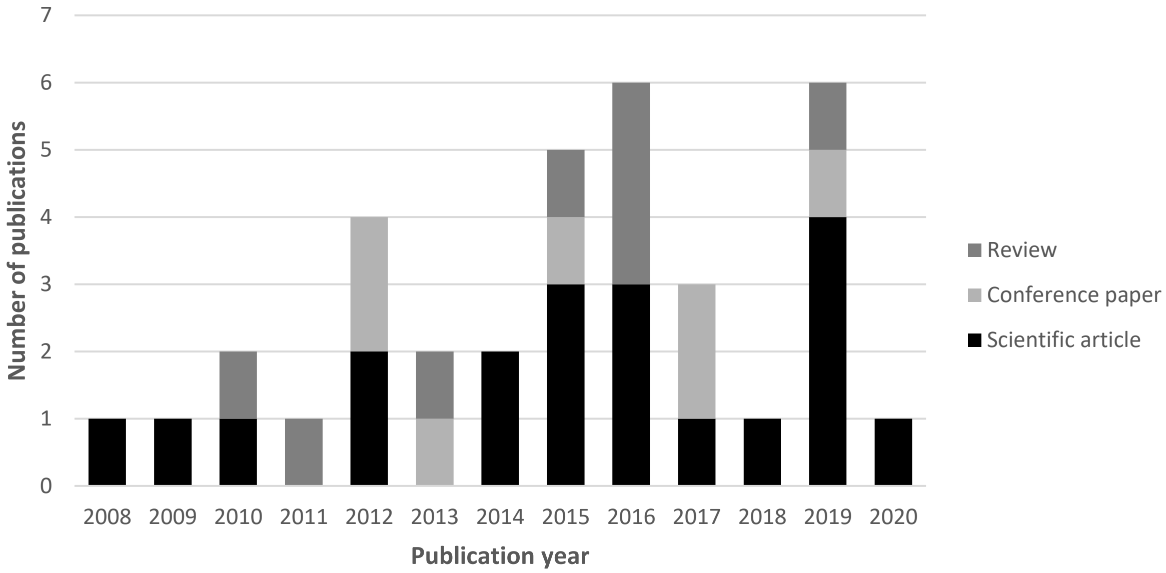


Figure 3.1. Number of eligible publications.

3.3.1. Qualitative and quantitative approaches

The data collected suggests that CB approach in 18 documents is purely qualitative, although quantitative concepts are introduced in 17 articles. As mentioned by Levin et al. (2015) control banding methodologies do not provide quantitative data; instead, the result is qualitative, based on quantitative and qualitative inputs and modelling, depending on the method used. However, it is feasible to combine these methods with quantitative approaches. Analyzing the tendency by year, in the past 6 years it is possible to recognize that the integration of quantitative concepts combined with CB is becoming more popular (Figure 3.2). Among the 17 publications that combine these two concepts is the one published by Bouhoulle et al., in which the authors applied two CB methodologies and also used measurement instruments, to assess the risk during laboratory tests with carbon black and Multi-Walled Carbon Nanotubes (MWCNT) (Bouhoulle et al., 2019). The authors used a condensation particle counter (CPC), a scanning mobility nanoparticle sizer (SMPS), a portative particle counter DiscMini and a mini particle sampler (MPS) to characterize the particles by Transmission Electron Microscopy (TEM). Their qualitative approach was based on the application of CB NanoTool 2.0 and Stoffenmanager Nano. Results of this study showed that both qualitative and quantitative methods lead to the same outcome for carbon black (medium risk level). Regarding MWCNT the results are not that consistent as CB Nanotool and Stoffenmanager Nano assigned the highest risk, while measurements of particles number revealed very low concentrations during tests and that almost no MWCNT fiber was detected.

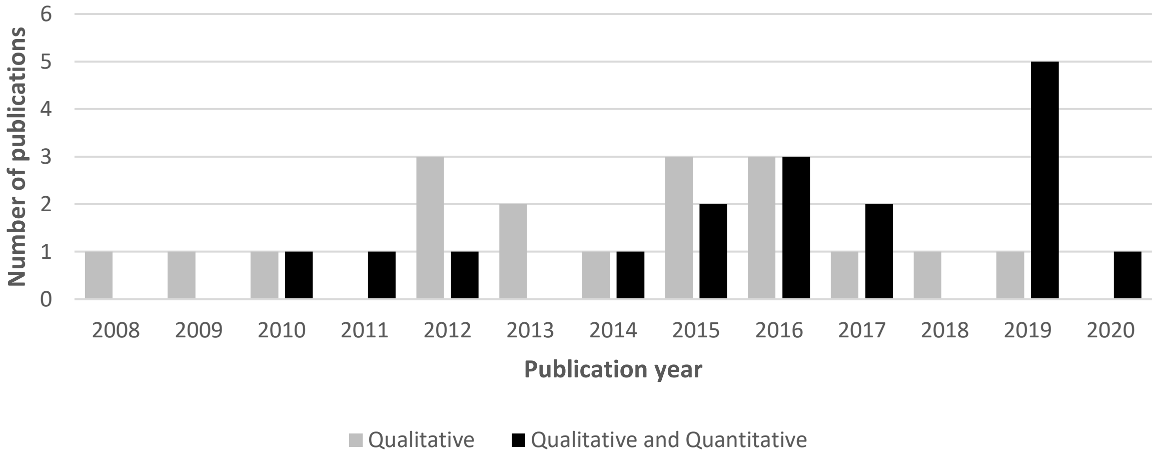


Figure 3.2. Number of eligible publications per year, considering the type of approach (fully qualitative or qualitative and quantitative).

Another study used the same qualitative methodologies and a Condensation Particle Counter (CPC), in this case to assess the risk of exposure to TiO_2 nanoparticles in a research laboratory (Silva et al., 2015a). The results obtained in the direct-reading equipment and using the CB Nanotool 1.0 were aligned as both indicated a low risk level. Stoffenmanager Nano presented a higher risk level, overestimating the risk. As mentioned by the authors of the study, combining qualitative and quantitative measures can help to reduce the overall uncertainty and to maintain a precautionary approach.

In 2019, a quantitative validation of CB Nanotool 2.0 was presented by its own authors (Zalk et al., 2019). This qualitative tool was applied to 20 activities performed at a research laboratory, as well as air monitoring for a qualitative study. The following equipment were used: Ultrafine Particle Counter, scanning mobility nanoparticle sizer (SMPS), filter sampling using a 2 -mm filter with a cyclone and/or filter sampling using a 37 mm closed-face cassette (CFC) sampler. In another laboratory 8 activities were also studied qualitative and quantitatively, using a Condensation Particle Counter (CPC), an Aerosol Spectrometer and filter sampling with 25 mm filters used in open-face configuration for microscopic analysis. From the 28 studied activities, 8 revealed qualitative results equal to quantitative ones. For the other 20 the risk was overestimated by CB Nanotool when comparing to strictly quantitative results.

3.3.2. Engineered and incidental nanomaterials

Regarding the type of nanomaterials under study, most publications focus on engineered nanomaterials (32 out of 35). Besides these publications, Gridelet et al. (2015) suggests a new control banding method applicable for industrial implementation for all powders and Lamon et al. (2019) present a review on grouping frameworks aimed at identifying hazard classes, mentioning articles that consider both ENM and incidental nanomaterials. Only one document shows a study dedicated exclusively to the exposure to incidental nanomaterials (Huang et al., 2016). In this study, Huang, Li, and Li, applied CB Nanotool 2.0 to incidental nanoparticles, generated in a thermal spraying process. It is mentioned by the authors that the various metal nanoparticles generated during the process have different composition, which affects some important toxicological factors considered in CB Nanotool. Plus, many characteristics of incidental nanomaterials and parent materials are not known. Therefore, when scoring severity, some factors were classified as “unknown” such as carcinogenicity, reproductive toxicity, mutagenicity, dermal toxicity, asthmagen and surface chemistry.

The result of the application of CB Nanotool 2.0 to this case study was an overall risk level of 3 out of 4 (4 being the highest risk level), meaning containment is the recommended control measure. Authors consider this result coherent.

3.3.3. Different Control Banding methodologies

The control banding methods for risk assessment mentioned and/or applied in the 35 publications designated in this review are diverse, as showed in Figure 3.3.

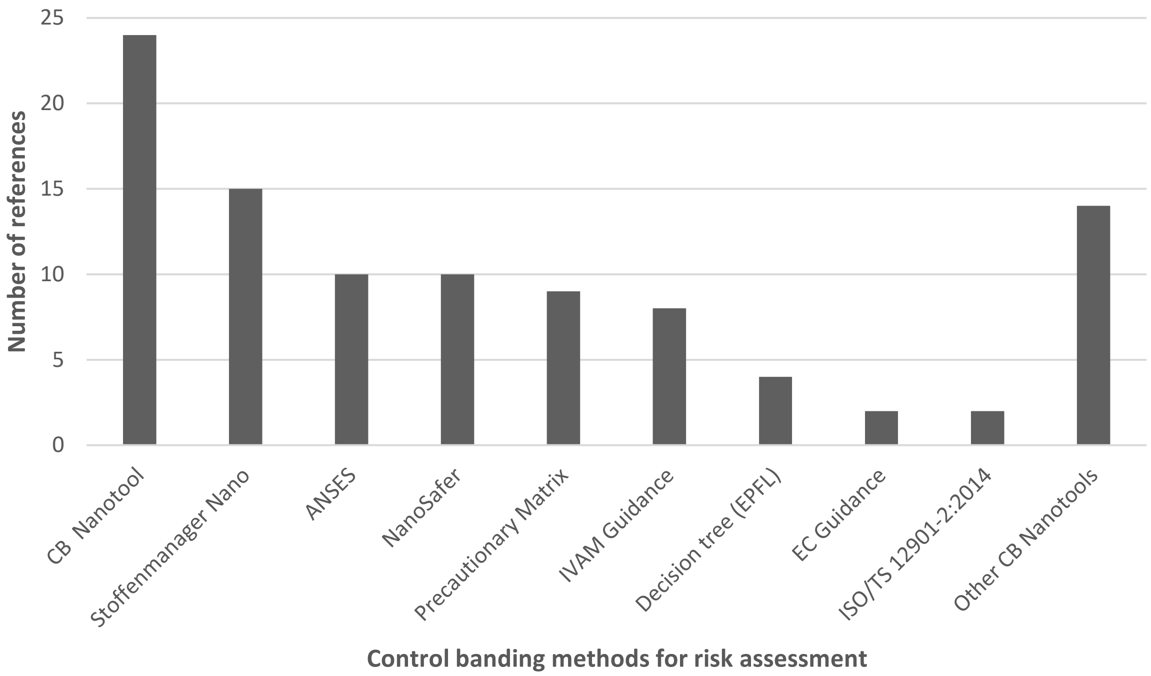


Figure 3.3. Control banding methods mentioned/used per publication.

A total of 24 publications apply or at least mention Control Banding Nanotool (CB Nanotool). This tool was developed by Paik et al. in 2008 aiming to assess and control the risk of exposure to nanoparticles of nanotechnology researchers at the Lawrence Livermore National Laboratory (California, United States of America), keeping a qualitative approach (Paik et al., 2008). One year after, it was adapted by Zalk et al., that reduced the maximum points in the severity scale, presenting CB Nanotool 2.0 (Zalk et al., 2009).

The concept of this method is to assign a severity score and a probability score (each corresponding to one axis), allowing the risk level to be determined using a four-by-four matrix. Severity is determined scoring 13 different factors related with properties of the nanomaterial under study (including physicochemical ones) and of its parent material, indicating the ability of particles to affect human health. The sum of all the points assigned to these 13 factors is the final score for severity. On the other hand, probability final score is given by sum of the results of 5 factors that are scored considering the interaction between the worker and the engineered nanomaterials under study (assessing the potential exposure) (Dimou & Emond, 2017).

Knowing the final score of severity and probability and matching them with the correspondent band, it is possible to determine the risk level (RL), using the matrix present in Figure 3.4. Each RL corresponds to a control band, meaning that RL 1 requires general ventilation; RL 2 demands fume hoods or local exhaust ventilation; RL 3, requires containment; and RL 4 suggests seeking specialist advice (Paik et al., 2008).

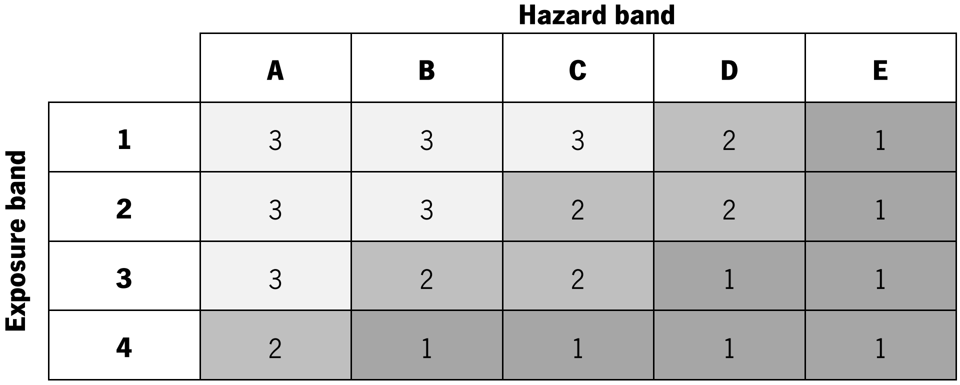
		Probability			
		Extremely Unlikely [0 - 25]	**Less Likely [26 - 50]**	**Likely [51 - 75]**	**Probable [76 - 100]**
Severity	**Very High [76 - 100]**	RL 3	RL 3	RL 4	RL 4
	High [51 – 75]	RL 2	RL 2	RL 3	RL 4
	Medium [26 – 50]	RL 1	RL 1	RL 2	RL 3
	Low [0 - 25]	RL 1	RL 1	RL 1	RL 2

Figure 3.4. CB Nanotool risk level matrix based on Paik et at. (2008), in which RL 1 corresponds to general ventilation; RL 2 to fume hoods or local exhaust ventilation; RL 3 to containment; and RL 4 to seeking specialist advice.

As mentioned before, among the articles studied in the present review, most mention and/or apply CB Nanotool, focusing ENM. However, Huang et al. (2016) applied CB Nanotool 2.0 to incidental nanoparticles, generated in a thermal spraying process. Allowing the classification of “unknown” in certain parameters, makes CB Nanotool eligible to assess the risk of exposure to incidental nanoparticles. Nonetheless, this literature review shows that this is not common practice. Another advantage of this tool is that it can be used by professionals and non-professionals (Dimou & Emond, 2017), although it is recommended to involve an expert (Brouwer, 2012), which may be an advantage while studying incidental NM. Another reason to consider this tool as appropriate for being eventually adapted to assess the risk of incidental nanomaterials, is that it is suitable for industrial environments, where many incidental nanomaterials are found and represent risk to workers exposed (Juric et al., 2015).

Other methods were found to be used when studying occupational exposure to ENM, as demonstrated in Figure 3.3. For example, Stoffenmanager Nano, created in The Netherlands, was mentioned in 15 articles analyzed in the present review. This tool intends to be used by non-experts (Brouwer, 2012) and its online version allows a comfortable solution when quantitative assessment is not feasible (Silva et al., 2015). Its authors claim that this qualitative risk assessment method features health risks associated with the exposure to manufactured nano-objects and it helps defining control measures. It is emphasized that information on shape and size of the manufactured nano-objects is fundamental to appropriately classify hazards, a detail that can exclude its suitability to assess the risk of exposure to incidental nanomaterials (Duuren-Stuurman et al., 2012).

Stoffenmanager Nano defines five hazard bands(considering hazardous properties of the nano-object such as particle diameter and length, solubility, morphology, bioavailability, among others; parent material characteristics may also be considered) and four exposure bands (considering nine modifying factors as, for example personal behavior, substance emission potential and surface contamination), allowing the user to determine the risk priority band using the risk matrix presented in Figure 3.5. There are three risk prioritization bands, 1 having the highest priority and 3 the lowest (Duuren-Stuurman et al., 2012).



Hazard band

Exposure band	A	B	C	D	E
1	3	3	3	2	1
2	3	3	2	2	1
3	3	2	2	1	1
4	2	1	1	1	1

Figure 3.5. Stoffenmanager Nano risk priority band matrix adapted from Duuren-Stuurman et al. (2012) in which 1 corresponds to high priority; 2 to medium priority; and 3 to low priority.

CB Tool from French Agency for Food, Environmental and Occupational Health & Safety method (ANSES) and NanoSafer were both mentioned in 10 articles studied in the present review, showing that these control banding methods are also highlighted when assessing the risk of occupational exposure to nanomaterials.

The French Agency for Food, Environmental and Occupational Health & Safety created a CB Tool, hereinafter called ANSES, aiming the development of a CB tool suitable for small and large enterprises, allowing them to evaluate the occupational risk of exposure to manufactured nanomaterials (Riediker et al., 2012). It proposes a 5-hazard band classification, based on physicochemical and toxicological properties of the nanomaterial, and a 4-exposure band classification, specified according to the nanomaterial emission potential. The control band of each case study is defined by using the matrix presented in Figure 3.6, that can vary from CB1 (natural or mechanical general ventilation) to CB5 (full containment and expert advice).

		Emission potential bands			
		EP1 **Solid**	**EP2** **Liquid**	**EP3** **Powder**	**EP4** **Aerosol**
Hazard band	**HB1** **Very low**	CB1	CB1	CB2	CB3
	HB2 **Low**	CB1	CB1	CB2	CB3
	HB3 **Moderate**	CB1	CB1	CB3	CB4
	HB4 **High**	CB2	CB2	CB4	CB5
	HB5 **Very high**	CB5	CB5	CB5	CB5

Figure 3.6. ANSES control bands based on Riediker et al. (2012) in which CB1 corresponds to natural or mechanical general ventilation; CB 2 to local ventilation; CB 3 to enclosed ventilation; CB 4 to full containment; and CB 5 to full containment and review by a specialist required.

NanoSafer is described by its authors as a control banding and risk management online tool designed for small and medium-sized enterprises working with manufactured nanomaterials (Jensen et al., 2014). It was developed by Denmark's National Research Centre for the Working Environment. Relying on technical information sheets and safety data sheets of the material to collect physical and toxicological data (water solubility for example) and other information about the bulk analogue compound, it is possible to determine the hazard band score. This can be difficult (or even impossible) data to collect when discussing incidental NM, so an adaptation of this method would be necessary to study these materials, particularly in input data.

This method proposes 4 hazard bands and 5 exposure bands. This last one is estimated considering the principles of the source-to-receptor model described in Schneider et al. (2011). Finally, based on the matrix presented in Figure 3.7, the risk level is determinate, ranging from RL1 (low hazard and low exposure potential) to RL5 (high hazard and/or moderate to very high exposure potential).

		Toxicity			
		[0.76 – 1.00]	**[0.51 – 0.75]**	**[0.25 – 0,50]**	**[0.00 – 0.25]**
Exposure	**> 1.00**	RL5	RL5	RL5	RL5
	[0.51 – 1.00]	RL5	RL5	RL4	RL4
	[0.26 – 0.50]	RL5	RL4	RL4	RL3
	[0.11 – 0.25]	RL4	RL4	RL3	RL2
	< 0.11	RL4	RL3	RL2	RL1

Figure 3.7. NanoSafer risk levels based on Jensen et al. (2014) in which RL5 corresponds to high hazard and/or moderate to very high exposure potential and RL1 to low hazard and low exposure potential.

The Precautionary Matrix for Synthetic Nanomaterials was developed by the Swiss Federal Office of Public Health and the Federal Office for the Environment, in 2008, and it has been revised into its current version 3.1 (Höck et al., 2018). It assesses the risk by combining hazard and exposure potential in a single score (Brouwer, 2012) and adds a new element in comparison to other CB tools created so far: it aims the protection of not only employees but also consumers and the environment during the life cycle of nanomaterials (Höck et al., 2018). Nevertheless, it is focused on the prevention of exposure to engineered nanomaterials (Dimou & Emond, 2017), not mentioning its possible applicability to incidental ones. The Precautionary Matrix for Synthetic Nanomaterials allows the user to differentiate the risks and opportunities related to the nanomaterial in two different categories – Class A or Class B, as shown in Figure 3.8. According to Dimou & Emond (2017), it requires expertise to ensure accurate interpretation of the results.

Score	Classification	Significance
[0 – 20]	A	The nanospecific need for action for the considered materials, products and applications can be rated as low and does not need further clarification
> 20	B	Nanospecific action is needed. Existing measures should be reviewed, further clarification undertaken and, if necessary, measures to reduce the risk associated with development, manufacturing, use and disposal implemented in the interests of precaution.

Figure 3.8. Nanospecific action requirement based on Höck et al. (2018).

The IVAM Guidance (Cornelissen et al., 2011) was created to deliver a guidance to work safely with ENM and nanoproducts. This method is based on a stepwise decision tree, consisting in 8 steps. At the fifth step a control approach band for activity is already selected, based on 3 hazard bands and 3 exposure bands according to the matrix presented in Figure 3.9. In this decision matrix, A is the lowest risk having as suggested measure applying sufficient (room) ventilation, if needed local exhaust ventilation and/or containment of the emission source and use appropriate personal protective equipment; B means that according to the hierarchic Occupational Hygienic Strategy, the technical and organizational feasible protective measures are evaluated on their economic feasibility. Control measures will be based on this evaluation; and C means the hierarchic Occupational Hygienic Strategy will be strictly applied and all protective measures that are both technically and organizationally feasible will be implemented.

		Description of the hazard category for nanoproduct		
		Hazard category 1: (water) soluble nanoparticles	**Hazard category 2:** Synthetic, persistent nanomaterials (non-fibrous)	**Hazard category 3:** Fibrous, non-soluble nanomaterials for which asbestos like properties cannot be ruled out
Possibility of exposure to nanoparticles during a	**Exposure category I:** Emission of free nanoparticles minimized due to working in full containment	A	A	B
	Exposure category II: Emission of nanoparticles (1-100 nm) embedded in a larger solid or liquid matrix (100 nm - 100 μm) is possible	A	B	C
	Exposure category III: Emission of primary nanoparticles (1-100 nm) is possible	A	C	C

Figure 3.9. The IVAM Guidance decision matrix based on Cornelissen et al. (2011)

IVAM Guidance was mentioned in 8 articles from the selection of this review and, probably because of its 8 steps so well outlined for ENM and nanoproducts, not applied to incidental nanomaterials. Finally, the decision tree of the Ecole Polytechnique Fédérale de Lausann (EPFL) was mentioned in 4 articles from the present review (Groso et al., 2010, 2016). This method consists in a decision tree for research laboratories producing and using ENM, so the main concept may be by itself an impediment to use this tool to assess the risk of incidental nanoparticles present in industrial workplaces. Summarizing, this decision tree method allows the classification of the risk in three different levels between Nano1 (low) to Nano3 (high), each one of them with associated control measures proposed by the method (Silva et al., 2015).

3.4 Conclusions

This review provided an overview on different Control Banding approaches for occupational risk assessment of nanomaterials, showing the clear tendency to apply these methods to study engineered nanomaterials. Nevertheless, considering the abundancy of incidental nanomaterials and their potential exposure risks, namely in workplaces, this review intended to highlight this approach application for incidental nanomaterials.

Besides showing various Control Banding methods, the results of the current review show that although some of these CB tools have potential of being used for managing the risk of exposure to incidental nanomaterials, so far it is not common to use such approach. Most authors of the tools highlight the fact that their purpose is to protect workers against consequences of exposure to manufactured nanomaterials, meaning that if these methods are ever used to incidental ones, an adaptation will be needed for most (if not all) of them.

Extensive changes would be necessary to adapt methods like IVAM Guidance, decision tree of the EPFL, ANSES and the Precautionary Matrix for Synthetic Nanomaterials, to incidental nanomaterials since their approach is clearly outlined for ENM and lacks flexibility for a different application. On the contrary, CB Nanotool does not require much adaptation for incidental nanomaterials, as it allows the user to classify factors as "unknown", making it suitable for this purpose. Other tools, like Stoffenmanager Nano and NanoSafer, may eventually be suitable for incidental nanomaterials, but this application would require several modifications, especially on their inputs as some of them are not easily obtained for incidental materials (for example shape, solubility, and toxicological data).

Screening the characteristics of the different CB methods mentioned in this review, the major challenge to use either of them to incidental nanomaterials is most likely the input data, as there are no safety materials datasheets available or information accessible through literature review. Additionally, inputs for exposure bands require data related to the emission, which is more challenging to for incidental nanomaterials than for engineered nanomaterials. Therefore, scoring the parameters for hazard and exposure bands may be a difficult obstacle to overcome.

Nevertheless, as a qualitative approach, Control Banding concept has great potential when applied to nanomaterials, including incidental ones, and there is, therefore, an opportunity to explore and improve this approach to manage the risk of exposure to incidental nanomaterials.

CHAPTER 4. OCCUPATIONAL EXPOSURE TO ULTRAFINE PARTICLES IN METAL ADDITIVE MANUFACTURING: A QUALITATIVE AND QUANTITATIVE RISK ASSESSMENT

Paper published in 2021:

Sousa, M., Arezes, P., Silva, F. (2021). Occupational Exposure to Ultrafine Particles in Metal Additive Manufacturing: A Qualitative and Quantitative Risk Assessment. International Journal of Environment Research and Public Health. 18(18), 9788. https://doi.org/10.3390/ijerph18189788.

Abstract

Ultrafine particles (UFPs) can be released unintentionally during metal additive manufacturing (AM). Experts agree on the urgent need to increase the knowledge of the emerging risk of exposure to nanoparticles, although different points of view have arisen on how to do so. This article presents a case study conducted on a metal AM facility, focused on studying the exposure to incidental metallic UFP. It intends to serve as a pilot study on the application of different methodologies to manage this occupational risk, using qualitative and quantitative approaches that have been used to study exposure to engineered nanoparticles. Quantitative data were collected using a condensation particle counter (CPC), showing the maximum particle number concentration in manual cleaning tasks. Additionally, scanning electron microscopy (SEM) and energy dispersive X-ray analyzer (EDS) measurements were performed, showing no significant change in the particles' chemical composition, size, or surface (rugosity) after printing. A qualitative approach was fulfilled using Control Banding Nanotool 2.0, which revealed different risk bands depending on the tasks performed. This article culminates in a critical analysis regarding the application of these two approaches in order to manage the occupational risk of exposure to incidental nanoparticles, raising the potential of combining both.

4.1 Introduction

Metal manufacturing processes have evolved significantly in the past couple of centuries. Nowadays, a metallic product can be manufactured using different technologies, such as casting, molding, forming, machining, and, more recently, additive manufacturing (AM), commonly known as 3D printing. AM is no longer exclusively a prototyping technology. It is now seen as a production process that is able to produce end-use parts for various applications, such as in the automotive industry, medicine, jewelry, and visual arts (Vaneker et al., 2020). One of the advantages of metal 3D printing over more conventional manufacturing processes is the fact that it requires less material and less post-processing activities, which can lead to lower costs. On the other hand, one of the disadvantages is a lack of knowledge and consistent information on the occupational risks of 3D printing. Therefore, it is important to study the health implications of a variety of factors, including (but not limited to) exposure to raw materials and emissions, the safety criteria of 3D printing systems and machines, emissions toxicology, and best practices to control overall exposure (Baumers et al., 2017).

Additionally, there is evidence that ultrafine particles (UFP) are emitted during these processes, with different emission rates depending on the source materials, technology, modelling, and temperature used (Sousa et al., 2019). The UFPs' nanometer scale allows them to reach and penetrate the lungs as well as bloodstream and internal organs (Viitanen et al., 2017). Three different types of UFP can exist within workplaces: engineered nanoparticles (ENP), incidental particles, and/or environmental background particles (natural and/or anthropogenic). Incidental nanoparticles are anthropogenic but are generated unintentionally and are usually physically and chemically heterogeneous compared to ENP, which are manmade with very specific properties to suit a certain purpose (Schulte & Salamanca-Buentello, 2007). There is now an increased concern centered on the consequent risks to and impact on human health when working with engineered nanomaterials. The number of studies recently published on this topic is proof of this concern (Schulte et al., 2019). However, there are workers exposed to incidental nanoparticles without research on the related risks. Occupational incidental nanoparticles usually originated from industrial processes that require high temperature or massive energy (Viitanen et al., 2017), such as metal additive manufacturing, which uses, for example, electron beams and lasers as heat sources. Recent studies have been published on this topic, showing the importance of studying the occupational risk of exposure to UFP in metal AM workstations (Graff et al., 2017; Jensen et al., 2020; Ljunggren et al., 2019). Some metal-based nanoparticles can cause adverse effects at cellular and subcellular levels. Due to their size and characteristics, they can interact with DNA and proteins and are able to induce inflammatory responses and toxic effects in humans (Schrand et al., 2010). Therefore, increasing our knowledge on how to protect workers exposed to incidental nanoparticles in metalworking environments is crucial, especially considering the scarcity of standardized and systematic risk management methods for this purpose (Sousa et al., 2019). Consequently, pertinent questions arise and are yet to be answered: which approach should be used to manage risks related to incidental metal UFP exposure? Are current methodologies used to study the risk of exposure to ENM sufficient and adequate for incidental ones? The common approach to industrial hygiene is to define occupational exposure levels (OELs) for different coarse and fine fractions. However, currently, there are no regulations or limits for most types of incidental nanoparticle exposure. Therefore, different approaches have been proposed and used to study, monitor, and control exposure to metal nanoparticles, although mostly for ENP. In occupational contexts, it is common to use direct-reading instruments such as condensation particle counters (CPCs), optical particle counters (OPCs), electrical low-pressure impactors (ELPIs), and/or scanning mobility particle sizers (SMPSs). Other strategies use filter-based samples and later analyze the collected material via, for example, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and/or energy-dispersive X-ray analyzers (EDSs), which provide a structural and chemical analysis (Bau et al., 2018; Kim et al., 2015; Miller et al., 2009; Pavlovska et al., 2016; Pietroiusti et al., 2018; Shepard & Brenner, 2014). However, former experience in chemical safety assessments and industrial hygiene shows that quantification is not enough to protect workers and avoid negative health impacts. It is necessary to establishing reference levels, such as OELs or derived no effect levels (DNELs), which create a connection between risk assessment and control measures. These limits have been difficult to establish due to a lack of information on particle toxicology, metrics considerations, the high diversity of particles, and uncertainties about their hazardous properties (Mihalache et al., 2017). Therefore, qualitative approaches to assessing the risk of exposure to nanoparticles should provide an alternative or complementary addition to quantitative analysis (Aschberger et al., 2011). This article aims to investigate potential exposure to incidental ultrafine particles during metal AM through a case study conducted in an industrial workplace using laser cladding technology. Additionally, this study will serve as a pilot study to explore the suitability of combining both quantitative and qualitative approaches to manage this occupational risk.

4.2 Materials and Methods

4.2.1. Operation Conditions and Materials

Data for this study were collected in a company specialized in technical coatings for industrial applications using laser cladding. This equipment can use different inert gas-atomized powders, specifically designed for laser cladding applications. Therefore, two raw materials were considered: a cobalt–chromium–silicon–carbon alloy (Powder 1) and a tungsten carbide–nickel alloy (Powder 2) (Figure 4.1).

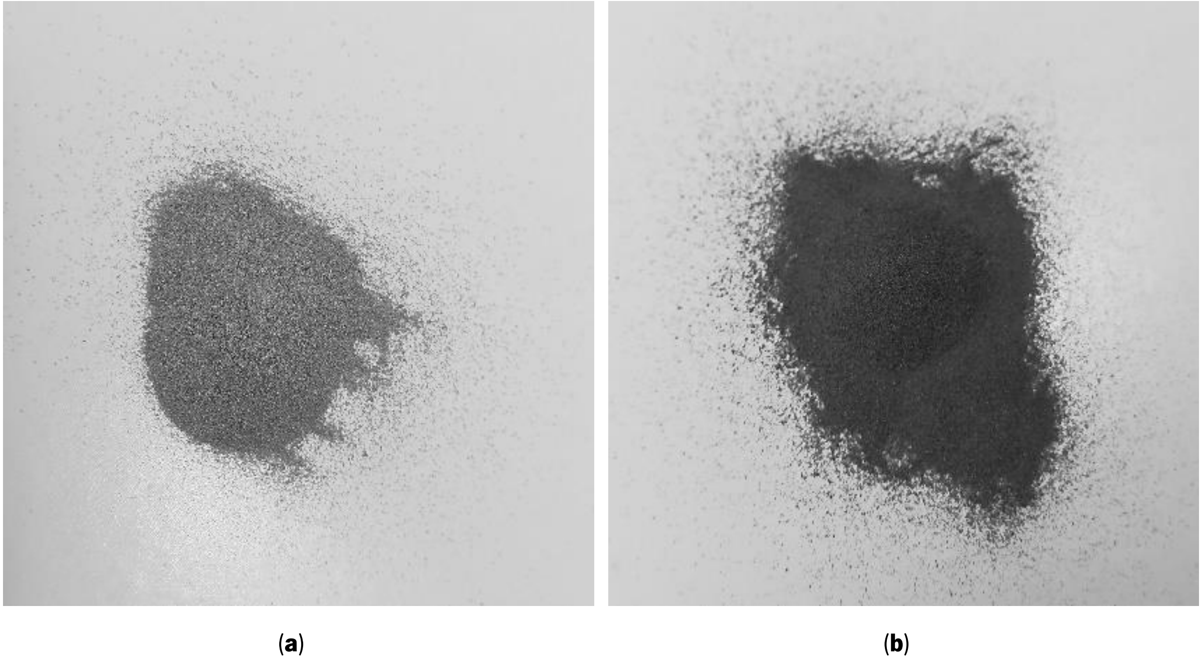


Figure 4.1. Photograph of inert gas atomized powders used for laser cladding applications: (a) Cobalt-Chromium-Silicon-Carbon alloy (powder 1); (b) Tungsten Carbide-Nickel alloy (powder 2).

Data gathering included a sample of each raw powder, technical sheets, and material safety data sheets of the powders, as well as details on operation conditions for each material and on-site measurements.

4.2.2. Quantitative assessment

The following equipment was used for the on-site measurements:

- A condensation particle counter (CPC), TSI® Model 3007, to measure the particle number concentration, with a particle size range of 10 nm to >1 µm in 1-s time resolution;
- A thermo-hygrometer, TSI® Model 9545, to measure air velocity, room temperature and relative humidity;
- A personal air sampling pump (SKC AirChek® TOUCH) to collect samples for subsequent Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) analysis. The samples were collect using mixed cellulose ester (MCE) membrane filters (0,8 µm pore), which meet NIOSH specifications for analysis of airborne metals. Additionally, these filters can collect particles with high efficiency, including particles much smaller than their nominal pore size (Soo et al., 2016).

Initially, background measurements were performed, before any printing activity and with the machine still turned off. Later, two trials were performed: trial nr. 1 while laser cladding with a Cobalt-Chromium-Silicon-Carbon alloy as raw material (powder nr. 1) and trial nr. 2 while using a Tungsten Carbide-Nickel alloy (powder nr. 2) (Figure 4.1). Each trial consisted of three measurements during three different tasks, during which the worker is considered to be more exposed to AM emissions. These tasks are listed in Table 4.1.

Table 4.1. Description of the tasks under study.

Task 1	Manual handling the powder to fill the machine container with raw powder
Task 2	Removing and cleaning the final part from the machine after coating process is completed (inside the machine operating area)
Task 3	Removing the remains of powder and cleaning the powder container

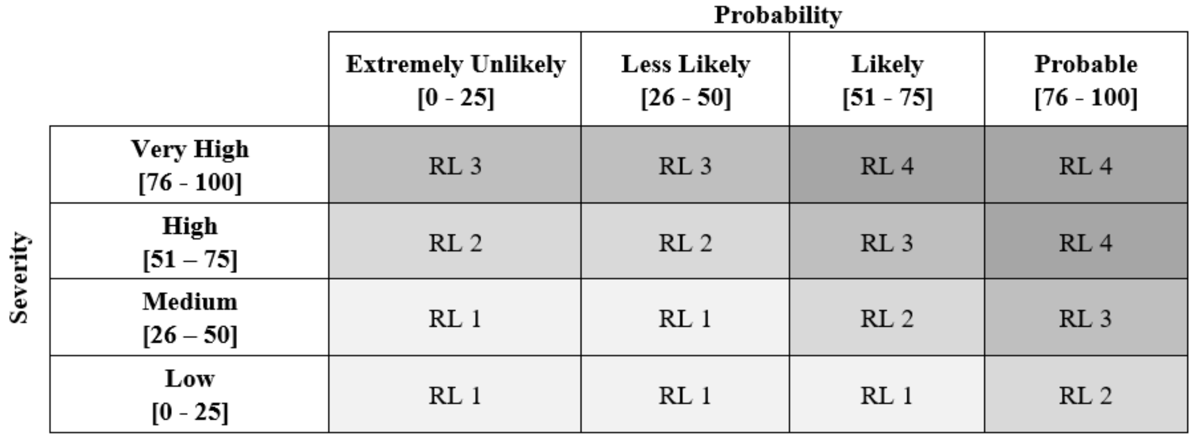
It is important to highlight the fact that measurements during the additive manufacturing process itself (that is, with the machine working) were not performed, since the machine works fully closed and has an incorporated exhausting system working during printing activity. While the machine is working, the worker stands outside the chamber, near the control panel, thus significantly reducing exposure.

4.2.3. Qualitative assessment

Regarding qualitative approaches, control banding methodology has been used to study exposure to nanoparticles, mostly ENP. In 2016, it was highlighted as the approach that can deliver better endorsement for occupational analysis in this field (Erbis et al., 2016). Among different control banding models, Control Banding Nanotool (version 2.0) was the one chosen for this case study, since it shows potential to be used to study occupational exposure to incidental nanoparticles (Sousa et al., 2021a).

The pilot CB Nanotool was created in 2008 by Paik et al. (Paik et al., 2008) and adapted one year later by Zalk et al. (2009). In 2019, the authors validated this CB model (Zalk et al., 2019). This method was designed to assess the risk of exposure to engineered nanomaterials. Regardless this method has been previously applied for incidental nanoparticles (Huang et al., 2016).

CB Nanotool 2.0 assigns a severity score and a probability score to a particular operation, allowing the determination of the risk level using a four-by-four matrix (Figure 4.2).



		Probability			
		Extremely Unlikely [0 - 25]	**Less Likely [26 - 50]**	**Likely [51 - 75]**	**Probable [76 - 100]**
Severity	**Very High [76 - 100]**	RL 3	RL 3	RL 4	RL 4
	High [51 – 75]	RL 2	RL 2	RL 3	RL 4
	Medium [26 – 50]	RL 1	RL 1	RL 2	RL 3
	Low [0 - 25]	RL 1	RL 1	RL 1	RL 2

Figure 4.2. CB Nanotool risk level matrix adapted from Zalk et at. (2009).

In Figure 4.2, RL stands for Risk Level and each of the four risk levels is related to a control band: RL 1 corresponds to general ventilation; RL 2 to fume hoods or local exhaust ventilation; RL 3 to containment; and RL 4 to seeking specialist advice.

Severity score is dependent on factors related to the nanomaterial (70% of the severity score) and to the parent material (30% of the severity score). Nanomaterial (NM) factors include:

- Surface Chemistry (points: high = 10; medium = 5; low = 0; unknown = 7.5);
- Particle Shape (points: tubular, fibrous = 10; anisotropic = 5; compact/ spherical = 0; unknown = 7.5);
- Particle Diameter (points: 1-10 nm = 10; 11-40 nm = 5; >40 nm = 0; unknown = 7.5);
- Solubility (points: insoluble = 10; soluble = 5; unknown = 7.5);
- Carcinogenicity (points: yes = 6; no = 0; unknown = 4.5);
- Reproductive Toxicity (points: yes = 6; no = 0; unknown = 4.5);
- Mutagenicity (points: yes = 6; no = 0; unknown = 4.5);
- Dermal Toxicity (points: yes = 6; no = 0; unknown = 4.5);
- Asthmagen (points: yes = 6; no = 0; unknown = 4.5).

On the other hand, parent material (PM) factors are scored considering:

- Occupational Exposure Limit (OEL) (points: <10 μg/m^3 = 10; 10-100 μg/m^3 = 5; 101-1000 μg/m^3 = 2.5; unknown = 7.5; >1000 μg/m^3 = 0);
- Carcinogenicity (points: yes = 4; no = 0; unknown = 3);

- Reproductive Toxicity (points: yes = 4; no = 0; unknown = 3);
- Mutagenicity (points: yes = 4; no = 0; unknown = 3);
- Dermal Toxicity (points: yes = 4; no = 0; unknown = 3);
- Asthmagen (points: yes = 4; no = 0; unknown = 3).

Probability score considers factors related to the workers exposure to nanomaterials:

- Estimated amount of material used (points: >100 mg = 25; 11-100 mg = 12.5; 0-10 mg = 6.25; unknown = 18.75);
- Dustiness/mistiness (points: high = 30; medium = 15; low = 7.5; unknown = 22.5);
- Number of employees with similar exposure (points: > 15 = 15; 11-15 = 10; 6-10 = 5; 1-5 = 0; unknown = 11.25);
- Frequency of operation (points: daily = 15; weekly = 10; monthly = 5; >monthly = 0; unknown =11.25);
- Duration of operation (points: >4 h = 15; 1-4 h = 10; 30-60 min = 5; <30 min = 0; unknown = 11.25).

4.3 Results

4.3.1. Quantitative assessment results

4.3.1.1. On-site measurements results

Temperature, relative humidity, and air velocity were measured to characterize the environmental conditions of the workplace under study and to give insight on these conditions for follow-up experiments. The results are presented in Table 4.2.

Table 4.2. Results of the measurements performed with the thermo-hygrometer: air velocity, room temperature and relative humidity.

Assessed parameters	**Background (before coating operations)**	**Near the machine powder tank**	**Inside the chamber (machine)**
Temperature [°C]	22.5	23.1	22.6
Relative Humidity [%]	44.7	45.2	45.0
Air Velocity [m/s]	<0.01	<0.01	<0.01

CPC allowed measuring the particle number concentration, before any task was performed (background measure) and during each one of the three tasks considered likely to expose workers to metal UFP, for each trial (as described in Table 4.1). The corresponding results are presented in Table 4.3. Additionally, on Figure 4.3, it is possible to verify the evolution of the concentration of airborne particles over time, for the three tasks under study and for each one of the trials performed.

Table 4.3. Results of *the measurements performed with the condensation particle counter (CPC).*

	Task 1	Task 2	Task 3	Background
Trial nr. 1 - Mean Particle number concentration [particles/cm^3]	16 421.69	28 895.80	18 279.44	13 358.94
Trial nr. 2 - Mean Particle number concentration [particles/cm^3]	16 716.12	37 568.52	22 708.98	

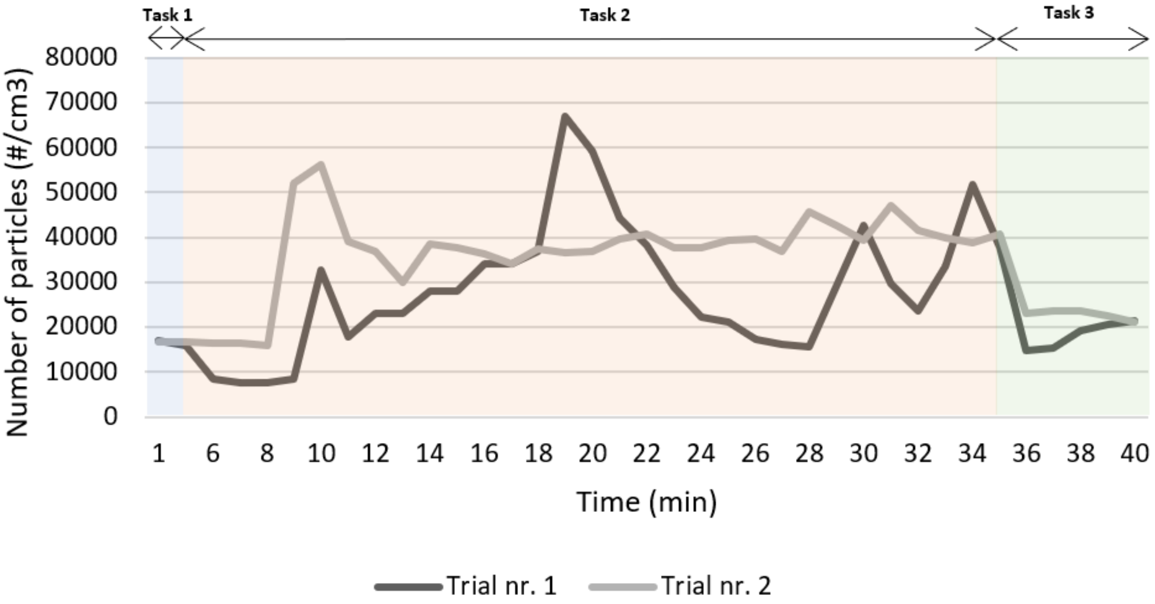


Figure 4.3. Number particle concentration (#/cm^3) measured over operation period with CPC during both trials.

4.3.1.2. SEM and EDS results

Scanning electron microscopy (SEM) was performed in the collected samples to increase data on size and shape characterization of the raw materials and particles released into the work environment. Additionally, Energy-dispersive X-ray spectroscopy (EDS) analysis was carried out to verify the elementary composition of both raw materials and consequent emissions after laser cladding. SEM and EDS analysis results of the raw powders (before laser operation) are presented in Figures 4.4 to 4.7. Figures 4.8 to 4.11 show SEM and EDS results of the individual samples collected during the two trials.

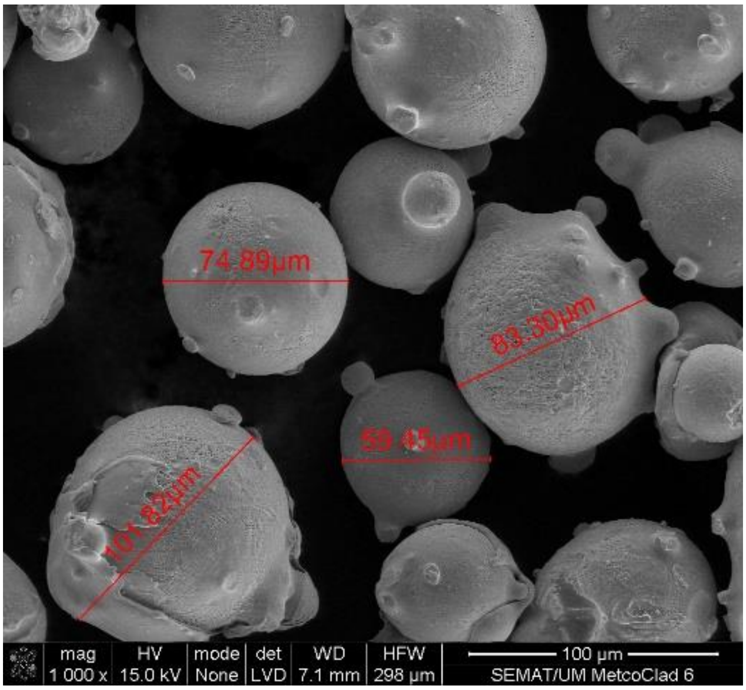


Figure 4.4. SEM analysis results: Raw powder nr. 1 sample – Cobalt-Chromium-Silicon-Carbon alloy.

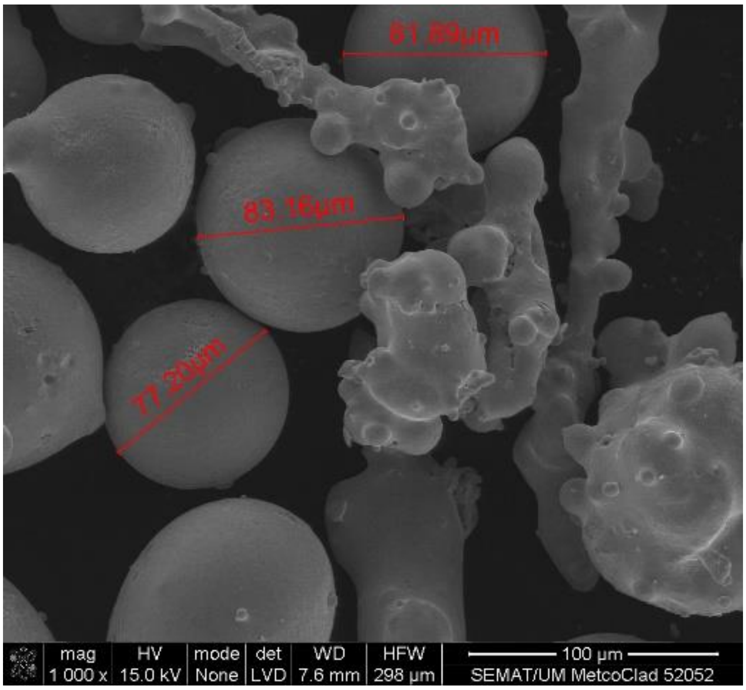


Figure 4.5. SEM analysis results: Raw powder nr. 2 sample – Tungsten Carbide-Nickel alloy.

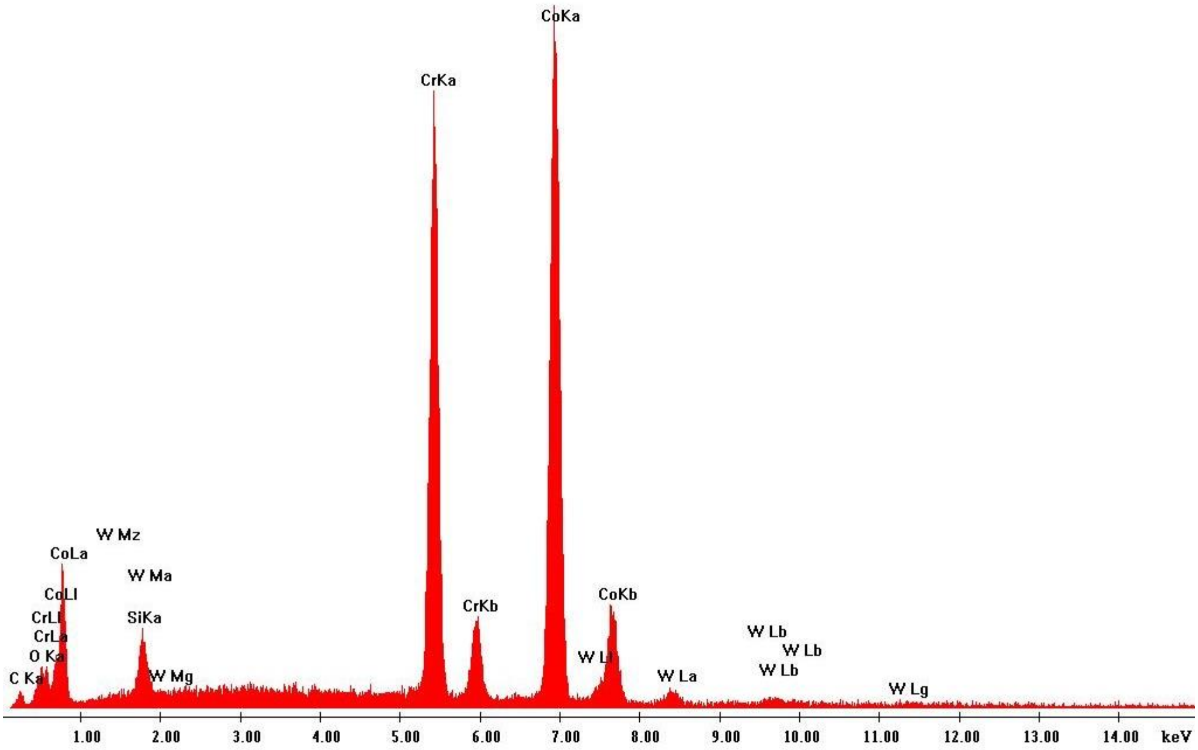


Figure 4.6. EDS analysis results: Raw powder nr. 1 (Cobalt-Chromium-Silicon-Carbon alloy).

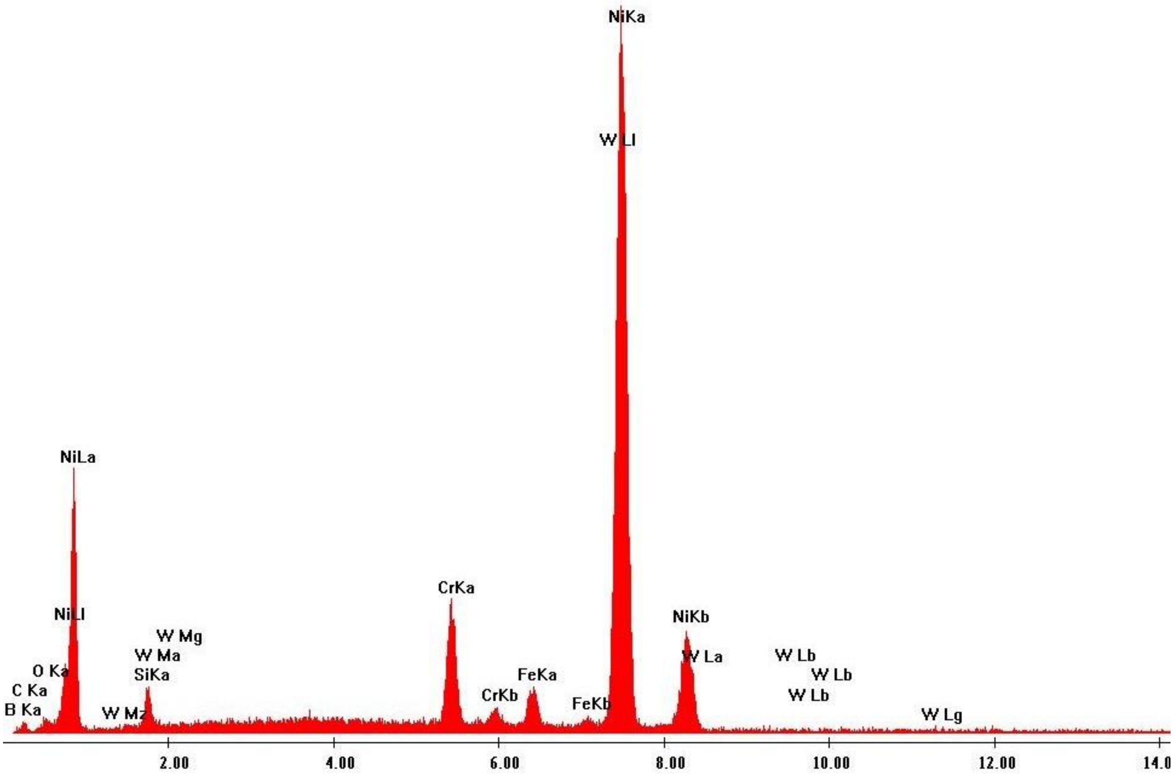


Figure 4.7. EDS analysis results: Raw powder nr. 1 (Tungsten Carbide-Nickel alloy).

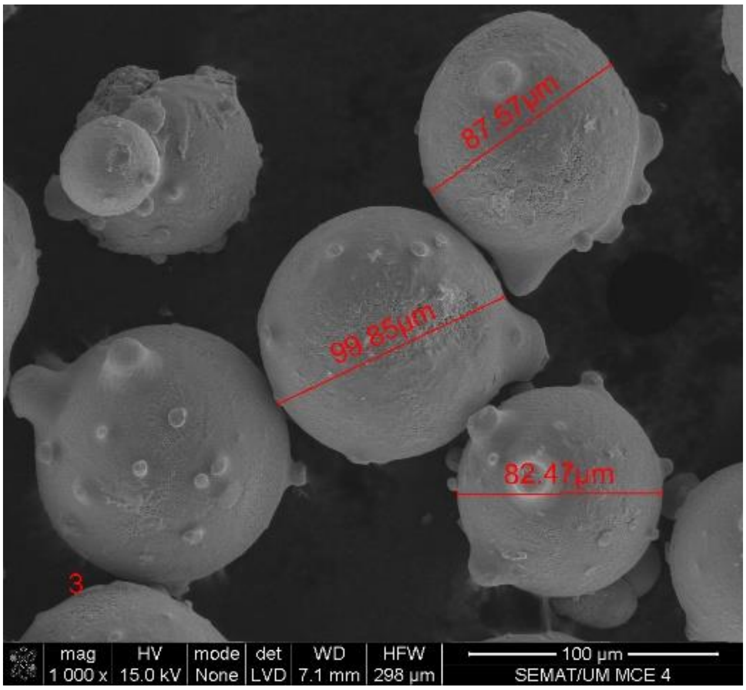


Figure 4.8. SEM analysis results: Sample collected during trial nr. 1 with Cobalt-Chromium-Silicon-Carbon alloy.

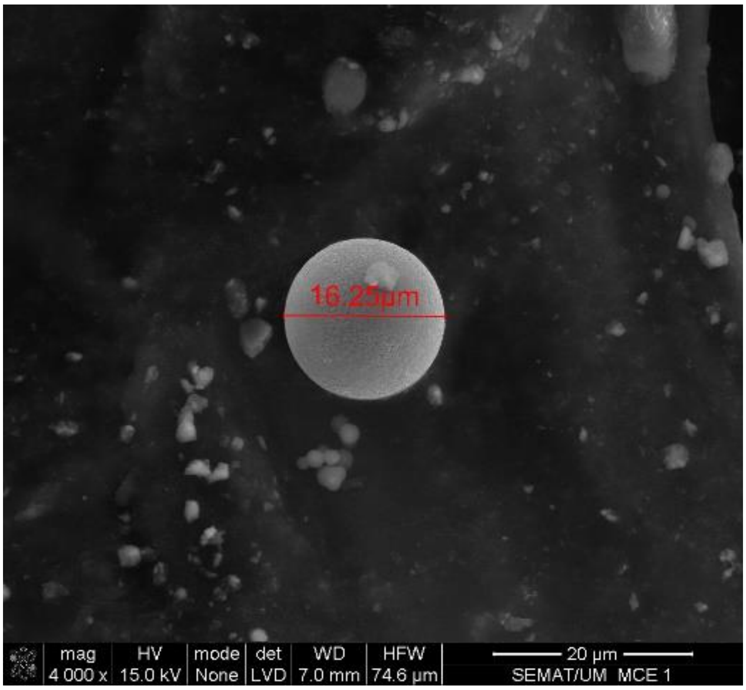


Figure 4.9. SEM analysis results: Sample collected during trial nr. 2 with Tungsten Carbide-Nickel alloy.

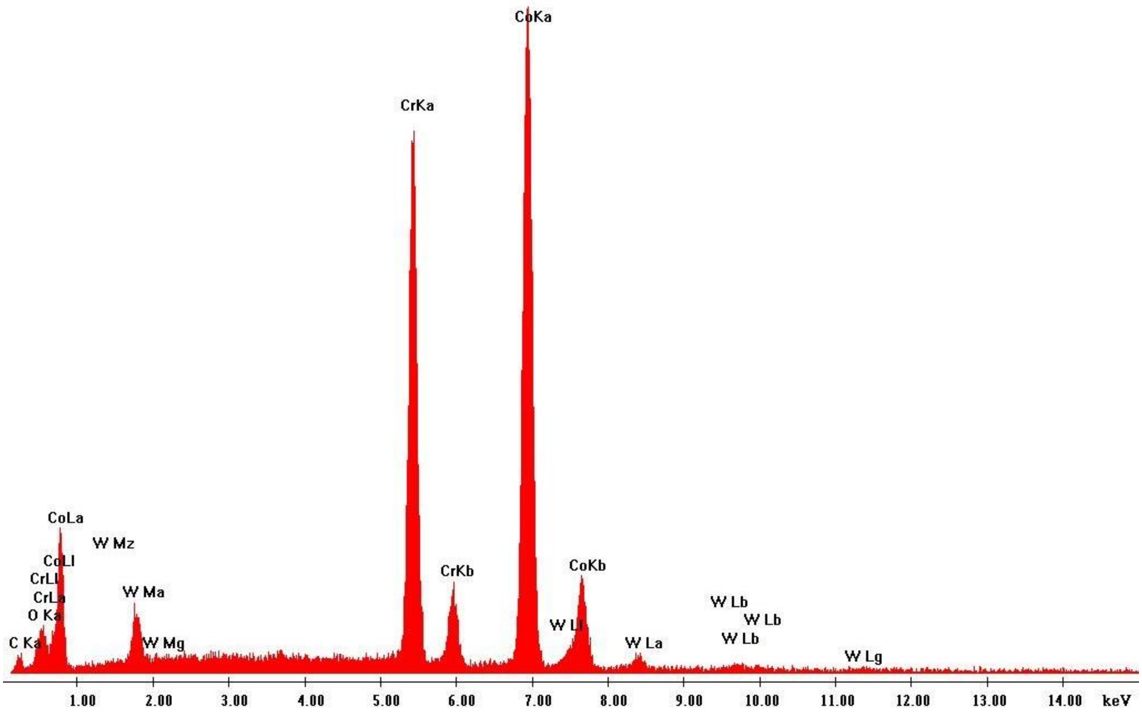


Figure 4.10. EDS analysis: sample collected during trial nr. 1 with Cobalt-Chromium-Silicon-Carbon alloy.

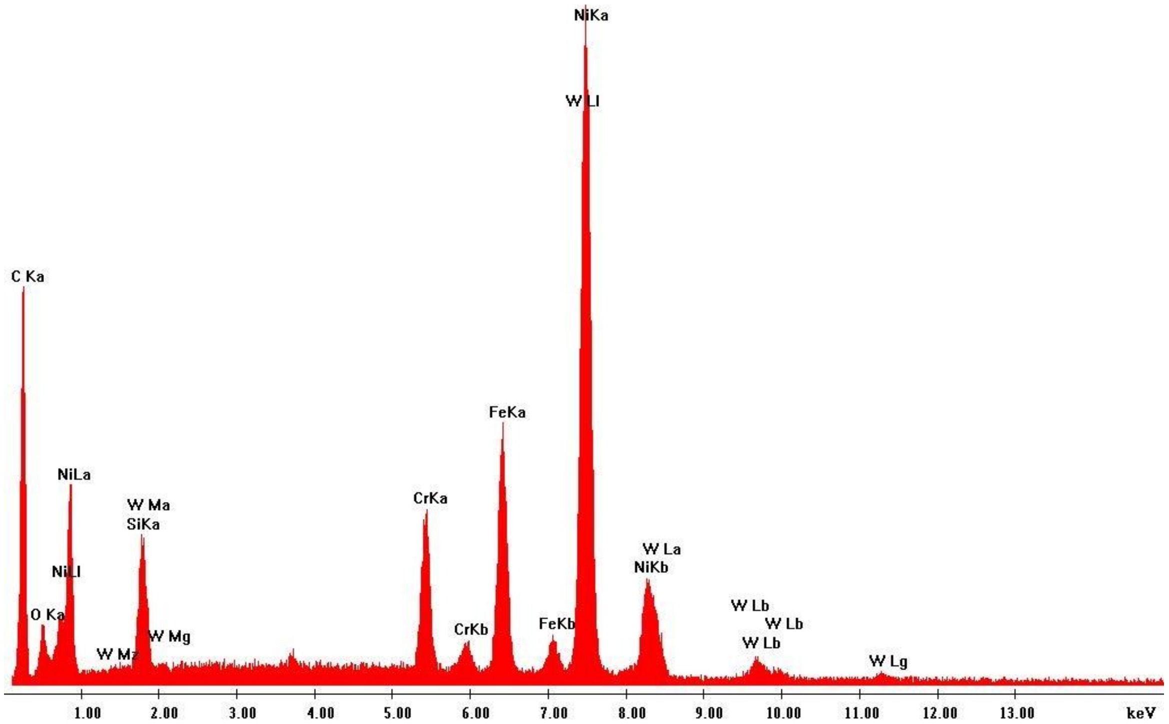


Figure 4.11. EDS analysis: sample collected during trial nr. 1 with Tungsten Carbide-Nickel alloy.

4.3.2. Qualitative assessment results

CB Nanotool 2.0 was used to assess the risk of exposure to incidental nanoparticles on both trials. Table 4.4 shows the results of the application of this method for laser cladding with powder nr. 1 as parent material (PM). On the other hand, Table 4.5 shows the results considering alloy nr. 2 as PM.

Table 4.4. Results of the application of CB Nanotool version 2.0 for the conditions of trial nr. 1.

CB factors	**Task 1**	**Task 2**	**Task 3**
PM OEL	20 µg/m^3 [1]	20 µg/m^3 [1]	20 µg/m^3 [1]
PM Carcinogenicity	No	No	No
PM Reproductive	Yes [2]	Yes [2]	Yes [2]
PM Mutagenicity	No	No	No
PM Dermal Toxicity	Yes [3]	Yes [3]	Yes [3]
PM Asthmagen	Yes [4]	Yes [4]	Yes [4]
NM Surface Chemistry	unknown	unknown	unknown
NM Particle Shape	unknown	unknown	unknown
NM Particle Diameter	unknown	unknown	unknown
NM Solubility	unknown	unknown	unknown
NM Carcinogenicity	unknown	unknown	unknown
NM Reproductive Toxicity	unknown	unknown	unknown
NM Mutagenicity	unknown	unknown	unknown
NM Dermal Toxicity	unknown	unknown	unknown
NM Asthmagen	unknown	unknown	unknown
Severity Score | Band	**72 | High**	**72 | High**	**72 | High**
Estimated amount of material used	>100 mg	>100 mg	>100 mg
Dustiness/mistiness	High	High	High
Number of employees with similar exposure	1-5	1-5	1-5
Frequency of operation	Daily	Daily	Daily
Duration of operation	< 30 min	1-4 hours	30-60 min
Probability Score | Band	**70 | Likely**	**80 | Probable**	**75 | Likely**
Overall Risk Level Without Controls	**RL 3 - Containment**	**RL 4 - Seek specialist advice**	**RL 3 - Containment**

[1] Considering the lowest OEL recommended in Portugal: Cobalt inorganic compounds (Portuguese Institute of Quality, 2014)

[2] Repr. 2, H361f according to the material safety data sheet

[3] Skin Sens. 1, H317 according to the material safety data sheet

[4] Resp. Sens. 1, H334 according to the material safety data sheet

Table 4.5. Results of the application of CB Nanotool version 2.0 for the conditions of trial nr. 2.

CB factors	Task 1	Task 2	Task 3
PM OEL	200 µg/m^3 [1]	200 µg/m^3 [1]	200 µg/m^3 [1]
PM Carcinogenicity	Yes [2]	Yes [2]	Yes [2]
PM Reproductive	No	No	No
PM Mutagenicity	No	No	No
PM Dermal Toxicity	Yes [3]	Yes [3]	Yes [3]
PM Asthmagen	No	No	No
NM Surface Chemistry	unknown	unknown	unknown
NM Particle Shape	unknown	unknown	unknown
NM Particle Diameter	unknown	unknown	unknown
NM Solubility	unknown	unknown	unknown
NM Carcinogenicity	unknown	unknown	unknown
NM Reproductive Toxicity	unknown	unknown	unknown
NM Mutagenicity	unknown	unknown	unknown
NM Dermal Toxicity	unknown	unknown	unknown
NM Asthmagen	unknown	unknown	unknown
Severity Score | Band	**63 | High**	**63 | High**	**63 | High**
Estimated amount of material used	>100 mg	>100 mg	>100 mg
Dustiness/mistiness	High	High	High
Number of employees with similar exposure	1-5	1-5	1-5
Frequency of operation	Daily	Daily	Daily
Duration of operation	< 30 min	1-4 hours	30-60 min
Probability Score | Band	**70 | Likely**	**80 | Probable**	**75 | Likely**
Overall Risk Level Without Controls	**RL 3 - Containment**	**RL 4 - Seek specialist advice**	**RL 3 - Containment**

[1] Considering the lowest OEL recommended in Portugal: Nickel inorganic compounds (Portuguese Institute of Quality, 2014)

[2] Carc. 2, H351 according to the material safety data sheet

[3] Skin Sens. 1, H317 according to the material safety data sheet

4.4 Discussion

4.4.1. Quantitative assessment

Considering that metal AM processes have the potential of emitting UFP, lowest mean number particle concentration was expected on background measurements. This condition was verified for both trials, as shown in Table 4.3.

Observing the same table, it is possible to confirm that both trials produced similar results. In both cases, the highest mean particle number concentration was obtained during task nr. 2. Figure 4.3 shows that the highest value was measured during this task, inside the machine operating area, while the worker removes and cleans the metal part. For task nr. 2 the mean value measured exceeds more than twice the background levels, being higher when printing with the Cobalt-Chromium-Silicon-Carbon alloy (presenting 181% increase).

The lowest mean particle number concentration, after background, was obtained while pouring the raw powder into the machine container (this task is performed outside the machine's operating area). Using the data of Table 4.3, it is possible to infer that the CPC results revealed around 25% increase in concentration comparing to background levels during task nr. 1 on both trials, and during task nr. 3 there was an increase of 37% on trial nr. 1 and 70% on trial nr. 2.

CPC results show consistency, given that the lowest and highest value of mean particle number concentration were obtained for the same tasks, independently which powder was being used (as emphasized in Figure 4.3). These results suggest greater exposure to particles while worker is inside the machine operating area, after the AM process occurs.

EDS analysis for both samples of raw powder corroborate the information of the technical data sheet of each material on the material chemical elemental composition (Figures 4.6 and 4.7). The composition of powder nr. 1 is mainly Cobalt and Chromium, although other metals are naturally present in the alloy. The main elements of powder nr. 2 are Tungsten and Nickel. Figures 4.10 and 4.11 show EDS analysis to the samples collected during AM process on the environment, showing that the chemical composition of the particles emitted is identical to their raw material. Although for powder nr. 2 there are some subtle differences that may indicate oxidation.

SEM detected medium-size particles (range from 1 to 100 μm), as shown in Figures 4.4 and 4.7. These images reveal that particles did not show any visible alteration on their size or surface (rugosity) after laser action.

After analyzing all quantitative results obtained on this case study, it is not possible to clearly assess the risk of exposure to UFP, as there is no occupational limit value for incidental nanoparticles to function as a reference. Even after the processing of quantitative data collected, results are not sufficient to say with certainty that workers are exposed (or not) to UFP concentration levels that may have an impact on his health and safety conditions. Without OELs, or at least more reference levels, results are also lacking information on whether the workstation under analysis requires the implementation of additional control measures to protect workers from the risk of exposure to UFP.

4.4.2. Qualitative assessment

The criteria considered during the application of CB Nanotool 2.0 on trial nr. 1 are present in Table 4.4. As the main composition of the alloy is Cobalt and Chromium, Cobalt compounds' OEL was considered as parent material OEL, since this metal has the lowest OEL (most penalizing). Nevertheless, cumulative effects may be the worst-case scenario. Parent Material carcinogenicity, reproductive, mutagenicity, dermal toxicity and asthmagen factors were rated based on the classification of this product according to CLP-Regulation: Repr. 2, H361f, Skin Sens. 1, H317 and Resp. Sens. 1, H334.

Nanomaterial factors were classified as "unknown", since there is no evidence of these characteristics for the incidental nanoparticles released. Different analysis and equipment would be necessary to classify the incidental nanoparticles considering surface chemistry, solubility, carcinogenicity, and other characteristics questioned in this method. Assuming these nine criteria as "unknown", to make no assumptions, the score of the severity band was the same for the three tasks: 72 points. On the other hand, regarding probability, different scores were obtained for each task, as exposure time is different in each task.

The same line of thoughts was considered on trial nr. 2, with Tungsten and Nickel alloy. The results are presented in Table 4.5. Nickel compounds have the lowest OEL so for that reason it was considered as PM OEL. Since this metal powder is classified as Carc. 2 (H351) and Skin Sens. 1 (H317) according to CLP-Regulation classification (material safety data sheet data), PM carcinogenicity and dermal toxicity were considered applicable. Similar to trial nr. 1, no information on incidental nanoparticles was available to score NM factors other than "unknown". Therefore, severity score was 63 for all tasks, 9 points lower comparing to trial nr. 1. Concerning probability score, as exposure time is higher for task nr. 2 and lower for nr. 1, different scores were obtained for the three tasks.

After using CB Nanotool 2.0 for both case studies, a Risk Level 4, seek specialist advice, was obtained for task nr. 2 in both trials. For tasks nr. 1 and nr. 3, regardless the raw powder used, Risk Level band obtained was 3, meaning containment is the recommended control measure to reduce the risk of exposure to nanomaterials.

Contrary to quantitative data, one of the outcomes of this approach is a tangible risk level, that allows the user to conclude about the complementary control measures needed, even if based on some assumptions.

4.4.3. Comparison between qualitative and quantitative assessments

The results of quantitative and qualitative analysis are consistent on this pilot study since both approaches underscore task nr. 2 in relation to others, specially to task nr. 1.

The qualitative approach used in this case study leads to two important results: a quantifiable risk level and specific control measures to prevent workers exposure. The control banding approach allows the user to understand which step to take towards reducing and preventing the risk of exposure, based on the risk level obtained.

As mentioned before, CB Nanotool 2.0 was designed for engineered nanomaterials and, although it allows the classification of "unknown" in certain parameters, there is a level of uncertainty introduced by these assumptions for incidental nanoparticles. These hypotheses may overestimate the risk. Nonetheless, with adjustments and more background data on incidental nanoparticles under study, this tool has potential to be eligible to assess the risk of exposure to incidental nanoparticles.

On the other hand, a quantitative approach offers less biased data and information that may be very useful for decision making. Results show higher mean particle number concentration when the worker is inside the machine and lower during background measurements, precisely as expected. Thus, results suggest reliable measurements, they lack information on exposure to UFP and moreover a clear understanding of the occupational risk of exposure. There are no established OELs, reference values or similar guidelines for incidental nanoparticles, which makes it difficult to interpret the results and, consequently, define adequate control measures to reduce risk of exposure to UFP.

However, this research may corroborate the potential in using both approaches combination. Quantitative results appear to be more accurate and less biased, not being dependent on the user's interpretation. Thus, this approach, considering the information available nowadays on incidental nanoparticles, lead to doubts on the meaning and interpretation of the values obtained. Still, these results may be a good input for a more accurate qualitative approach, which is built on many assumptions. For incidental nanoparticles there is not much background information, so any available data on UFP, for example on concentration, chemical composition, shape, and size is valuable.

4.5 Conclusions

The main objective of this case study was to investigate the potential exposure to incidental nanoparticles during metal AM and to be pilot research on studying the suitability of both quantitative and qualitative approaches to manage this occupational risk.

The results of the quantitative analysis revealed less biased, although it also highlighted the lack of occupational limits for comparison. This is a significant limitation when using a quantitative approach to study incidental nanoparticles. Additionally, the quantitative approach does not give insights on how to control the risk of exposure to UFP. In this case study, this insight was given by the qualitative method used (CB Nanotool 2.0). However, this method was not designed to manage risks related to incidental nanoparticles, so there is some uncertainty associated with the analysis. The biggest difficulty in using this approach for incidental nanoparticles is the lack of background information on the particles (such as size, shape, solubility, among others). Therefore, one of the most significant findings of this case study was that qualitative methods to assess the risk of exposure to incidental nanoparticles should have different inputs than the ones designed for ENP. If not, more qualitative data is needed for incidental nanoparticles.

In conclusion, it is possible to realize that there is an opportunity when using these approaches combined: on one hand, the qualitative assessment gives inputs on control measures and, on the other hand, the quantitative approach provides a more detailed information about UFP, that may provide more accurate inputs for the qualitative methodology used. This pilot study may give a good insight for future research, to explore the potential of combining these two approaches to create solutions to manage the risk of exposure to incidental NM.

Author Contributions: Conceptualization, M.S., P.A. and F.S.; methodology, M.S., P.A. and F.S.; validation, P.A. and F.S.; investigation, M.S.; writing—review and editing, M.S., P.A. and F.S.; supervision, P.A. and F.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Acknowledgments: The results of this study would not be possible to obtain without the support of the company specializing in technical coatings, where measurements were performed. We wish to acknowledge the help provided by the board of the company and workers involved in the study.

Conflicts of Interest: The authors declare no conflict of interest.

CHAPTER 5. OCCUPATIONAL EXPOSURE TO INCIDENTAL NANOMATERIALS IN METAL ADDITIVE MANUFACTURING: AN INNOVATIVE APPROACH FOR RISK MANAGEMENT

Paper submitted for publication in October 2022 to the International Journal of Environment Research and Public Health.

Abstract

The benefits of metal 3D printing seem unquestionable. However, this additive manufacturing technology brings concerns to occupational safety and health professionals, since recent studies show the existence of airborne nanomaterials in these workplaces. This article explores different approaches to manage the risk of exposure to these incidental nanomaterials, on a case study conducted in a Portuguese organization using SLM technology. A monitoring campaign was performed using a CPC, a SMPS and air sampling for later SEM and EDS analysis, proving the emission of nano-scale particles and providing insights on number particle concentration, size, shape and chemical composition of airborne matter. Additionally, Control Banding Nanotool v2.0 and Stoffenmanager Nano v1.0 were applied in this case study as qualitative tools, although de-signed for engineered nanomaterials. This article highlights the limitations of using these quantitative and qualitative approaches when studying metal 3D Printing workstations. As a result, this article proposes the IN Nanotool, a risk management method for incidental nanomaterials designed to overcome the limitations of other existing approaches and to allow non-experts to manage this risk and act preventively to guarantee the safety and health conditions of exposed workers.

5.1 Introduction

Freedom of design, time efficiency, reduction of labor and machine costs are few examples of the several advantages mentioned when the subject is metal 3D Printing, also known as metal Additive Manufacturing (AM) (Duda & Raghavan, 2016). Regardless its considerable potential, metal AM has been raising some concerns regarding occupational health and safety (Graff et al., 2017). Among other occupational risks, it is known that during these processes incidental metal nano-objects are emitted and it is essential to manage the risk of exposure to this airborne matter, to reduce possible negative ill-health effects on workers (Ljunggren et al., 2019).

Different approaches have been used to assess and/or manage the occupational risk of exposure to incidental nanomaterials in AM processes, but the definition of standardized methods still remains an urgent need (Leso et al., 2021). Looking at this occupational risk from the point of view of the common industrial hygiene approach, it is possible to monitor and to quantify the airborne matter released during metal 3D printing. Recent publications in this field endorse the use of direct-reading instruments (for example condensation particle counter - CPC, optical particle counter - OPC and scanning mobility particle sizer – SMPS) and/or the collection of samples and subsequent structural and chemical analysis, by using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and/or energy dispersive X-ray analyzers (EDS) (Dugheri et al., 2022; Graff et al., 2017; A. C. Jensen et al., 2020; Ljunggren et al., 2019; Mellin et al., 2016; Sousa et al., 2021b). However, this attempt at a more industrial hygiene conservative approach has limitations, that cross all these studies: the lack of clearly defined and standardized occupational exposure limits for metal incidental nanomaterials and the lack of standardized sampling strategies. Some of these studies use as comparison reference values for nanomaterials proposed by different competent local entities and institutes, but so far, no specific limits have been proposed for metal incidental nanomaterials. The most common approach is to compare the results to the recommended benchmarks defined by the Nanosafety Research Centre of the Finnish Institute of Occupational Health (FIOH), i.e. 20,000 nanoparticles/cm^3 (with a density higher than 6000 kg/m^3) for an 8-hour exposure time. This limit was later adopted by the Institute for Occupational Safety and Health of the German Social Accident Insurance (IFA DGUV) and the IVAM Environmental Re-search UVA BV in the Netherlands (Dugheri et al., 2022; Hendrikx & Broekhuizen, 2013). Even if this value is assumed as an appropriate reference for metal AM case studies, the quantitative risk assessment still has limitations, namely the possible lack of access to equipment and laboratory analysis for these monitoring campaigns and also the lack of experts to perform them and interpreter the results.

Another possibility to assess this risk during metal AM has been to apply qualitative methods originally designed for engineered nanomaterials (ENM), namely control banding based ones. Sousa et al. (2021b) and Dugheri et al. (2022) applied Control Banding Nanotool v2.0 to assess the risk of exposure to ultrafine particles during metal 3D printing operations. Sousa et al. (2021b) highlight some difficulties on using this approach for incidental nanoparticles, specially the lack of background information on the particles (such as size, shape, and solubility, among others). These authors suggest the design of new methods for incidental nanomaterials, with different inputs than the ones for ENM, to reduce the uncertainty associated with the assessment. Dugheri et al. (2022) also emphasize the importance of searching different strategies to assess this occupational risk.

This article aims to explore different approaches to study the potential exposure to incidental nanomaterials during metal AM, through a case study conducted in an organization using Selective Laser Melting (SLM) technology. The main purpose of this article is to propose a risk management tool, entitled IN Nanotool, designed for incidental metal nanomaterials originated from metal AM processes, to overcome the limitations of other existing approaches.

5.2 Materials and Methods

5.2.1. Facility, operation conditions and materials

This study was conducted in an organization that uses Selective Laser Melting (SLM) technology for metal additive manufacturing. The SLM printer is located in a room dedicated to prototyping, with approximately 85 m2 and 3 meters in height. On the data collection day, no other equipment besides the printer was operating.

The printing process consists in the deposition of layers of a metal powder, usually 20 to 70 microns depending on materials, followed by the application of an infrared laser light scan (1064nm) of 250W that melts the powder to reproduce a three-dimensional part, previously defined in a CAD program. The material used was a nitrogen gas atomized spherical powder for additive manufacturing: stainless steel 316L, with particle size between 20 and 53 μm. Stainless steel 316L is an alloy of iron (>75%) and chromium (≈17%) which also contains nickel (≈12,5%), molybdenum (≈2,5%) and other elements in less significant amount. In this case study, 59,15 cm^3 of this powder were used during the printing process but the final part only had 0,35 cm^3 (approximately 0,59%).

In addition to the initial preparation for printing (which includes CAD design and filling the powder in the printer), the worker's tasks can be divided into 3 distinct phases, as described in Table 5.1.

Table 5.1. Description of the tasks under study.

Task 1	Supervision of printing process
Task 2	Removing the part from the printer and cleaning it with a brush
Task 3	Removing the remains of powder, sieving it for reuse and cleaning the powder container

Data gathering included a sample of powder before and after printing process, technical and material safety data sheets of the powder, information on operation conditions and on-site measurements.

5.2.2. Quantitative approach

In the attempt to study the risk of exposure to airborne nanomaterials using a quantitative assessment, the following equipment was used:

- A thermo-hygrometer, TSI® Model 9545, to measure air velocity, room temperature and relative humidity.
- Portable condensation particle counter (CPC), TSI® model 3007, to measure the total particle number concentration from 10 nm to > 1000 nm in 1-s time resolution.
- A scanning mobility particle sizer (SMPS), TSI® Model 3910, to measure nanoparticle size distributions and concentrations, with a size distribution from 10 to 420 nm. The number of particles per size was measured by an internal CPC which counts single particles to provide accurate counts, even at low concentrations.
- A personal air sampling pump, SKC AirChek® TOUCH, to collect samples for subsequent Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) analysis. The samples were collect using a polycarbonate membrane filter (with 25 mm diameter and 0,4 µm porosity) and a heat-treated quartz filter (DPM Cassette with 0,8 µm Impactor), since these type filters were used in previous studies and proved to be effective for nanomaterials (Dewalle et al., 2011; Tsai et al., 2015; Tsai et al., 2009).

The monitoring campaign started with background measurements before any printing activity. Then, measurements were performed during three different tasks, previously described in Table 5.1.

Even though the printer works closed and has an exhausting system working during the printing activity to avoid emissions, the operator stands frequently near the control panel. For that reason, measurements were carried out during this task, to better know the risk of exposure to potential emissions while parts are being printed.

5.2.3. Qualitative approach

Control Banding has been often used for studying the risk of exposure to ENM and has been suggested as a potential approach to assess the risk of exposure to incidental nanomaterials (Sousa et al., 2021b). In 2021, Sousa et al. published a review on control band, focusing the occupational exposure to incidental nanoparticles. This study provided an overview on different Control Banding approaches designed for ENM and their potential to be used for incidental nanomaterials, highlighting CB Nanotool and Stoffenmanager Nano as potential methods in this field, considering some adaptations. Therefore, Control Banding Nanotool (version 2.0) and Stoffenmanager Nano (version 1.0) were used in this case study. Although both methods are control banding based, their approach is significantly different, especially regarding the inputs for the determination of bands and the risk control considerations.

CB Nanotool 2.0 was proposed in 2009 (Zalk et al., 2009) and revalidated by its authors 10 years later (Zalk et al., 2019). Applying this method, it is possible to determine the risk level of a particular operation using a four-by-four matrix, based on severity and probability scores. The severity score depends on factors associated with the nanomaterial (70% of the severity score) and with the parent material (30% of the severity score). Nanomaterial (NM) factors include: surface chemistry; particle shape; particle diameter; solubility; carcinogenicity; reproductive toxicity; mutagenicity; dermal toxicity; and asthmagen. The parent material (PM) factors are scored considering: Occupational Exposure Limit (OEL); carcinogenicity; Reproductive Toxicity; Mutagenicity; Dermal Toxicity; and Asthmagen. The second step is to reach the probability score, for which the following factors are considered: estimated amount of material used; dustiness/mistiness; number of employees with similar exposure; frequency of operation; and duration of operation. Finally, after reaching a severity and probability score, this tool leads to one of four risk levels (RL) which correspond to a certain control measure: RL 1 - general ventilation; RL 2 - fume hoods or local exhaust ventilation; RL 3 - containment; and RL 4 - seeking specialist advice.

On the other hand, Stoffenmanager Nano 1.0 is a risk-banding tool created to prioritize the risk of exposure to manufactured nano-objects and to help defining control measures (Duuren-Stuurman et al., 2012). This tool defines five hazard bands (A being the least hazardous until E which is the most hazardous), considering hazardous characteristics of the nano-object under study, such as particle size, water solubility, persistent fibers or other structure and classification based on data available on the nano-object or on the hazardous potential of its parental material. Four exposure bands are also determined (1 to 4, with 1 being the lowest exposure), considering nine modifying factors related to source emission, transmission, and immission (receptor): substance emission potential, handling (activity emission potential), localized controls, segregation, dilution/dispersion, personal behavior, separation (personal enclosure), surface contamination, and respiratory protective equipment. The online tool guides the user through six steps:

- Step 1 - General: allows the user to select the source domain of potential release of nanomaterials, among four options: release of primary particles during actual synthesis; handling of bulk aggregated/agglomerated nanopowders; spraying or dispersion of a ready-to-use nanoproducts; or fracturing and abrasion of manufactured nano-objects-embedded end products.
- Step 2 – Product characteristics: includes information provided by product information sheets and/or material safety data sheets (if available), such as dustiness, moisture content, concentration, presence of fibers, and inhalation hazard.
- Step 3 – Handling/process: considers information to characterize tasks such as the way the product is handled, duration and frequency of the task, distance to the breathing zone of employees and number of employees performing the task.
- Step 4 – Working area: takes into account information on frequency of room cleaning, inspections and maintenance, as well as volume and ventilation conditions of the working room.
- Step 5 – Local control measures and personal protective equipment (PPE): includes information regarding control measures, location of the employees and type of PPE used during the task.
- Step 6 – Risk assessment: inputs of the 5 previous steps are considered to calculate the exposure-hazard-class and show the risk priority band using the risk matrix. Overall, 1 represents the highest priority and 3 the lowest priority.

5.2.4. Semi-quantitative approach – Proposal for a new risk management method

After applying the previously mentioned qualitative and quantitative approaches in this case study, a different approach was designed. As highlighted by Sousa et al. (2021), the existing qualitative and quantitative approaches have significant limitations when aiming to manage the risk of exposure to incidental nanomaterials, mainly during metal 3D printing. Therefore, in this study a new semi-quantitative risk management tool was designed and verified.

The IN Nanotool is based on control banding and aims to enable the risk management of exposure to incidental metal nanomaterials released in AM processes. The existing control banding methods for studying the risk associated with exposure to nanomaterials in workplaces were designed for engineered nanomaterials (Sousa et al., 2021a). However, there is a need to create methods to study the risk of exposure to incidental ones, since the number of workers exposed to them is significantly higher than the ones exposed to ENM (Viitanen et al., 2017).

Therefore, IN Nanotool was designed taking into consideration the limitations and opportunities already identified in previous studies regarding exposure to incidental nanomaterials in addition to the results of this particular case study.

5.3 Results

5.3.1. Quantitative approach

5.3.1.1. On-site measurements

Temperature, relative humidity, and air velocity were determined to characterize the background environmental conditions of the prototyping room and the conditions near the 3D printer while it was printing, as shown in Table 5.2.

Table 5.2. Environmental characterization provided by the thermo-hygrometer: air velocity, room temperature and relative humidity.

Measured parameters	Background (before printing)	Near the printer (close to the door)
Temperature [°C]	27.4	28.1
Relative Humidity [%]	54.2	53.7
Air Velocity [m/s]	<0.01	0.17

The CPC provided the particle number concentration, from 10 nm to > 1000 nm, during the three tasks under study, in addition to the background measurement. Table 5.3 indicates the mean particle number concentration for these four distinct periods. Additionally, Figure 5.1 illustrates how the concentration of this airborne particles changed over time during the trial.

Table 5.3. Results provided by the CPC.

	Background	Task 1	Task 2	Task 3
Time [min]	15	105	8	15
Mean particle number concentration [particles/cm^3]	6 003.07	12 636.92	12 734.70	11 121.98

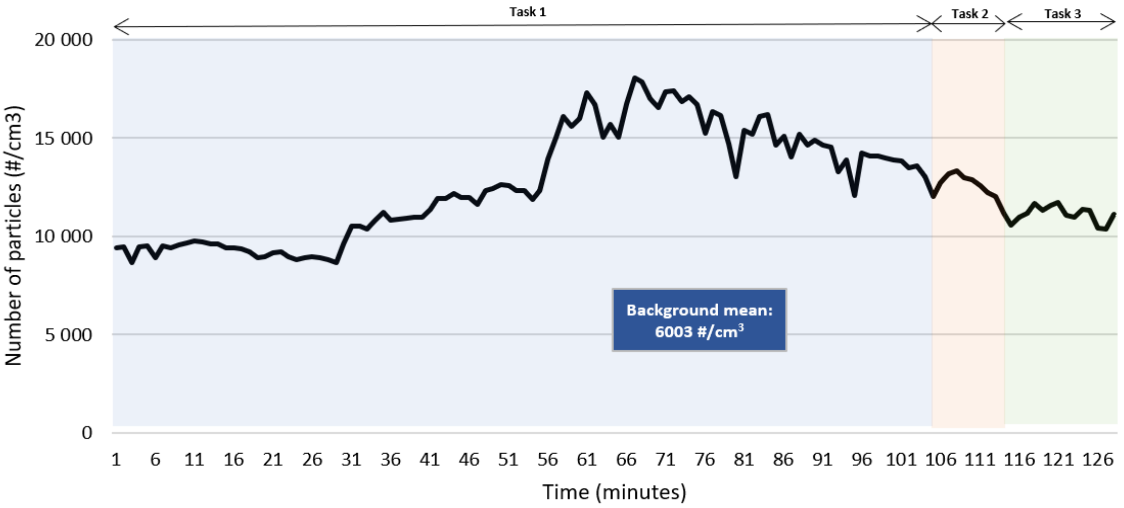


Figure 5.1. Number particle concentration (#/cm^3) over time measured by the CPC.

The SMPS allowed to better understand the potential exposure to smaller particles, by providing the size distributions from 10 to 420 nm. The corresponding results are presented in Table 5.4 and Figure 5.2.

Table 5.4. Results provided by the SMPS: Mean particle number concentration [particles/cm^3] by particle size.

	11.5	**15.4**	**20.5**	**27.4**	**36.5**	**48.7**	**64.9**	**86.6**	**115.5**	**154.0**	**205.4**	**273.8**	**365.2**	**Total**	**GSD**$^{(1)}$
Background	219.69	461.75	458.70	630.35	709.28	684.59	602.07	502.39	347.25	153.61	3.89	0.00	0.00	**4773.58**	40.63
Task 1	1080.31	1379.35	788.44	1129.11	1250.13	1010.95	654.65	430.89	278.75	129.33	13.35	0.00	0.12	**8145.38**	30.66
Task 2	883.65	1611.25	1146.33	1365.82	1430.65	1206.07	836.94	527.58	274.65	72.86	0.00	0.00	0.00	**9355.81**	30.27
Task 3	714.64	1436.72	1118.46	1292.11	1353.58	1177.73	856.14	543.37	266.28	54.00	0.00	0.00	0.00	**8813.04**	31.19

$^{(1)}$ Geometric Standard Deviation

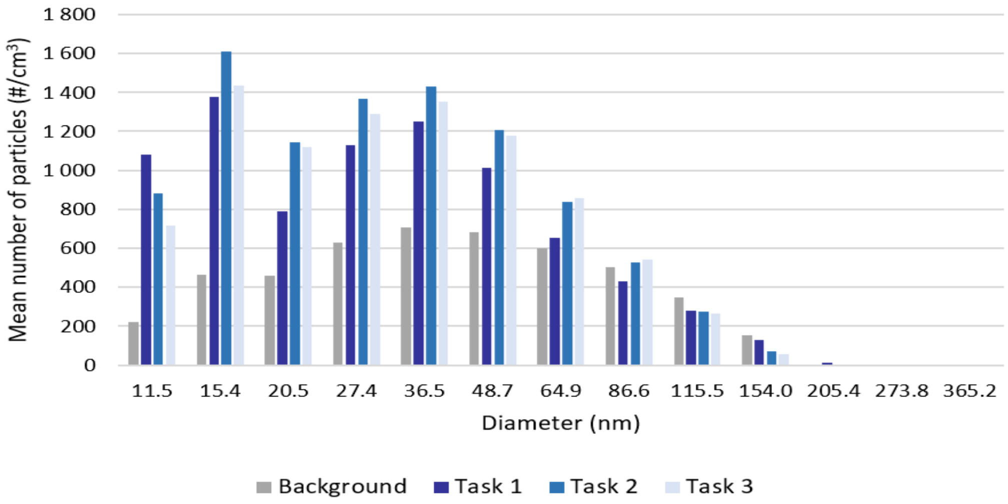
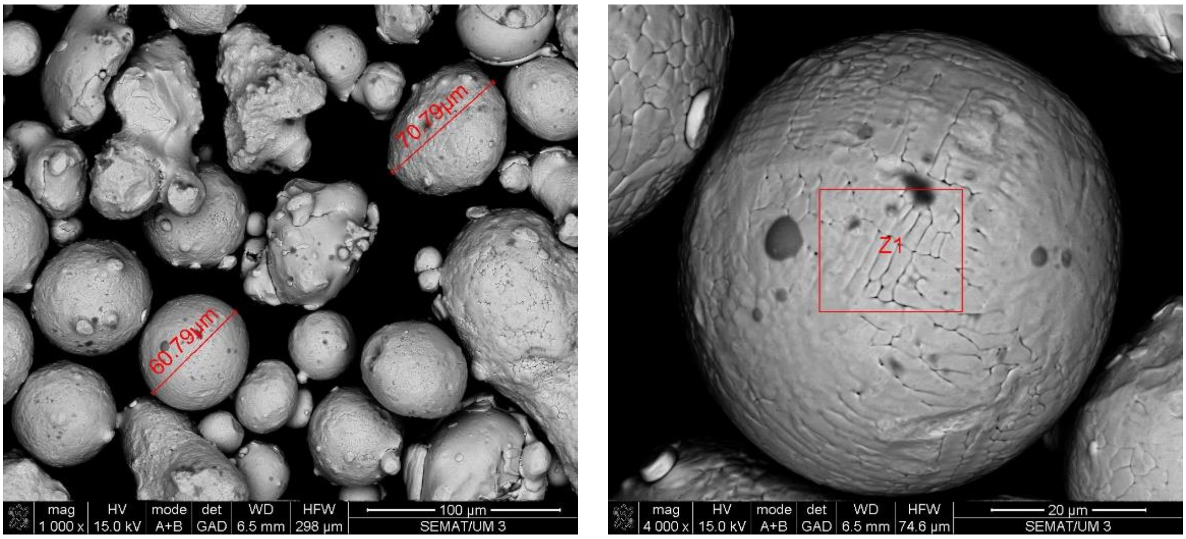


Figure 5.2. Results provided by the SMPS: Mean particle number concentration [particles/cm^3] by particle size range.

5.3.1.2. SEM and EDS

Data collection included two samples of stainless steel 316L: one of the raw powder before printing and other of the powder after the laser action, which is collected after printing to be reused in future prints. Scanning electron microscopy and energy-dispersive X-ray spectroscopy analysis were performed to these two samples, to study possible changes in size, shape and/or chemical composition. Results are shown in Figures 5.3 to 5.6.



(**a**) (**b**)

Figure 5.3. SEM analysis results: Stainless steel 316L raw powder, before any AM process (a) Size and shape of particles in the sample; (b) Image of the particle analyzed by EDS (results in Figure 5.4).

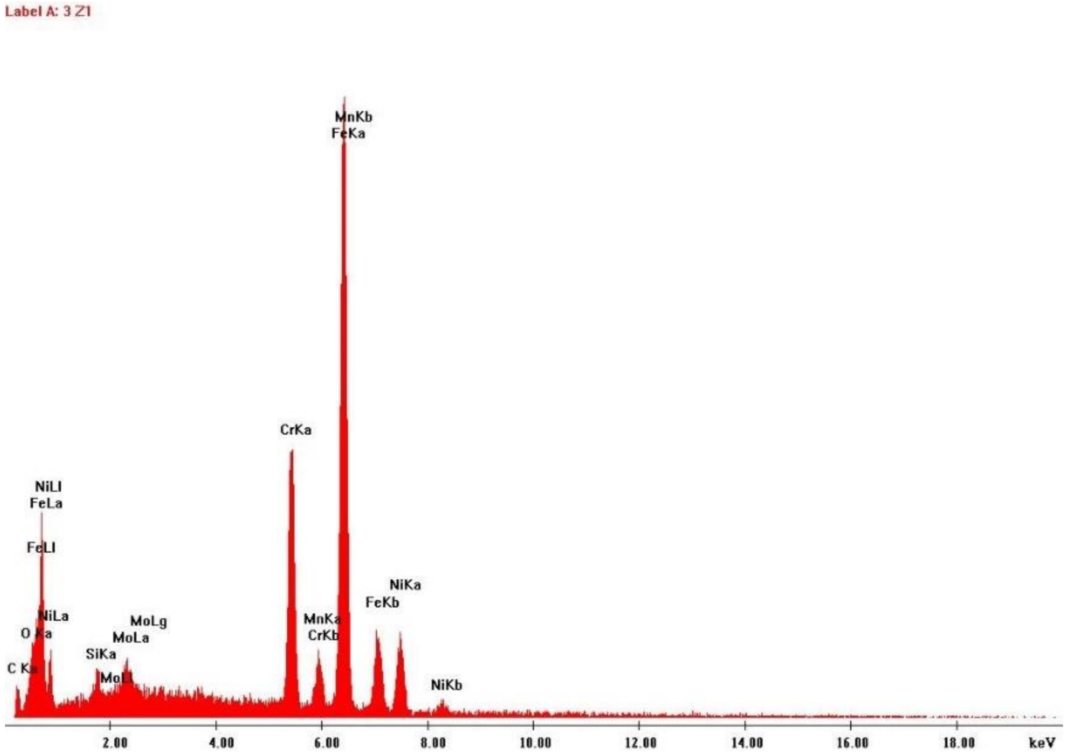
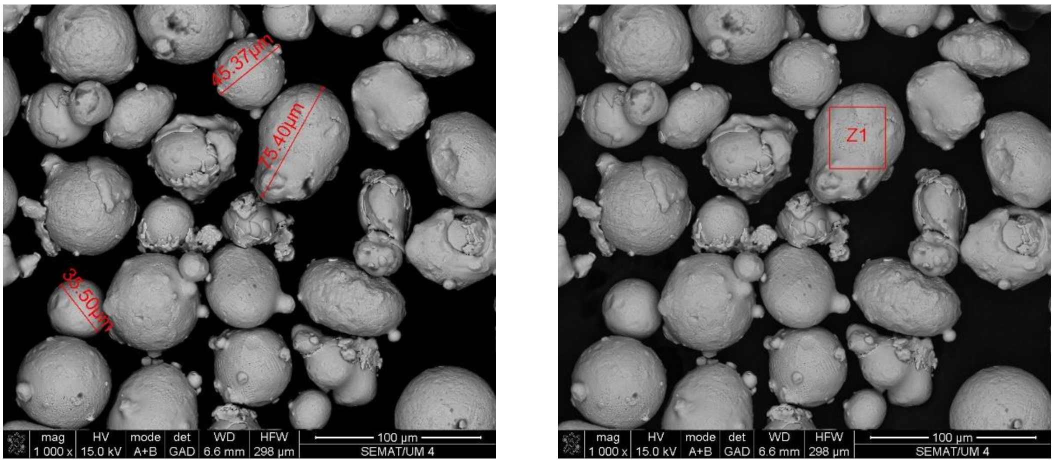


Figure 5.4. EDS analysis results: stainless steel 316L raw powder, before any AM process.



(**a**) (**b**)

Figure 5.5. SEM analysis results: Stainless steel 316L powder after AM process (a) Size and shape of particles in the sample; (b) Image of the particle analyzed by EDS (results in Figure 5.6).

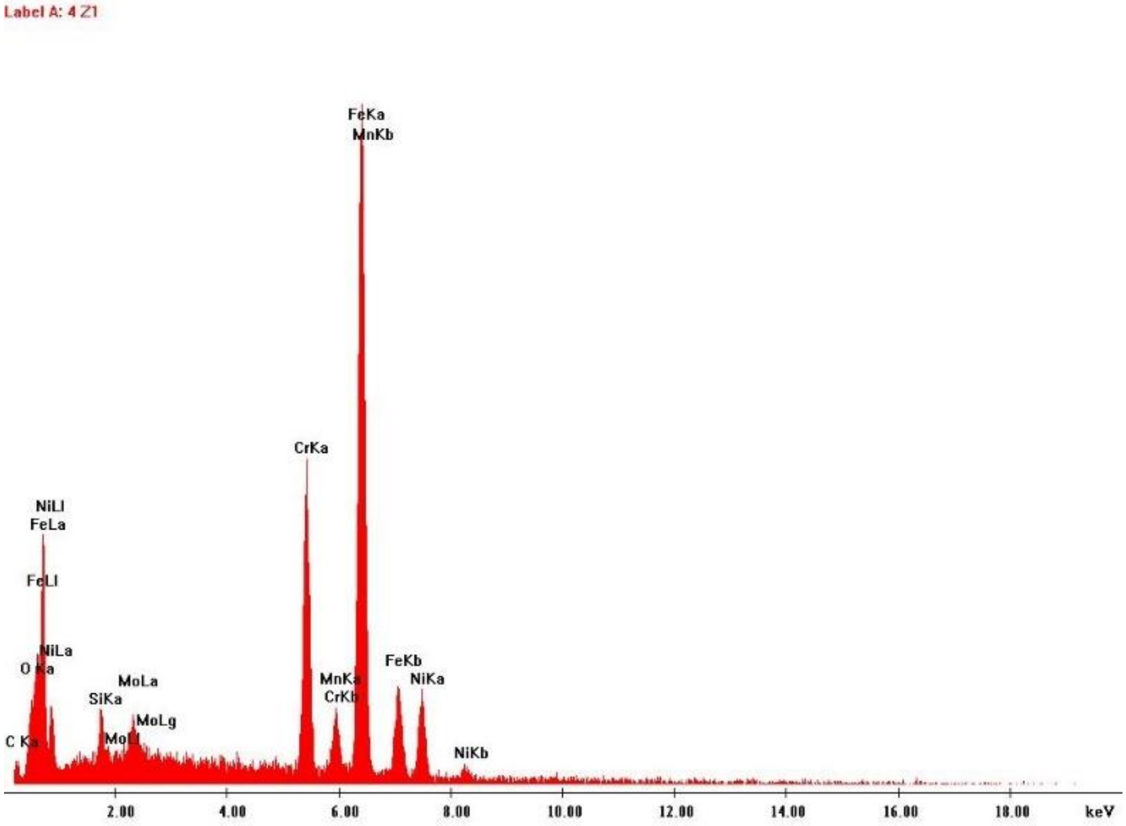
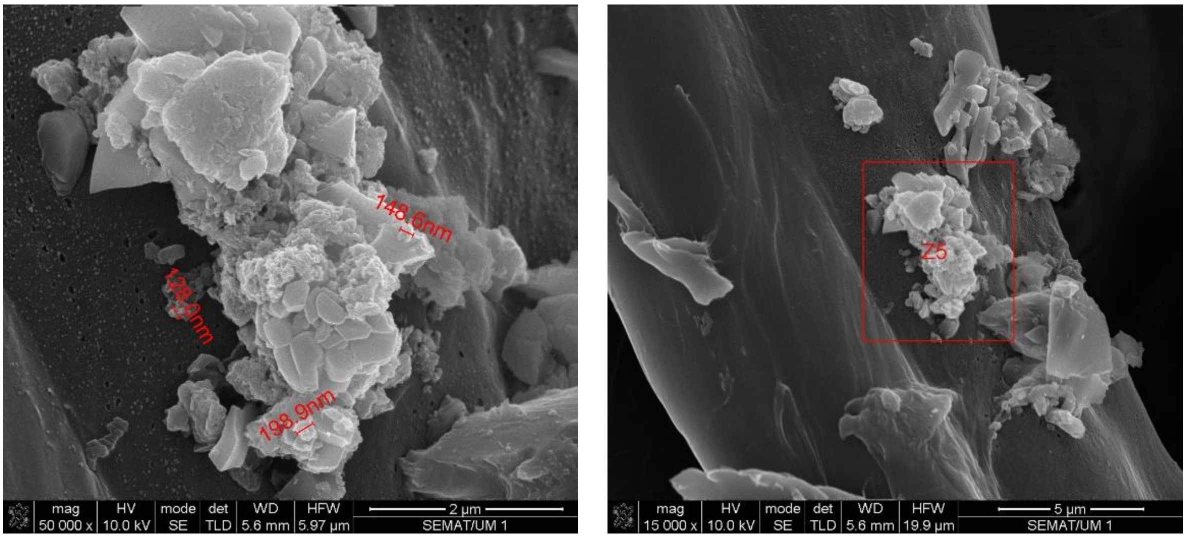


Figure 5 6. EDS analysis results: stainless steel 316L powder after printing.

To better characterize the size and shape of the particles released to the work atmosphere during this AM process, the air samples collected on the polycarbonate membrane filter and on the heat-treated quartz filter were subjected to SEM. EDS analysis was also carried out to verify the elementary composition of these samples. Figures 5.7 to 5.10 illustrate these results.



(**a**) (**b**)

Figure 5.7. SEM analysis results: airborne sample collected on quartz filter (a) Size and shape of particles in the sample; (b) Image of the particle analyzed by EDS (results in Figure 5.8).

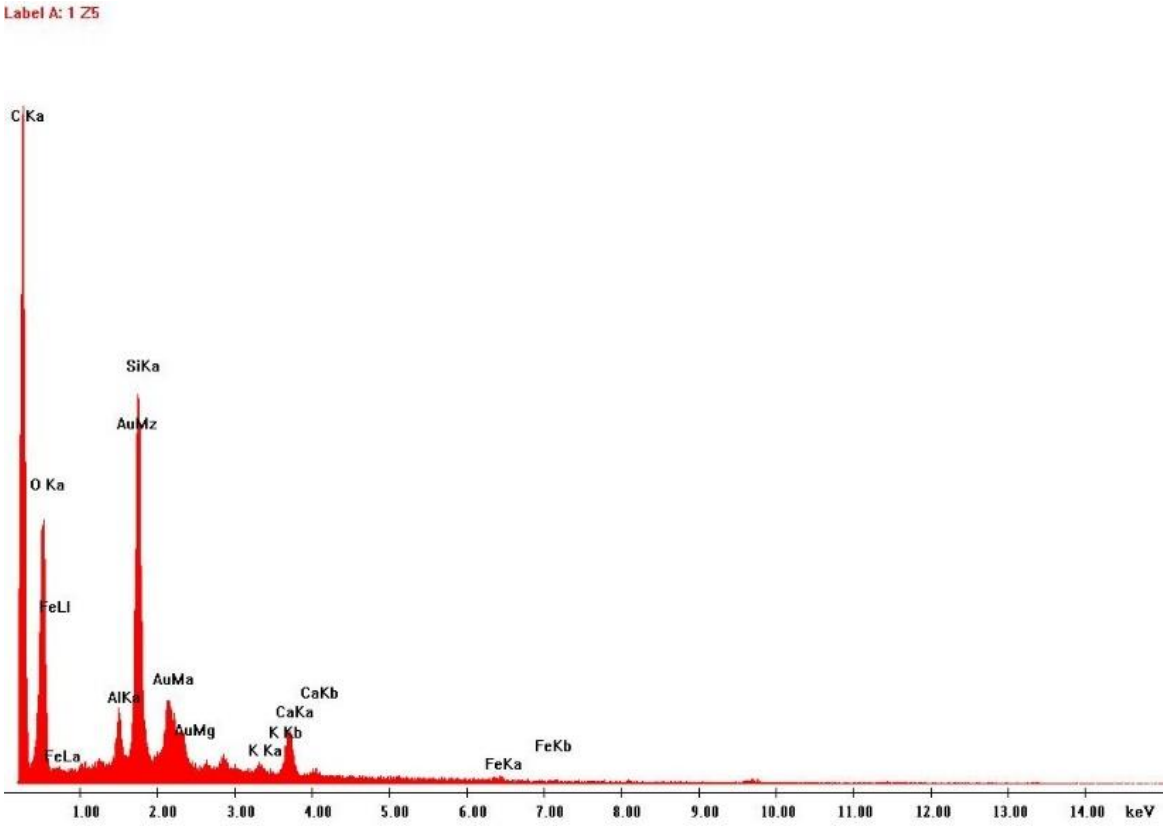
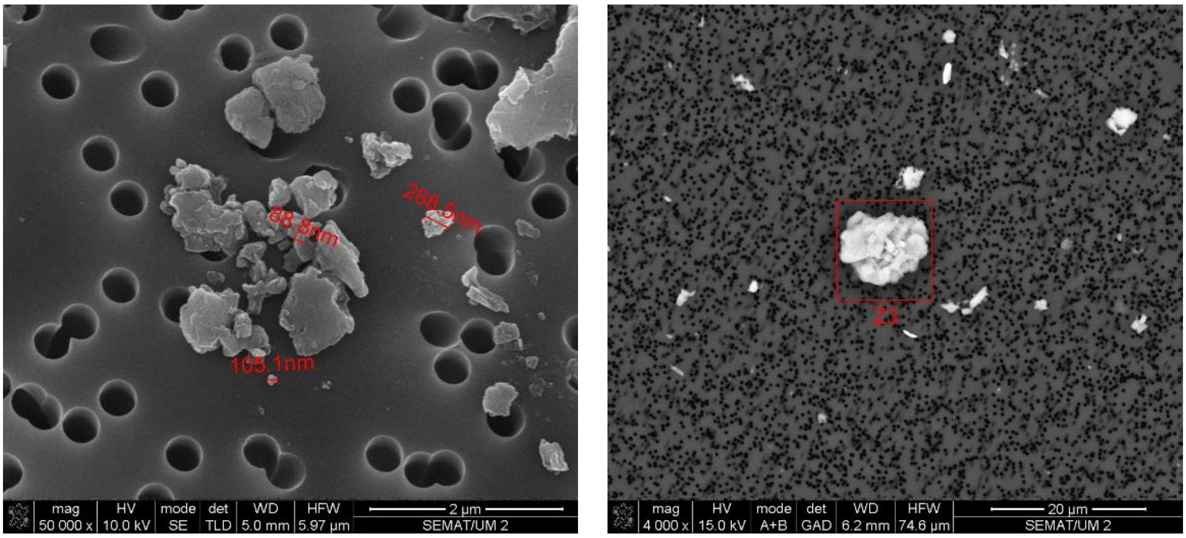


Figure 5.8. EDS analysis results: airborne sample collected on quartz filter.



(**a**) (**b**)

Figure 5.9. SEM analysis results: airborne sample collected on polycarbonate filter (a) Size and shape of particles in the sample; (b) Image of the particle analyzed by EDS (results in Figure 5.10).

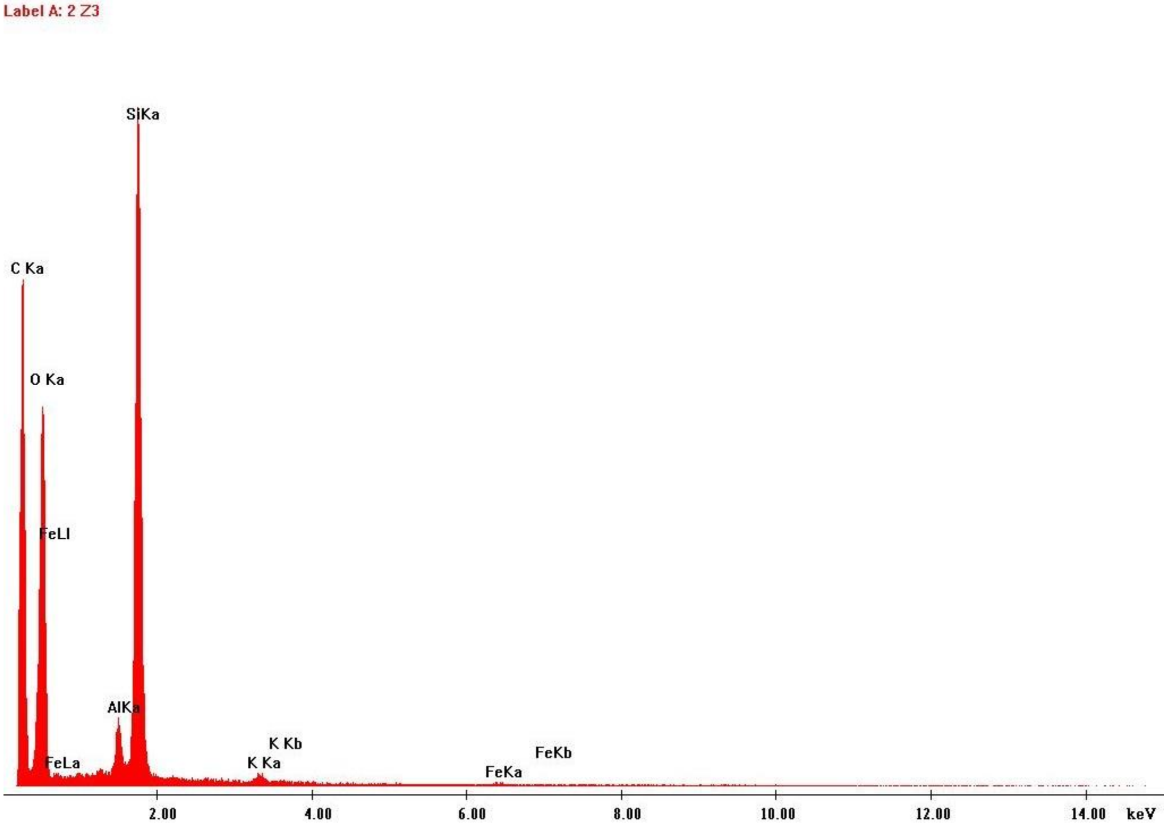


Figure 5.10. EDS analysis results: airborne sample collected on polycarbonate filter.

5.3.2. Qualitative assessment results

5.3.2.1. Control Banding Nanotool 2.0

As mentioned before, CB Nanotool 2.0 was one of the methods used to qualitatively assess the risk of exposure to incidental nanoparticles during the tasks understudy. Table 5.5 summarizes the considerations and results of the application of this qualitative method.

Table 5.5. Results of the application of CB Nanotool version 2.0.

CB factors	Task 1	Task 2	Task 3
PM OEL	200 µg/m^3 [1]	200 µg/m^3 [1]	200 µg/m^3 [1]
PM Carcinogenicity	yes [2]	yes [2]	yes [2]
PM Reproductive Toxicity	no	no	no
PM Mutagenicity	no	no	no
PM Dermal Toxicity	yes [3]	yes [3]	yes [3]
PM Asthmagen	no	no	no
NM Surface Chemistry	unknown	unknown	unknown
NM Particle Shape	unknown	unknown	unknown
NM Particle Diameter	unknown	unknown	unknown
NM Solubility	unknown	unknown	unknown
NM Carcinogenicity	unknown	unknown	unknown
NM Reproductive Toxicity	unknown	unknown	unknown
NM Mutagenicity	unknown	unknown	unknown
NM Dermal Toxicity	unknown	unknown	unknown
NM Asthmagen	unknown	unknown	unknown
Severity Score | Band	**63 | High**	**63 | High**	**63 | High**
Estimated amount of material used	>100 mg	>100 mg	>100 mg
Dustiness/mistiness	high	high	high
Number of employees with similar exposure	1-5	1-5	1-5
Frequency of operation	daily	daily	daily
Duration of operation	> 4 hours	< 30 min	< 30 min
Probability Score | Band	**85 | Probable**	**70 | Likely**	**70 | Likely**
Risk Level and recommended controls	**RL 4 - Seek specialist advice**	**RL 3 – Containment**	**RL 3 - Containment**

[1] Considering the lowest OEL recommended in Portugal: Nickel inorganic compounds (Portuguese Institute of Quality, 2014)

[2] Carc. 2, H351 according to the material safety data sheet

[3] Skin Sens. 1, H317 according to the material safety data sheet

5.3.2.2. Stoffenmanager Nano 1.0

The results of the application of Stoffenmanager Nano 1.0 to assess qualitatively the risk of exposure to incidental nanoparticles during the tasks understudy are in Table 5.6.

Table 5.6. Results of the application of Stoffenmanager Nano 1.0.

CB factors	**Task 1**	**Task 2**	**Task 3**
Product appearance	powder	powder	powder
Dustiness	very high	very high	very high
Moisture content	dry product	dry product	dry product
Exact concentration of the nano component	unknown	unknown	unknown
Concentration	small (1-10%)	small (1-10%)	small (1-10%)
Fibers or fiber like particles in the product	no	no	no
Inhalation hazard	unknown	unknown	unknown
OECD components	other MNOs	other MNOs	other MNOs
PM with one or more of the R phrases: R40, R42, R43, R45, R46, R49, R68 [1]	yes	yes	yes
Hazard Band	**E**	**E**	**E**
Task characterization	Handling of products in closed containers	Handling of products with low speed or little force	Handling of products with low speed or little force
Duration task	30 – 120 min/day	1 – 30 min/day	1 – 30 min/day
Frequency task	≈ 4 to 5 days/week	≈ 4 to 5 days/week	≈ 4 to 5 days/week
Distance head-product (breathing zone)	> 1 m	< 1 m	< 1 m
More than one employee performing the task simultaneously	no	no	no
Room cleaned daily	yes	yes	yes
Inspections and maintenance of machines/ ancillary equipment performed at least monthly	no	no	no
Volume of the working room	100 – 1000 m^3	100 – 1000 m^3	100 – 1000 m^3
Ventilation of the working room	Mechanical and/or natural ventilation	Mechanical and/or natural ventilation	Mechanical and/or natural ventilation
Local control measures	Containment of the source with local exhaust ventilation	none	none
The employee is situated in a cabin	no	no	no
Personal Protective Equipment used	none	Filter mask P3 (FFP3)	Filter mask P3 (FFP3)
Exposure Band	**1**	**2**	**2**
Risk Level	**RL 1 – Highest priority**	**RL 1 – Highest priority**	**RL 1 – Highest priority**

Recommended controls	- Product elimination - Task elimination - Product substitution - Automation of tasks - Enclosure of the source - Local exhaust ventilation - Enclosure of the source in combination with local exhaust ventilation - Wetting of powders/substance - Applying glove boxes/bags - Use of a spraying booth - Use of work cabins with clean air supply - Use of work cabins without clean air supply - Respiratory protection	- Product elimination - Task elimination - Process adaptations - Product substitution - Automation of tasks - Enclosure of the source - Local exhaust ventilation - Enclosure of the source in combination with local exhaust ventilation - Wetting of powders/substance - Applying glove boxes/bags - Use of a spraying booth - Use of work cabins with clean air supply - Use of work cabins without clean air supply - Respiratory protection

[1] Defined in Annex III of European Union Directive 67/548/EEC, no longer in force; replaced by CLP Regulation No 1272/2008

[2] Carc. 2, H351 according to the material safety data sheet

[3] Skin Sens. 1, H317 according to the material safety data sheet

5.3.3. IN Nanotool – Design

5.3.3.1. Framework

As previously mentioned, one of the main goals of this study was to design a more accurate control banding based method to manage the risk of exposure to incidental nano-scale matter in metal AM workplaces. This was only possible after studying and understanding the limitations and potential of the currently used methods.

The IN Nanotool redefined inputs by adapting them to incidental nanomaterials originating from metal powders. Additionally, this tool added quantitative data as a potential input, given the possibility to include information on shape and size of nanomaterials, taking into consideration that many authors consider this information fundamental to classify hazards (Duuren-Stuurman et al., 2012).

IN Nanotool defines four hazard bands, considering metal powder properties and airborne nanomaterials properties, and four exposure bands, considering materials and operation conditions and existing control measures. Then, it allows the determination of the risk level associated with the exposure to nanomaterials during metal AM, according to previously determined hazard and exposure bands, using a four-by-four matrix. Finally, this method recommends additional control measures depending on the risk level, as an increment to the existing ones.

IN Nanotool was thought to be used by occupational safety and health (OSH) professionals, including non-experts. Therefore, it aims to be an intuitive and user-friendly tool, maintaining the necessary accuracy for an assertive risk management, guaranteeing the safety and health conditions of exposed workers. The assessment steps are described in detail on the following subsubsections.

5.3.3.2. Hazard Band determination

The hazard band is determined by the sum of all points from 11 different factors related to the metal powder characteristics (50 possible points out of 100) and the airborne nanomaterials characteristics (50 possible point out of 100), as summarized in Table 5.7.

Table 5.7. Hazard factors and points per factor.

Metal powder characteristics

1. Powder Carcinogenicity: score is assigned based on whether the material is carcinogenic or not. It is possible to confirm this information on the material safety data sheet, for example, by checking if any of these hazard statements are included in its hazard identification: H350, H351 (according to CLP Regulation).

yes: 6 no: 0 unknown: 4.5

2. Powder Reproductive Toxicity: score is assigned based on whether the material is a reproductive hazard or not. It is possible to confirm this information on the material safety data sheet, for example, by checking if any of these hazard statements are included in its hazard identification: H360, H361, H362 (according to CLP Regulation).

yes: 6 no: 0 unknown: 4.5

3. Powder Mutagenicity Toxicity: score is assigned based on whether the material is a mutagenic or not. It is possible to confirm this information on the material safety data sheet, for example, by checking if any of these hazard statements are included in its hazard identification: H340, H341 (according to CLP Regulation).

yes: 6 no: 0 unknown: 4.5

4. Powder Dermal Toxicity: score is assigned based on whether the material is a dermal hazard or not. It is possible to confirm this information on the material safety data sheet, for example, by checking if any of these hazard statements are included in its hazard identification: H310, H311, H312 (according to CLP Regulation).

yes: 6 no: 0 unknown: 4.5

5. Powder Inhalation Toxicity: score is assigned based on whether the material is toxic if inhaled or not. It is possible to confirm this information on the material safety data sheet, for example, by checking if any of these hazard statements are included in its hazard identification: H330, H331, H332, H333 (according to CLP Regulation).

yes: 6 no: 0 unknown: 4.5

6. Other health hazards of the powder: score is assigned based on other hazards of the material besides the ones already scored in factors 1 to 5. It is possible to confirm this information on the material safety data sheet, for example, by checking if any hazard statement starting with H3 is included in its hazard identification (besides the ones already mentioned in factors 1 to 5).

yes: 4 no: 0 unknown: 3

7. Lowest OEL applicable to powder [µg/m^3]: a different score is given depending on the lowest OEL defined for the metal powder's components.

<100 µg/m^3: 8 100-1000 µg/m^3: 4 1001-10000 µg/m^3: 2 >10000 µg/m^3: 0 unknown: 6

8. Powder Solubility: score is given depending on the water-solubility of the material, considering it is soluble if the solubility higher than 1g/L. If this property is unknown, 3 points are given.

insoluble (< 1 g/L): 4 soluble (> 1 g/L): 0 unknown: 3

9. Powder Average particle size [µm]: the score is assigned according to the available information or analyzes performed. If unknown, 3 points are given.

<50 µm: 4 50 – 1000 µm: 3 > 100 µm: 1 unknown: 3

Airborne nanomaterials characteristics

10. Shape: the score is assigned according to available information, for example, to SEM or TEM analyzes results, considering the most common shape verified. If unknown, 18.75 points are given.

tubular, fibrous: 25 anisotropic: 12.5 compact/ spherical: 6.25 unknown: 18.75

11. Size: the score is assigned according to available information, for example, to SEM or TEM analyzes results, considering the main size of airborne materials. If unknown, 18.75 points are given.

< 100 nm: 25 100 – 500 nm: 12.5 > 500: 6.25 unknown: 18.75

Regarding the properties of the metal powder, the first six factors are related with the hazard classification of the powder: carcinogenicity, reproductive toxicity, mutagenicity, dermal toxicity, inhalation toxicity and/or other significant health hazards. These properties can be verified, for example, on the second section of the material safety data sheet (MSDS) of the product (hazard identification), confirming if any of the related hazard statements are included. Other CB methods for ENM also include some of this information (Duuren-Stuurman et al., 2012; Paik et al., 2008; Zalk et al., 2009). Regardless, IN Nanotool attempts to better catalog these hazards in different factors and also to simplify the process of classification by using as guideline the related hazard statements, according to European Classification, Labelling and Packaging (CLP) Regulation. Many authors considerer that standardized communication, such as MSDS, should be the source of hazard information, including Stoffenmanager authors (Juric et al., 2015).

There are three more factors for the characteristics of the metal powder: lowest Occupational Exposure Limit (OEL) applicable, solubility, and average particle size. The first one is based on the CB Nanotool factor *Parent Material OEL*, considering it is important to take into account the known and already established occupational exposure limits. These limits may originate from bibliography, legislation, standardization or other reliable source. Next factor, solubility, is a physicochemical property considered in most CB approaches to study exposure to ENM (Lamon et al., 2019). A material is not considered water-soluble unless the solubility limit exceeds 1g/L or is listed as soluble or highly water-soluble. Points are given considering that even if the material is soluble does not mean there is no hazard; thus nano-specific properties are expected to be lost when particles are in solution (Duuren-Stuurman et al., 2012). Finally, the average particle size factor is taken into account, since the size of primary particles is an important input for a precautionary approach (Höck et al., 2018). The particle size can sometimes be found in the material safety data sheet of the product or in its technical sheet. Alternatively, it is possible to obtain this information by performing a SEM or TEM analysis. The points are given depending on a range of sizes, that goes from smaller than 50 µm to higher that 100 µm. Even though, in SLM technology it is very common to use metal powders with a typical particle size of 40 µm (Mellin et al., 2016), there are other technologies that use different size ranges. For instance, several AM technologies use metal powder between 15 to 100 µm (Tang et al., 2020).

To complete the hazard band determination, there are two significant factors related with the properties of airborne nanomaterials: shape and size. Shape is also an input in CB Nanotool 2.0 for the severity band of ENM (Zalk et al., 2009) and it is was also considered in IN Nanotool given its relevance. It can be scored considering, for example, results of a SEM or TEM analysis. Regarding size, despite the definition of nanomaterial, cells and organisms are also affected by particles whose external dimensions are bigger than 100 nm, since cells are capable of absorbing particles of up to approximately 500 nm (Höck et al., 2018). Therefore, it is possible to assign different scores in this last factor, depending on the main size range: lower than 100 nm, between 100 and 500 nm or higher than 500 nm. This factor can be scored considering, for example, results of a SEM or TEM analysis. If it is not possible to obtain accurate information on shape and size of airborne matter, IN Nanotool allows the user to assign 18.75 points to each factor, assuming it is unknown. In fact, for all 11 factors it is possible to classify the factor as unknown, giving the uncertainty in these studies.

After assigning scores to all 11 factors, the hazard band is determined depending on the sum of these points. There are four different hazard bands: low (0 – 25), medium (26 – 50), high (51 – 75) or very high (76 – 100).

5.3.3.3. Exposure Band determination

The exposure band is determined by the sum of all points from five distinct factors related to material operation conditions (60 possible points out of 100) and four factors associated with existing control measures (40 possible points out of 100), as presented in Table 5.8.

Table 5.8. Exposure factors and points per factor.

Operation conditions

1. Powder Dustiness: points are provided based on a judgment of whether the material's dustiness is high, medium, or low. If unknown, 11.5 points are given.

high: 15	medium: 10	low: 5	unknown: 11.25

2. Frequency of operation: points are provided depending on the regularity of the procedure.

daily: 10	weekly: 5	monthly: 2.5	> monthly: 0	unknown: 7.5

3. Duration of operation (per day): score is assigned based on the daily time dedicated to the operation.

> 4 hours: 10	1 – 4 hours: 5	30 – 60 min: 2.5	< 30 min: 0	unknown: 7.5

4. Task characterization: points are provided based on a judgment of whether the quantity of dust generated and dispersed during the task is large, low or negligible during manual handling. If there is no manual handling or it is performed in a closed container (for example printing operation in a closed printer), 0 points are assigned to this factor.

manual handling the powder where large quantities of dust are generated and dispersed: 15	manual handling the powder where low quantities of dust are generated and dispersed: 10	manual handling the powder where negligible quantities of dust are generated and dispersed: 5	no manual handling or handling in closed containers: 0

Existing control measures

5. Working room control measures: points are provided by confirming on-site ventilation conditions.

no general ventilation: 10	natural ventilation: 5	mechanical ventilation (alone or combined with natural ventilation): 0	unknown: 7.5

6. Source control measures: score is given by confirming the control measures on the source of emissions.

no control measures at the source: 15	use of a product that limits the emission: 10	local exhaust ventilation or fume hood: 5	containment of the source or glove box or glove bag: 0

7. Preventive procedures: score is assigned according to the existing cleaning and maintenance routines.

room cleaned daily and printer maintenance performed at least monthly: 0	cleaning and maintenance procedures less frequent than previous option: 10	unknown: 7.5

6. Worker related control measures: points are chosen considering the personal protective equipment (PPE) used by the worker.
The worker does not work in a separate room/ cabin and does not use any PPE: 5
The worker uses eye protection and/or protective clothing (including gloves): 4
The worker uses filter mask P2/FFP2: 4
The worker uses filter mask P2/FFP2 and protective clothing (including gloves) or eye protection: 3
The worker uses filter mask P2/FFP2, protective clothing (including gloves) and eye protection: 2.5
The worker uses filter mask P3/FFP3: 3
The worker uses filter mask P3/FFP3 and protective clothing (including gloves) or eye protection: 2.5
The worker uses filter mask P3/FFP3, protective clothing (including gloves) and eye protection: 1
The worker uses powered/supplied air respirator: 1
The worker uses powered/supplied air respirator and protective clothing (including gloves) or eye protection: 0.5
The worker uses powered/supplied air respirator, protective clothing (including gloves) and eye protection: 0
The worker works in a separate room/cabin with independent ventilation system: 0

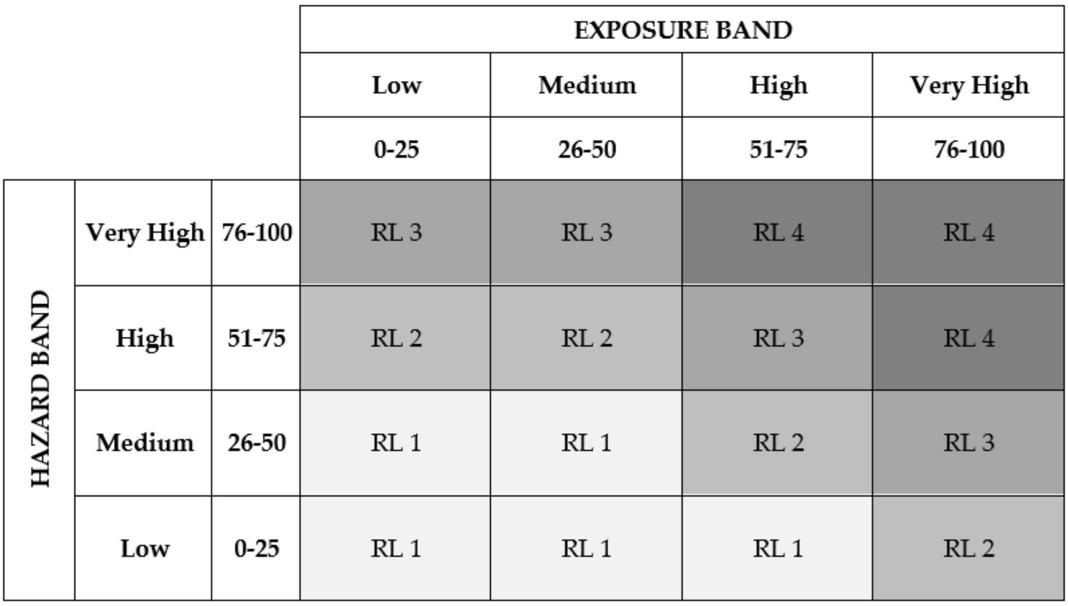
The first five factors are related with the material and operation conditions: dustiness, frequency of operation, duration of operation per day, task characterization and estimated amount powder used in that task. When handling a powdered material the main factor for intrinsic emission potential is dustiness (Schneider et al., 2011), therefore this is factor number 1 in the exposure band factors of IN Nanotool. Points are given based on a judgment of whether the material's dustiness is high, medium, or low. Most of these five factors are also considered in other nano CB approaches, since they are essential to study exposure to nanomaterials (Groso et al., 2010). In IN Nanotool, the number of employees exposure was not considered, since 3D printers usually are operated by only one or two workers, which means this is not a very relevant input to determine exposure in these workplaces.

The last four factors are related to existing control actions. Considering the already implemented control measures, it is possible to assess the actual exposure of the worker. Therefore, IN Nanotool follows a similar approach to Stoffenmanger Nano (Duuren-Stuurman et al., 2012), which does not compromise the subsequent proposal for additional control measures that can be implemented and effectively reduce the risk.

After summing the scores of the nine factors, the exposure band is defined according to the following criteria: low if the score is under 25, medium if the score is between 26 and 50, high if between 51 and 75 or very high if the sum is 76 or higher.

5.3.3.4. Risk Level determination

After defining the hazard and exposure bands, IN Nanotool allows the user to determine the risk level using a four-by-four matrix, as commonly used in other CB strategies (Dimou & Emond, 2017). This risk matrix is presented in Figure 5.11, and it is based on the matrix of CB Nanotool 2.0.



			EXPOSURE BAND			
			Low	**Medium**	**High**	**Very High**
			0-25	**26-50**	**51-75**	**76-100**
HAZARD BAND	**Very High**	**76-100**	RL 3	RL 3	RL 4	RL 4
	High	**51-75**	RL 2	RL 2	RL 3	RL 4
	Medium	**26-50**	RL 1	RL 1	RL 2	RL 3
	Low	**0-25**	RL 1	RL 1	RL 1	RL 2

Figure 5.11. IN Nanotool risk matrix.

5.3.4.4. Risk Control

IN Nanotool aims not only to assess the risk of exposure to incidental metal nanomaterials, but also to help users to properly manage this risk by providing recommendations for risk control. These recommendations depend on the risk level and on the control measures already implemented. They aim to be an increment to the already existing measures. For each risk level, there is more than one recommendation. The user must analyze the options and select one (or more) that is not yet implemented and that can ideally have an impact on the higher scored factors. A new risk assessment may be performed after the implementation of the recommended controls, to validate the risk level decrease. On the other hand, when selecting the control, the user can take advantage of the tool to assess the impact of that measure in the risk level, helping to choose the more effective control measure. Table 5.9 shows the list of recommended additional control measures based on risk level.

Table 5.9. Recommended additional control measures based on risk level.

Risk Level	Total Score	Recommended Additional Control Measures based on Risk Level
RL 4	151 – 200	Seek specialist advice Product replacement Task elimination or automatization Containment / Glove box / Glove bag Worker isolation (separate room/ cabin)
RL 3	101 – 150	Task elimination or automatization Containment / Glove box / Glove bag Worker isolation (separate room/ cabin) Local exhaust ventilation or fume hood Change operation conditions
RL 2	51 – 100	Worker isolation (separate room/ cabin) Local exhaust ventilation or fume hood Change operation conditions Mechanical ventilation Change Personal Protective Equipment
RL 1	≤ 50	Change operation conditions Mechanical ventilation Change Personal Protective Equipment Improve internal preventive procedures

5.3.4. IN Nanotool – Case study application

To experiment and verify the potential of IN Nanotool concept, this tool was applied to the SLM printer case study. The inputs had in consideration the MSDS and the technical sheet of the powder, the Portuguese Standard NP 1796:2014 (regarding the lowest OEL), SEM results presented in section 3.1, printer manufacturer information and *in situ* observation and consultation of workers. Table 5.10 shows the results of the application of IN Nanotool to this case study.

Table 5.10. Results of the application of IN Nanotool.

CB factors	Task 1	Task 2	Task 3
Powder Carcinogenicity	yes [1]	yes [1]	yes [1]
Powder Reproductive Toxicity	no	no	no
Powder Mutagenicity	no	no	no
Powder Dermal Toxicity	no	no	no
Powder Inhalation Toxicity	no	no	no
Other Hazards of the powder	yes [2]	yes [2]	yes [2]
Lowest OEL applicable to powder	200 µg/m^3 [3]	200 µg/m^3 [3]	200 µg/m^3 [3]
Powder Solubility	insoluble	insoluble	insoluble
Powder Average particle size	< 50 µm	< 50 µm	< 50 µm
Airborne NM Shape	anisotropic	anisotropic	anisotropic
Airborne NM Size	100 – 500 nm	100 – 500 nm	100 – 500 nm
Hazard Score | Band	**47 | Medium**	**47 | Medium**	**47 | Medium**
Powder Dustiness	high	high	high
Frequency of operation	daily	daily	daily
Duration of operation (per day)	1 – 4 hours	< 30 min	< 30 min
Task characterization	No manual handing	Manual handling the powder where large quantities of dust are generated and dispersed	Manual handling the powder where large quantities of dust are generated and dispersed
Estimated amount powder used	100 – 1000 g	100 – 1000 g	100 – 1000 g
Local control measure – Working room	Natural ventilation	Natural ventilation	Natural ventilation
Local control measures – Source	Containment of the source	No control measures at the source	No control measures at the source
Local control measures – Preventive procedures	Room cleaned daily and printer maintenance performed at least	Room cleaned daily and printer maintenance performed at least	Room cleaned daily and printer maintenance performed at least
Local control measures – Worker	The worker uses protective clothing	The worker uses filter mask P3/FFP3 and protective clothing	The worker uses filter mask P3/FFP3 and protective clothing
Exposure Score | Band	**46,5 | Medium**	**70 | High**	**70 | High**
Risk Level	**RL 1**	**RL 3**	**RL 3**
Recommended controls	-Change operation conditions -Mechanical ventilation -Change Personal Protective Equipment -Improve internal preventive procedures	- Task elimination or automatization - Containment / Glove box / Glove bag - Worker isolation (separate room/ cabin) - Local exhaust ventilation or fume hood - Change operation conditions	

[1] Carc. 2, H351 according to the material safety data sheet

[2] Skin Sens. 1, H317 and Stop RE 1, H372 according to the material safety data sheet

[3] Considering the lowest OEL recommended in Portugal: Nickel inorganic compounds (Portuguese Institute of Quality, 2014)

5.4 Discussion

5.4.1. Quantitative assessment

On-site measurements showed the lowest mean number particle concentration on the background trial, as expected, since the printer was not yet operating. After the AM operation started, the highest mean number particle concentration was obtained while the worker removed the part from the printer and cleaned it with a brush (task 2), as shown in Table 5.3. This number is very close to the one measured during the first task (printing). In reality, when analyzing Figure 5.1, it is possible to verify that the maximum values of number of particles occurred during the printing process, and not during the subsequent tasks. This result may be an indicator that, although the metal parts are printed in a closed chamber, there is still emission of matter during the process that may be released into the work atmosphere. The fact that the real-time measurement of air velocity near the door of the printer indicated 0.17 m/s, as shown in Table 5.2, endorses this possibility, since it is significantly higher than the background measurement (<0.01 m/s). Regardless this finding, several studies sharing the results of workplace airborne matter measurements during metal 3D printing do not consider the printing process (Dugheri et al., 2022; Jensen et al., 2020; Sousa et al., 2021b). In view of these results, further investigation is needed in this field, to verify if currently containment conditions are enough to prevent workers' exposure to nanomaterials during printing processes, or if containment improvement is required and/or if safety-by-design measures are needed at the printer manufacturing stage.

The results of the SMPS shown in Table 5.4 are consistent with the ones from the CPC (Table 5.3). When comparing these results to the previously mentioned recommended value of 20,000 nanoparticles/cm^3 for an 8-hour exposure time (mean number of particles between 10 and 100 nm lower than 9,300 particles/cm^3 for all tasks), it is possible to conclude that results are consistently lower, which doesn't mean absence of risk. In Figure 5.2, it is possible to confirm that SMPS measurements indicate that the smaller particles are released during the printing activity.

Another finding of this quantitative approach, by using EDS technology, was that there was no significant change in the chemical composition of the powder after laser action (Figures 5.4 and 5.6). The same results were achieved in similar studies (Mellin et al., 2016). The results of SEM analysis to the airborne samples (Figures 5.7 and 5.9) indicate the presence of agglomerates/aggregates of nanometer-scale particles, with an anisotropic shape.

This quantitative approach gives good insights on number particle concentration, size and shape of airborne matter, chemical composition, and environmental conditions.

5.4.2. Qualitative assessment

Qualitative assessments present risk levels as a result and allow the user to access information on recommended controls. Additionally, opposite to quantitative analysis, this approach does not require access to measuring equipment.

Table 5.5 summarizes the application of CB Nanotool 2.0 to this case study. Since stainless steel 316L is an alloy of iron and chromium and contains a significant quantity of nickel (≈12,5%), nickel inorganic compounds' OEL was considered as PM OEL, since it is the lowest one amount the significant components of this alloy. According to the material safety data sheet, the metal powder used is carcinogenic (H351) and skin sensitizing (H317), so PM carcinogenicity and PM dermal toxicity factors were scored as yes (this last one considering a precautionary approach). All nanomaterial related factors were classified as "unknown" since there is no information available for these airborne incidental nanomaterials. These considerations lead to a severity score of 63 (high band) for all tasks performed.

Regarding probability band, the amount of powder used in each task is similar (always more than 100 mg). So is the number of employees exposure and the frequency of the operation, thus scores were the same. Only the duration of the operation is different, so the probability score for task 1 (the longest one) is 85 (Probable band) and for task 2 and 3 the score is 70 (Likely band). According to these results, for task 1 it is recommended to seek specialist advice since risk level is the highest possible. For task 2 and 3 the recommendation is containment since the Risk Level is 3.

These results may be considered unexpected, since the highest risk level is usually associated with handling tasks, like sieving and cleaning (Chen et al., 2020). Another observation to CB Nanotool results, is related to the recommended controls. Containment may not be adequate for task 2 and 3, since it may not viable when removing the part from the chamber of the machine and when removing the remains of powder.

On the other hand, Stoffenmanager Nano 1.0 lead to different results, as presented in Table 5.6, since it is a source-receptor model (Brouwer, 2012). The criteria for the hazard band were the same for all tasks: dry powder with very high dustiness, small concentration of nanocomponents and unknown characteristics of the nanomaterials (concentration and inhalation hazard). In the factor related to OECD components, the option "other MNOs" was selected in the absence of another specific for incidental NM and, in the last factor, it was necessary to establish a relation between the current hazard identification and the one considered in this method, defined in Annex III of European Union Directive 67/548/EEC, which is no longer in force (replaced by CLP Regulation No 1272/2008). Hazard band E, the hazardous one, was therefore the result for the 3 tasks. In this method, hazard band E is assigned when the parental material is classified for carcinogenicity, mutagenicity, reproduction toxicity, or sensitization (Duuren-Stuurman et al., 2012).

About the exposure band, duration of each task was considered, as well as distance to the breathing zone of the worker and specific existing local control measures for each operation. Thus, exposure band 1 was the result for task 1 (lowest band) and exposure band 2 for the other tasks. Despite the different exposure bands, the overall risk level for all tasks was RL 1 (highest priority).

Subsequent controls recommended for each task are listed in Table 5.6 and they are different for tasks 1 as it shows lower exposure. The recommendations for printing operation include automation of tasks and enclosure of the source, which are already implemented. It also mentions controls that are not viable for this operation, such as wetting the powder or eliminating this task, since it would compromise all the manufacturing process. For task 2 and 3, recommendations also mention already implemented controls, such as respiratory protection, and not suitable solutions, like using a spraying booth or wetting the powder.

When applying Stoffenmanager Nano 1.0 to this case study, the hazard band E was obtained for all tasks, therefore risk level 1 the corresponding final result by default. In view of these results, it is possible to conclude that although this method considers relevant inputs for incidental NM and considers some control measures already implemented, it is a not suitable method for metal AM workstations, since it does not differentiate the level of risk of different tasks performed and it does not provide tailored control actions aiming the reduction of the exposure risk in these workplaces.

5.4.3. IN Nanotool

Considering all results and limitations from the previous described qualitative and quantitative approaches, IN Nanotool was designed for managing the exposure to incidental NM in metal 3D printing workstations and it was applied in this case study. The results of this application are presented in Table 5.10, in which it is possible to verify that the results obtained by using IN Nanotool are significantly different from the ones achieved by the other approaches.

When analyzing the hazard band, the first six factors were provided by the properties of the metal powder present in the MSDS of the product, being clear that it is a powder with carcinogenicity and other associated health hazards. The lowest OEL criteria was the same as the one used for CB Nanotool 2.0 application. According to its MSDS the powder is water insoluble, and the average particle size range is between 20 and 53 μm. The two remaining factors to define the hazard band (shape and size) were possible to score due to the results of SEM analysis (Figures 5.7 and 5.9). If these SEM results wouldn't be available, the score of these two factors would be 18.75 (unknown), which would increase the hazard band, since a precautionary approach is intended. The hazard band obtained for all three tasks is Medium (47 points), since the material used is the same throughout all 3D printing process.

Regarding the exposure band in this case study, material and operation conditions were determined by observing the conditions *in situ* and consulting the organization and the workers involved. The outcome was an exposure score of 46.5 (medium band) for task 1, mainly because it was considered that there is containment of the source and high dustiness, even though the time of exposure is higher, and no PPE were used during this period. For tasks 2 and 3 the exposure score was 70, meaning the exposure band is High. In this case, although the worker uses filter mask FFP3 and protective clothing, no eye protection is used and there is no containment of the source or isolation of the worker, when dustiness is high.

Using the risk matrix from Figure 5.11, it is possible to conclude that the printing process represents a Risk Level 1 and the other two tasks a Risk Level 3. These results are different from the ones obtained by applying CB Nanotool 2.0 and Stoffenmanager Nano 1.0. Using IN Nanotool, distinct risk levels are obtained for considerably different operations and it the results seem to support the belief that not contained manual handling processes are the ones with higher risk (Chen et al., 2020).

It should be highlighted that in this case study using IN Nanotool the highest risk level (RL4) was not assigned to any of the tasks understudy. This is aligned with the quantitative results, that show that the measured number particle concentration was not high when comparing to other metal 3D printing case studies (Jensen et al., 2020; Sousa et al., 2021b) and to previously mentioned nano reference values.

Finally, according to IN Nanotool, additional risk control measures should be considered. Critically analyzing the recommended controls for task 1 (see Table 5.10), in addition to the already containment of source, mechanical ventilation can be installed in the room, the operation conditions can change (for example, by reducing the frequency and/or duration), additional PPE can be used by precaution and/or internal procedures can be improved. For tasks 2 and 3, it is possible to clean the part with a brush and to sieve the powder in a glove box or bag, to install local exhaust ventilation or fume hood and/or to change operation conditions.

5.5 Conclusions

The difficulties to manage the risk of exposure to incidental nanomaterials and the lack of information on this matter have been recently discussed and are a cause of concern. Quantitative assessments require access to specific measurement equipment and don't provide control recommendations, requiring expert knowledge to assess and control the risk. On the other hand, limiting the risk management approach to the existing qualitative tools focused on ENM may be biased. Using those methods for incidental NM represents a significant difficulty in background data gathering, as shown in this case study.

The main objective of this study was to explore and highlight these difficulties and to design and test a tool to manage the risk of exposure to metal incidental NM in 3D printing processes. IN Nanotool redefined the inputs of CB approaches for incidental NM and added quantitative ones. Unlike quantitative approaches, this method does not necessary require special measurement equipment and it is not dependent from reference or limit values. Moreover, this method culminates in risk control recommendations, allowing to manage the risk of exposure to airborne incidental NM originated in metal AM processes, without the need to resort to a specialist. This tool was designed to enable this risk management, by providing a comprehensive and accessible approach to OSH professionals, including non-experts. However, there are limitations to this method. For instance, if the user does not have access to majority of background in-formation, the method allows to score factors as unknown, resulting in a high risk level. This precautionary result may lead to the suggestion of exaggerated control measures in relation to the real risk. Additionally, this tool requires additional testing and further validation. Regardless its limitations, IN Nanotool application to the present case study led to reliable results that are more in line with the state-of-the-art, showing its potential to fill the lack of methods for incidental NM.

Author Contributions: Conceptualization, M.S., P.A. and F.S.; methodology, M.S., P.A. and F.S.; validation, P.A. and F.S.; investigation, M.S.; writing—review and editing, M.S., P.A. and F.S.; supervision, P.A. and F.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Acknowledgments: The results of this study would not be possible to obtain without the support of the company specializing in technical coatings, where measurements were performed. We wish to acknowledge the help provided by the board of the company and workers involved in the study.

Conflicts of Interest: The authors declare no conflict of interest.

CHAPTER 6. CONCLUSIONS

6.1 Conclusions and main contributions

This thesis addressed risk management in workstations created by the modern technology of metal 3D printing, while focusing on an emerging risk: exposure to nanomaterials. As previously mentioned, the main goal was to create a risk management method regarding exposure to incidental nanomaterials emitted during metal AM.

The main conclusions of the present thesis can be summarized in five main aspects, which provide the answer to the research questions:

- Since 2016, studies have been published confirming the existence of airborne nanomaterials in metal 3D printing, which represent an occupational risk to operators on the workstations. The monitoring campaigns performed during this research also contribute to demonstrate this fact;
- Based on the state-of-the-art, it was possible to verify that a variety of approaches have been used to study the exposure to NM in these workstations, including quantitative approaches (direct reading equipment, SEM, TEM, biological markers, among others) and qualitative approaches, namely control banding. These studies disclosed important findings, but also showed some limitations. So far, there is no clear understanding of the most suitable or reliable approach to adopt to assess the risk of exposure to INM in metal AM. Additionally, a complete risk management process is rarely addressed in these investigations;
- Considering key findings on literature review and information provided by the case studies performed, it was possible to design and test a risk management method to manage the occupational risk of exposure to INM in metal AM workstations. By using the IN Nanotool (a CB based method), the user will reach a risk level for each task performed by the AM worker. The RL is established by determining a hazard band (with 11 factors related to the metal powder and the airborne nanomaterials characteristics) and an exposure band (with 5 factors related to material operation conditions and 4 factors associated with existing control measures), following a scoring system. This tool was designed to be intuitive, comprehensive, and accessible to all OSH professionals, including non-experts;
- One of the most relevant outcomes of this research project was the accomplishment of a risk management method, which is not limited to risk assessment. Besides providing a risk level for

each task performed, IN Nanotool helps users to effectively manage this risk by providing recommendations for risk control. These recommendations depend on the risk level and respect the hierarchy of control measures, including elimination, substitution, containment, engineering controls, procedural measures, and PPE;

- The IN Nanotool application to the case study presented in Chapter 5, led to consistent results that are in line with the state-of-the-art, showing its potential to fill the lack of methods for risk management of INM.

6.2 Limitations and future work

Like any other pilot study, there are some limitations to the IN Nanotool risk management method:

- By allowing to score majority of factors as unknown, if the user cannot access most background information, the method will provide a precautionary result showing a high risk level, which may lead to the suggestion of exaggerated control measures in relation to the real risk;
- Although promising, this method requires testing and validation.

Finally, it would be relevant to further investigate the following aspects:

- Apply IN Nanotool to other case studies (ideally not only to SLM printers but other metal AM technologies) and extend the study to other tasks such as maintenance.
- Use the acquired knowledge by this and other research projects on this field, to act preventively in the design phase of metal printers, in a perspective of safety-by-design.
- Investigate the similarities between the occupation risk exposure to INM in metal AM and in other metal manufacturing processes, in order to assess the feasibility of applying IN nanotool in other workplaces of the metalworking industry.
- Explore the possibility to include other important aspects in risk management, such as training, communication, and information, in IN Nanotool.
- Design and establish an online IN Nanotool, which allows OSH professionals to access IN Nanotool and share their results.

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