State of the art of particle emissions in thermal spraying and other high energy processes based on metal powders

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State of the art of particle emissions in thermal spraying and other high energy processes based on metal powders

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Abstract

Thermal spray is a high energy-based process, like additive manufacturing and powder atomization, leading to fine particle emission. But there is little information about these nanoparticles and their characteristics: workers' exposure, filtration efficiency, dustiness. This paper aims to update the knowledge of the thermal spray community, to focus on thermal spraying and to a lesser degree on powder atomization and additive manufacturing technology, regarding emissions due to the high energy-based process. The three processes are presented before introducing an updated survey of thermal spray activities in France. The main thermal spray equipment is wire arc and plasma spraying. The main metal used is Al and Ni. The paper also highlights the lack of knowledge among workers on thermal spray emissions. Most workers are not made aware of collective protection (emission filtration equipment used) and personal protection (PPE). A complete bibliographical review is presented on the problem of ultrafine particle emissions mainly for the thermal spray process. Ultrafine particles are always characterized inside a working environment. The objective of this article is to list all publications related to ultrafine particle emissions around the working environment of a thermal spray process to raise awareness of the academic and industrial communities about the actual risks associated with this exposure. Finally, the authors are looking at the list of dust filtration equipment by presenting their advantages and disadvantages for particle filtration.

Key words

Thermal spray; emissions; nanoparticles; dust equipment; filtering; safety

1. Introduction

High temperature processes related to metal powders (e.g. atomization, thermal spraying, additive manufacturing) lead to the production and release of fines and nano-sized metal particles (Trompetter et al., 2016; Stefaniak et al., 2019). There is a lack of knowledge about the properties of these emissions and their management (collection, confinement or remediation), although the consequences of these ultrafine particles on health have been widely demonstrated, in particular because of their inhalation without respiratory protection or collective aspiration (Reijnders et al., 2006).

The current French legislation requires reducing emissions into the environment in both gaseous and particulate form. This is particularly true for industries using powder metallurgy processes. Among the various existing processes, thermal spraying is probably the one with the most numerous configurations both in terms of energy sources (plasma, flame, electric arc) and materials used (metals, ceramics, polymers, composites, etc.). The principle of this technology is to combine a heat source with gases to melt a precursor material usually in the form of micrometric powder, and to accelerate the resulting molten particles towards a substrate.

Another powder metallurgy process which is currently on the rise is additive manufacturing, in particular selective laser melting of metal (so-called SLM technology). The energy source is a laser radiation applied to melt the powder. This process generates metal vapors. The operations are carried out in a closed chamber during the production phase.

The common approach of these two powder metallurgy processes is to use of a powder as a raw material. In the case of metals, one method to make these powders from a liquid molten bath is atomization. Different methods can be used: blowing the surface of the molten bath with a jet of cold gas or blowing a stream of molten metal liquid with cold gas from surrounding nozzles, in order to generate droplets atomization that quickly solidify to form the powder.

Whichever process is used among the three presented, an exhaust management device allows to treat particles emitted to collect and/or treat them. However, there is relatively little information on the performance of this system, especially since the characteristics of these emissions are not well known. In addition, gas and particulate emissions do not only affect the core of the process, but the challenge is to consider the entire manufacturing chain, particularly the pre- and post-process stages. Environmental management allows good practice of emission control. Different issues are at stake, including organizational structure, practices, procedures and processes. The main objective is to provide companies with more information about environmental issues and emissions, for example decisions on the substitution of raw materials, decisions on the implementation of central or decentralized treatment or control for wastewater/waste gas, etc. (Brinkmann et al., 2016).

The general purpose of this paper is to update our knowledge about emissions due to thermal spraying particularly, and to a lesser degree to additive manufacturing and powder atomization processes. The authors will first detail the different processes. The results of a survey conducted about thermal spraying in France will then be presented followed by a review of papers on thermal spray emissions. They will also discuss scientific results and survey data. Finally, the authors will present an overview of dust equipment for emission control.

2. High energy processes based on metallic powders

2.1 Metallic powder manufacturing

The metallic powder manufacturing currently benefits from the growth of additive manufacturing (Thomas, 2016; Tofail et al., 2018). The market is divided into two broad categories: plasma and gas atomization. For additive manufacturing or plasma spraying, the particle shape and size distribution are very important to optimize the use of the powder in the process and optimize the properties of the coatings or parts obtained. Powders resulting from plasma atomization perform better than other powder manufacturing processes (uniformity, spherical shape, very fluid). Gaseous atomization is the most popular technique used to produce metallic powders. The objective is to transfer kinetic energy from a high velocity gas stream expanded through a nozzle, to a filament of molten metal, resulting in disintegration into metal droplets. During this process, the material in the form of a metal bar is melted by induction in a crucible. Once the metal is completely liquid, the stopper bar used to prevent the liquid from transferring to the lower part of the process is removed to allow the molten metal to flow. The metal melt jet exits vertically by gravity from a hole/nozzle. The jet is surrounded by a gas flow from one or several jets which blow the liquid metal to generate a stream of droplets which solidify quickly to produce the powder (see Figure 1). The behavior of the metal liquid jet is important in determining the particle size distribution. Different atomization devices are available to generate metal powders.

The main global providers of metal powders using a plasma atomization process are located in Quebec: Tekna, AP&C and PyroGenesis Additive. Regarding gas atomization, a technique which is over 100 years old, manufacturers operate mainly in metallurgical industry: Carpenter and Praxair in the United States, VDM Metals in Europe and Sanyo Special Steel in Japan, for example. On the French territory, the main manufacturers are Toyal, Hermillon, Erasteel/Aubert & Duval, Tekna. Some research laboratories or technology platforms such as ICB-LERMPS, ONERA/MATMECA or Metafensch aim to develop specific metal powders or alloys.

2.2 Additive manufacturing

Additive manufacturing can be described as the transformation of a 3D model into a 3D object, using a raw material and a heat source (Niaki et al., 2000). Additive manufacturing is a family of processes including selected techniques depending on the state (solid, liquid) and nature (plastic, polymer, metal, etc.) of the filler material (Dobrzanski, 2017). First a virtual 3D CAD model is designed. This file is then converted to be understood by the additive manufacturing equipment (STL being the most commonly used). The software 'slices' the STL files into thin layers. Once the software has sent the instructions to the additive manufacturing equipment, the pattern is built layer upon layer (see Figure 2). The Selective Laser Melting (SLM) additive manufacturing process deposits a few ten micrometers thick bed on a support plate. The powder is melted locally with a laser spot based on the geometric parameters defined by the CAD file of the final part. The melted powder solidifies rapidly forming strings of solid material. At the end of this stage, the support plate goes down a little to allow the deposit of a new powder bed. This is repeated until completion of the finished product.

The additive manufacturing market is rapidly growing due to increasingly mature users and diversified uses (Debroy et al., 2019). Sales of equipment have seen an average annual growth of nearly 27% in recent years (Pipame, 2017). The R&D French sector includes 57 centers of excellence (Institut Carnot France, 2017) and 2,116 companies (BPI France, 2018). Aeronautics, space, medicine, luxury, mold/tool manufacturing, automotive are the main business sectors. In France, metallic materials are the most used with 40% of activities (Institut Carnot France, 2017). The metal additive manufacturing market is estimated at €60.6 million in France: 30% for powders, 40% for equipment, and 30% for the manufacture of parts (Observatoire de la métallurgie, 2019). The French market is expected to double between 2018 and 2025, notably through the expansion of part manufacturing, to reach €122M in 2025 (Pipame, 2017).

2.3 Thermal spraying

Thermal spraying is a common surface technique used in many industries such as transport, energy, biomedicine, electronics, etc. (Vardelle et al., 2016; Abbas et al., 2019). This technology belongs to the family of dry surface treatments. The principle is to spray a powder on a support to modify its properties, using a thermal and kinetic source (see Figure 3). Materials in the form of powders are usually injected into a heat source where they are heated and accelerated before being deposited on a substrate to form a coating. Thermal spraying shows great flexibility due to the following characteristics (Vuoristo, 2014): wide range of processes and sprayed materials (pure metals, metal alloys, hard metals, ceramics, polymers), attractive production rate, high deposit efficiency, versatility of processes and adaptability to the shape of the components. Selecting the type of gun/torch used involves looking at different thermal/kinetic properties (jet at higher or lower temperature, at higher or lower speed). This selection is decisive as it will determine the conversion of energy available in the jet for the treatment of injected materials. The thermal spray process is selected depending on the material to be used (which also depends on the coating application: anti-corrosion, anti-wear, reloading, reduction of friction, thermal or electrical insulation, etc.), the substrate nature, etc. (Fauchais et al., 2014). The different systems are Atmospheric Plasma Spraying (APS), High Velocity Oxy Fuel (HVOF), wire arc spraying, cold spray, etc. Among the various processes based on metallic powders and high energy, thermal spraying is undoubtedly characterized by the widest range of configurations of energy sources (plasma, flame, electric arc) and materials used. Thus, emissions are very diverse in terms of produced gases (ionization, recombination, combustion phenomena, etc.) and emitted particles (material, average size, reactivity, etc.) (Pawlowski, 2008). Moreover, the range of reactions complexity can vary. Thermal plasma is also used to manufacture nanoparticles (Samal, 2017).

A detailed survey of the INRS (French National Research and Safety Institute for the prevention of Occupational Accidents and Diseases) has mapped thermal spray facilities in France based on the processes and materials used, and the line of business (Savary, 2014). It shows that approximately 780 to 960 companies working in thermal spraying, with 75% of companies owning only one process in contrast with 2% of them working with five types of equipment. The main process was wire arc spray (more than 50% of companies). The APS process was five times fewer and the HVOF ten times fewer. This was consistent with the main material used, ZnAl (14%), followed by Ni base material (9%) and Al (8.5%). In France, thermal spray was mostly linked to small companies, using only one process.

3. CaRPE survey

To update the INRS work (Savary, 2014), a survey of French thermal spray companies was conducted in 2019. The questions were aiming at improving the understanding of their activities (processes, materials) regarding emission hazards (personal protective equipment) and capture systems (cleaning, filtration, measurements). The questions are listed in the Table 1, and the answers are presented in Figures 4 to 9.

Among around 100 companies, only 10 answered. As a result, the statistics presented barely give a qualitative trend for 2019. The key is to know the company working environment when it comes to thermal spray activities. Figure 4 shows that more than 80% of the French companies surveyed are equipped with wire arc spraying and APS processes. Then HVOF/HVAF reach 78%. These results are in line with the INRS wide survey (Savary, 2014). For APS and HVOF/HVAF, the base materials are Ni and Cr, as shown by the INRS survey (see Figure 5). For wire arc and flame spraying, Al, Cu and Fe base material are mostly used. In the INRS survey, Zn was predominant. These results indicate that small companies contacted for the survey probably did not answer due to lack of time or the primary purpose of the survey: emissions. Most of the time, companies are reluctant to discuss emissions and staff protection issues.

The survey shows that the majority of thermal spray booths is inaccessible during operations and the main air capture is usually located at the emission source and on the booth wall (see Figure 6). Furthermore, 67% of companies do not have suction over the powder feeder to evacuate aerosol formation during powder pouring.

Regarding the companies' dust exhaust system, the most popular one is filtration using a fibrous media, namely a cartridge (see Figure 7). It is interesting to highlight that 20% of companies do not really know which equipment is installed. Furthermore, the effectiveness of the media is unknown in most cases, and various classes of media are used (EPA, HEPA). This information shows companies' lack of interest in selecting a dust collector, because there is little information (scientific papers, studies) about the efficiency of dust collectors.

Figure 8 presents the protective equipment worn by operators during thermal spray operations. In most cases, it includes face masks and FFP3 cartridges. But there are still some companies where operators do not wear respiratory PPE. Despite information in the literature regarding emissions and exposure, a company policy is paramount. Furthermore, the right equipment must be worn for each step where there is a risk of contact with powder/dust (booth cleaning, powder pouring, etc.). Moreover, the efficiency class of respiratory protective equipment filters is not FFP3 equivalent for all. Booths are usually cleaned once a week. But the selected method to remove dust is still surprising. For example, 33% of operators use a broom and 22% use a compressed air-blower. Finally, Figure 9 confirms that 66% of companies set aside the emission problem and do not plan emission measurements, such as sampling on a workstation or on the dust collector exit.

4. Emissions from processes

Whatever the process (atomization, thermal spraying or additive manufacturing), using powder and a heat source leads to particle emissions. For thermal spraying, the range of materials is very large (almost all metals) with a powder size scaling from micrometers to sub-micrometers and nanometers, depending on the surrounding atmosphere around the process (air, neutral gas, vacuum). Emissions vary greatly based on these conditions. Moreover, the thermal spray deposition efficiency range is largely dependent on the process, 10 to 99.9% (Fauchais et al., 2014). A significant proportion of particles, residues and matter gets lost in the booth. The initial average size of the powder ranges from 5 to 150 micrometers. But after spraying, some matter is vaporized, sprayed out of the substrate, lost after rebounding at the surface. To date, the conversion rate of micrometric particles into ultrafine particles is not known. No study has investigated this question. In most cases, an aerosol is generated. For powder atomization, the process is based on aerosol manufacturing by the blowing of a liquid jet. Selective laser melting generates matter emissions when the laser spot melts the powder. Figure 10 illustrates these emissions around the thermal source.

The scientific community has been studying emissions from powder metallurgy processes for several years. Regarding metal powder atomization, the aim is to collect all particles generated by the process. Most of them enter the final container under the atomization tower. But some of them accumulate inside the tower leading to possible emissions during maintenance. As it is a closed-circuit process, emissions are channeled inside during the manufacturing phase. No study was found on the characterization of emissions during metal atomization.

Selective laser melting with metals usually occurs inside a specific device in a closed loop. During metal processes, emissions are channeled inside the equipment, whereas for plastic and polymers, some equipment do not use any exhaust and filtration system. As a result, the operator is exposed to emissions of ultra-fine particles. On plastics, these emissions have been found in very high concentrations (Stephens et al., 2013; Azimi et al.). Regarding metal particles, Keller et al. (2018) and Bau et al. (2019) highlighted the high number of nanoparticles generated during the additive manufacturing process near the source inside the process: $2.5.10^6$ to $4.5.10^6$ #/cm^3. Operators who handle metal powders run the risk to be exposed to particles (Graff et al., 2017; Mellin et al., 2016). Another study confirms the presence of nanoparticles (around 15 nm) around metal additive manufacturing equipment (Gomes et al., 2019). A review of Chen et al. confirms these results, showing that these emissions are very real and unintentional during the operator’s handling (Chen et al., 2020). A methodology must be developed to avoid exposures, especially regarding the management of this risk (Souza et al., 2019) and the design of the working environment of the process (Ljunggren et al., 2019).

For thermal spraying, the available studies essentially focus on describing thermal spray activities in terms of processes, materials and applications. Some scientific papers nevertheless look at characterizing emissions for a few combinations of materials, in most cases around the process. In France, the INRS has carried out studies in thermal spray activities (Mater and Savary, 2014). Their survey reveals that in 12% of French thermal spray companies, employees do not wear respiratory protective equipment (Savary, 2014), as confirmed by our CaRPE survey. Moreover, even if there is a ventilation system in the booth, a significant number of employees enter without respiratory equipment (Savary, 2015). A study was carried out on the emissions of arc-wire spray processes that emit metal vapors (Grippari, 2012). The measurements showed numerous particles with an aerodynamic diameter less than 100 nm. The INRS also raises the alarm against the large quantity of ultrafine particles below 100 nm generated by the arc-wire spray process and recommends a number of technical measures to use filtration to treat the nature of effluents (Bémer et al., 2010). This same institute has also published some emission data on NiCr alloy and some elements of information on aluminum and zinc materials in various processes (first level information only). A study conducted by another French health institute measured levels 15 times higher than the occupational exposure limit value for CrVI for sprayed materials containing chromium or chromium oxides (CARSAT, 2013). Similarly, operators who thermally spray Cr using plasma are exposed to CrVI with concentrations above VLEP-8h of 1 $\mu g/m^3$ (Jacoby et al. 2017). Levels of urinary excretion of Ni metal for exposed thermal spray operators, all processes combined, are relatively high compared to those unexposed. Viana et al. and Salmatodinis et al. show that high concentrations of ultrafine particle emission are measured during the APS process ($3.7 \times 10^6/cm^3$), with a particle size distribution between 28 nm and 45 nm (Viana et al., 2017; Salmatodinis et al., 2018). These emissions of nanoparticles can transfer outside the spray enclosure where workers are not necessarily protected by PPE (Salmatodinis et al., 2020). With the HVOF process, the same trend is found with exposure concentration of dust particles reaching 140 mg/m^3 (Huang et al., 2016). A study compared three spray processes for material residues (cobalt, chromium, and nickel) in the urine of operators (Chadwick et al., 1997). The plasma process is the most emissive. In Greece, a thermal spray company completed some measurements to control air quality (Petsas et al., 2007). It appears that concentrations of particles and heavy metals were predominant during the cleaning and maintenance phases of the spray booth. The INRS survey indicates that 23% of operators use a broom or a blow gun to clean work areas (Savary, 2015). The Thermal Spray Society (2013) publishes documents on risks surrounding the process and recommended protections. However, these documents only give an overview of the issues encountered and do not provide a clear answer on how to ensure health and safety in the workplace.

The scientific literature demonstrates the unintentional manufacturing of nanoparticles during thermal spraying. As the deposition efficiency is mostly around 50-60%, a part of the initial feedstock loss is transformed into ultrafine particles under the heat source. Some of these particles are sucked by the extraction system, but nanoparticles can deposit around different parts in the booth (robot, coated piece, booth corners, etc.). So, at the end of spraying, the operator is always exposed to nanoparticles through his actions in the booth (object displacement, walking on the ground, air flow due to his movements, etc.). The release due to the induced air motion can play a role in the exposure. The CaRPE survey demonstrates that wearing protective equipment is not ubiquitous and not all companies are aware of the risks of exposure to ultrafine particles. Operators wear protections without any knowledge regarding the risks and consequences of not wearing any. This is even more damaging because the two most used materials are Cr and Zn. Several analyses show that Cr can be found in urinary samples, and CrVI can be formed during spraying via different processes. Zn material mainly used with wire arc spray process under atmospheric conditions can generate ZnO oxide at the nanometer scale which could induce a health hazard (Subramanian et al., 2018). To make matters worse, according to the INRS and CaRPE surveys, booth cleaning is often carried out with a broom or a compressed-air blower only to induce the resuspension of ultrafine particles in the air. Normally, nanoparticles are quickly sucked by the air extraction systems, limiting the operator's exposure. But as shown by Bemer et al. (2010) (2013b), the most widely used dust collector with a cartridge fibrous media is rapidly clogged up with nanoparticles. The difficulty to clean cartridges, even by gas pulse, can explain the pressure drop inside the exhaust pipe of the booth. As a result, dust particles from the thermal spray remain at high levels in the booth, increasing the operator's exposure after the coating manufacturing.

5. Dust equipment for emission control

Thermal spraying induces gaseous emissions that contain particles of various average sizes, morphologies, compositions. Around the process, the waste gas generated can be divided into ducted and diffuse emissions. The first type can be cleaned whereas the second one can only be prevented. Industrial emissions can usually be classified as shown in Table 2 (Brinkmann et al., 2016).

Waste gas treatment devices aim at processing different chemical elements such as gas, particles, vapors of volatile liquid substances, gaseous air contaminants. The system is linked to a unique emission source as the treatment unit is exclusively designed for a specific waste gas composition. Most processes show material melting through their heat source at relatively high temperatures. The raw material is a powder in a melting state, upstream (thermal spraying, additive manufacturing) or downstream (powder atomization) of the process. The induced emissions consist of a variety of gases and particles (composition, particle size, concentration, etc.).

An aerosol is defined as a set of solid or liquid particles in suspension (maximum limit speed of fall <0.25 m/s) in a gaseous medium (Kulkarni et al., 2011). This term includes both fumes, dusts and mists, but not vapors. Fumes are defined as dispersions of very fine solid particles resulting sometimes from condensation or incomplete combustion. Dust is defined as any suspended solid particles. A particle is defined as a small part of solid or liquid material suspended in the air or likely to be. Within an emission, particles are mainly distinguished by their size (see Figure 11):

- PM10 particles: aerodynamic diameter less than 10 µm;
- PM2.5 aerodynamic diameter less than 2.5 µm;
- PM1 aerodynamic diameter less than 1 µm.

This classification was created based on inhalation hazards level. Particle characteristics are linked to the deposit area in the pulmonary system. The fraction of inhaled particles depends on their aerodynamic diameter (diameter of a sphere with the density of 10^3 kg/m^3 and a falling rate in calm air environment which is equal to that of the particle in the same conditions) and on the type of breathing (nose, mouth). The pulmonary area will depend on the inhalable fraction of well-defined sub-fractions: thoracic and alveolar. Regarding the three processes based on metallic powders and high energy (thermal spraying, powder atomization, additive manufacturing), the main components of emissions are solid particles. So, the waste gas treatment device will depend on the particle characteristics.

A dust collector is designed to collect the dust containing particles and separate these particles from the gas . The choice of process starts with an efficient characterization of the fumes to be treated, including:

- solid or liquid particles,
- temperature, because it will alter the density, the viscosity, the humidity, the conductivity of particles and affect the selection of the material for filters, for example;

- granulometry;
- concentration at the capture inlet and at the outlet;
- vector fluid;
- fluctuating, pulsed or continuous gas flow;
- neutral, corrosive or flammable medium;
- pressure.

Dust collectors can be wet (removal of dust from the air by water filtration) or dry (removal of dust from the air through filter media or electrostatic forces). The collected air is filtered by dust extractors. In order to capture the dust, different attraction methods are available: gravity, molecular (cohesion and adhesion forces) and electrical (or repulsion).

Therefore, different types of equipment were designed to filter or sort this dust, among which 5 main techniques (Siret, 2001):

- settling chambers;
- centrifugal separators or cyclones;
- electrostatic precipitators;
- filtration by fibrous media;
- wet dust collectors.

5.1 Dry collectors

Settling chambers consist of an empty chamber where the fumes/waste gases circulate with a low speed. This leaves time for gravity to separate particles from gas(>10-50 µm). To improve the deposition efficiency of particles, it is necessary to:

- adjust the chamber design with baffles or lamellae to reduce gas velocity;
- increase the active force of particles by centrifugal force (baffled precipitator, centrifugal separator) or electric force (electrostatic precipitators);
- capture particles in liquid droplets (hydraulic dust collectors, wet electrostatic precipitators);
- agglomerate particles by electrical or sonic agglomeration.

Settling chambers are often used as a first device in filter systems to remove large particles.

In a centrifugal separator, fumes will be rotated to use inertia to collect particles. Centrifugal force moves the dust towards the wall to be collected (cyclone effect) thanks to a double vortex. Cyclones are sedimentation chambers where the effect of gravity is increased by centrifugal force. The largest particles are removed. Performances are set by the geometry of the system (height, diameter, tangential velocity). Efficiency increases with high airspeeds in a small diameter and long cylinder. This is the cheapest and most robust equipment with a very wide operating amplitude (temperature, pressure). However, performance is limited to particle sizes greater than 10 microns. The efficiency is 95% for particles> 15 µm. The smallest ones should be separated with another device. Wet cyclones aim to increase efficiency when separating fine particles.

There are two main types of cyclones:

- reverse flow cyclone (lateral inlet);
- straight-through cyclone (axial inlet);

Other less used types are: electro cyclones with an electrode that charges particles to hit the walls, multi-cyclones.

Electrostatic precipitators (ESP) use an electric force applied to the charged particles by ionization of the fumes. A wire placed in a tube or pulled between two plates is brought up to a highly negative voltage creating a corona discharge. The gases that make up the smoke are then excited, tearing out electrons that, by collision, create ions and radicals that will charge particles. They are then subjected to an electric field to be attracted to a counter electrode where they will pile up and form a deposit. There are different separators: dry wire plate or pipe ESP, wet wire plate or pipe ESP. However, this equipment has been listed as a possible explosion risk due to its technical configuration and its electrostatic property which can be a source of ignition (Chhabra, R. et al., 2019). ESPs are not recommended for materials with explosive properties (Peukert et al., 2001). The authors believe that ESP would be suitable to remove ultrafine oxidized dust. In the case of metal dust, a pre-combustion step would be required to avoid the formation of an explosive atmosphere in the ESP. Ultrafine metal dust is likely to react with water to produce hydrogen (e.g. aluminum dust) and in that case, neither dry ESPs nor humid ESDs can be used exposed to air. If the risk analysis shows that such a system could be used (e.g. passivated powders, mixture with inert solid particles, low flow rate associated with a sufficient ventilation rate), it is likely that an explosion mitigation system should be implemented such as an explosion vent.

The dust collector by fibrous media (fabric filter) consists of a main box (filter elements, high-pressure air pulse cleaning system, hopper collecting dust). Polluted air enters at the bottom of the dust collector to come out above after passing through the filters. Unlike with cyclones where disposal is continuous, with fibrous media collectors, particles accumulate on the outer surface of the filter media and form a deposit that will induce a pressure drop during the operation of the dust collector. These filters are cleaned to limit the pressure drop caused by clogging fibers, fabrics or other felts. There are different cleaning methods:

- shaking, where the filter is gently shaken in all directions on a mechanical device;
- counterflow gas, where the suction is stopped and air is blown through the filters in the opposite direction to that of the filtration;
- gas pulse, where a pulse of medium air pressure is propelled inside the sleeve, generating a wave of pressure and deformation that will allow the dust cake to come off. This type of unclogging is possible without the need to isolate the whole box, and sleeves nearby can continue to operate. The benefits of this method are its high efficiency and the possible use of non-compartmentalized filters. In contrast, the sleeves are more stressed and wear faster.

These actions remove the cake made of particles which is collected in a hopper. Unclogging is performed at regular intervals depending on the pressure drop. The first unclogging operations make it possible to find pressure drop values close to those of a new fibrous media, for the first cycles. Once deposited on the fibrous media, particles remain either on the surface or inside the media. This phenomenon increases during the process. After a while, the filter elements become irremediably clogged and must be replaced. The presence of ultra-fine particles accelerates the clogging phenomenon. The media is less efficient due to the strong adhesion of particles. To delay the clogging, it is advisable to reduce the filtration speeds by increasing the filtration area, or to add a coarser filter (prefilter for large particles). There are three filter media technologies:

- fibrous media;
- consolidated porous media, such as sintered ceramics but generating high-pressure losses;
- unconsolidated granular porous media, such as sand columns but showing low efficiency against fine particles.

When filtering an aerosol, a particle is screened by a fibrous filter (particle size larger than the pore size). In the absence of external force fields such as a magnetic field, particles are captured via gravity through a fiber filter in 3 steps:

- inertia: particles cannot follow the current line during fiber crossing and collapse against it (diameter greater than 1 μm);
- direct interception when particles follow the current line but approach the fiber at a distance shorter than their radius (greater than 100 nm);
- Brownian scattering for particles smaller than 100 nm, where their trajectory passes close enough to the fiber to undergo a deflection under the influence of the Brownian motion.

Electrostatic forces can also be added with a metal media before calculating the filter efficiency. Between 100 nm and 500 nm, a minimal degree of operational efficiency is reached because the three capture mechanisms are not preponderant. Some particles are too large to be affected by the diffusion phenomenon and too small to be intercepted or impacted. These are the most penetrating particles (MPPS: Most Penetrating Particle Size). It is in this area that the efficiency of high efficiency particles (HEPA) and ultra-low penetration (ULPA) air filters is calculated. The fiber filters consist of natural, metallic, or synthetic fibers. Generally, fibers consist of fiberglass, polyester or cellulose. They are defined by different factors:

- compactness: volume of the fibers/volume of the filter;
- basis weight: filter mass/filter area;
- thickness;
- size distribution of the fibers;
- nature of the fibrous filters: fibrous woven, felt or nonwoven.

These fibrous filters can be mounted on different filtration systems: bag filters, cartridge filters. They can operate alternatively or continuously (it is possible to isolate the filter to be unclogged without stopping the ventilation). Each of these filters exists in various ranges of efficiency depending on the industrial field and the fumes particles characteristics: very high efficiency (nuclear, clean room), high efficiency (indoor air, air conditioning), average efficiency (industrial effluents). For a medium and high efficiency, the deposition of particles (cake) on the surface of the media is eliminated mechanically whereas for very high efficiency, particles are captured inside and therefore filters must be changed.

An absolute filter is composed of a high-density pleated media made of fiber glass. Particles from the waste gas are collected. The design is often a cylindrical cell, and a pre-filter is necessary to remove the biggest particles. The absolute part is set for ultra-fine particles and nanomaterials.

The Carpe survey shows that the most popular filter is the cartridge filter (see Figure 7). But 20% of companies are unaware of their filter characteristics. In the thermal spray community, fibrous media filters are the most adapted to filter emitted particles. However, difficulties related to the regeneration of filters clogged by metallic nanoparticles are still relevant today. The rapid increase of the pressure drop with ineffective unclogging is still being investigated to control this issue (Khirouni et al., 2020a). To date, it means a frequent replacement of filter media.

5.2 Wet collectors

A wet collector, often named wet dust scrubbing, uses a liquid to intercept particles contained in the fumes. This device is widely used for its efficiency in reducing particulate emissions and especially soluble compounds such as acid gases and heavy metals. Wet collectors are often associated with other technologies, especially electrostatic precipitators. There are two mechanisms for dust capture: by impaction on a wet wall (packed column) or by collision with a dispersion of liquid droplets injected into a gas (venturi, spray column). The most common principle is impaction by inertia.

There are therefore several types of wet separators (Siret, 2001):

- spray towers: the spray occurs from top to bottom. They are widely used but not for dusting due to their low efficiency. The stripping mattress is composed of a mesh of fine ordered or disordered fibers, which capture particles. The efficiency is very good up to 1 μm;
- cross-current: the spraying is perpendicular to the flow of smoke. They are suitable for dust (99% efficiency for particles> 2 μm) but have a fairly high energy consumption (pump);
- foam: fumes cross a liquid layer supplemented with a surfactant. The phenomenon of diffusion explains an efficiency rate of 90% for 500 nm particles. There are a few pressure losses, but the cost is quite high;
- venturi type: this type is especially designed for dust while the previous ones basically focus on the purification of gaseous compounds. Gases are accelerated, which facilitates the interaction between the aerosol and the liquid regardless of the significant pressure loss. The efficiency rate is 99% for a dimension of 1 μm but the energy consumption is important;

- bubble columns: the transported dust meets liquid bubbles and mixes with them, establishing a transfer from one phase to another;
- fibrous packing, moving-bed, plate, etc.

Tables 3 and 4 show the main characteristics of the different filters (abatement efficiency, benefits and limitations).

6. Thermal spray and emissions control efficiency

Thermal spraying combines micrometric powder and high energy sources (flame, plasma, electric arc). The formation of the coating from the precursor generates nanoparticles that can be found in the spray booth or in the environment close to the cabin. The exposure of operators is then obvious and protective equipment has to be worn (Heriaud-Kraemer et al., 2003). In most cases, the nanoparticles are the result of the process as the initial feedstock is micrometer sized, even if nanoparticles (ceramics) can be used (Toma et al., 2008). Moreover, the solution precursor plasma spray process uses only salt solution feedstocks to manufacture coatings with physical and chemical reactions inside the heat source (Bertolissi et al., 2012). The use of plasma spraying under very low pressure allows vaporizing the initial powder creating nanoparticles and nanostructures (Fan et al., 2019; Darut et al., 2019). So, the resulting fine dust generated by the process must be captured by the exhaust system which has to be selected or configured based on the thermal spray dust properties. This way, an efficient ventilation flow inside the booth facilitates the capture of nanoparticles in the filtration system. The air velocity impacts directly on the dust drive to suctions panels. It is linked to power characteristics of the exhaust filtration system and to pressure losses in the pipes and filter media. If the velocity is too low, dust accumulates on the booth floor or walls. That is why cartridge media (major filter system in thermal spray activity (Bemer et al., 2013b) as confirmed by the CaRPE survey) are cleaned by compressed air jet to prevent pressure loss and allow good ventilation. But with some processes, in particular wire arc spraying, filtration cartridges are often clogged. Bemer et al. underline the irreversible character of clogging due to the nature of the dust collected (Bemer et al., 2013a). Even with the use of a counter-current pulse-jet, cleaning seems to be inefficient. Granular beds, based on Brownian diffusion mechanism to capture ultrafine particles, could be a good alternative to conventional cartridge filters but no industrial pilot has yet been tested (Bemer et al, 2015a; Bemer et al., 2015b). A recent work of the INRS shows the possibility to improve cartridge cleaning using a pre-deposit (micrometer particles) on the surface of the filter media in order to improve the removal of ultrafine particles that would be deposited on the surface (Khirouni et al., 2020b). A different approach was proposed by Cho et al.:

spraying compressed air directly on the external surface of the filter rather than injecting pulse-jet air on its internal surface (Cho et al., 2020). This so-called air-washing cleaning method allows successful cleaning and regenerate the fibrous media, but also to reduce particle emissions. Some modeling has been developed to study the concentration of released nanoparticles during a thermal spray process (Ribalta et al., 2016). The measurements confirm the results of previous studies. When the thermal spray process occurs in a booth, a negative pressure is applied to confine dust inside. A problem can occur: the filtering system does not collect nanoparticles efficiently. The negative pressure can reintroduce the polluted air in the booth, according to the positioning of the exhaust system outlet in relation to the air compensation entry. In any case, nanoparticles will be rejected into the environment if the exhaust system is not appropriate.

7. Conclusions

Nanoparticles emission is crucial for processes based on metal powders and high energy such as thermal spraying, powder atomization and additive manufacturing. During processes, particles are in a liquid/vapor state in the thermal source. Generated nanoparticles are incidental. As a result, companies and operators must be aware of the risk and release into the environment. The different surveys on thermal spray activity demonstrate the lack of information and communication between the industry and scientific community. Various published papers state the health risk for unprotected operators around the process. A significant number of operators work without a protection adapted to thermal spray activity. It would therefore be necessary to characterize these emissions, and to make operators aware of monitoring and reduction. Different filtration devices can be used to treat thermal spray effluents and therefore adapted to the ultrafine particles generated. However, the use of fibrous media (filter cartridge essentially) is the most appropriate to retain this waste. The clogging issue of these media and therefore the suction flow pressure drop in the spray enclosure are still relevant. The risk is an increase of particles in the working booth and their presence at the end of the spraying, in contact with the operator.

The main recommendations for the thermal spray activity as well as the risks that may be encountered will be studied in a second part of this project. Various sampling operations and emission analyses of plasma spraying equipment will be carried out. Different areas will be targeted, such as at the level of emissions channeled upstream and downstream of the filtration system, at the workstation level as well as fugitive emissions. Various measurements will be carried out: real-time particle size distribution, mass concentration of total suspended dust, heavy metals, sampling characterization by EDX/MET, etc.

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Figure captions

Figure 1: Powder atomization principle

Figure 2: Additive manufacturing principle

Figure 3: Thermal spray principle

Figure 4: Different processes used by the French companies (CaRPE survey)

Figure 5: Sprayed metal-based materials used by French thermal spray companies (CaRPE survey)

Figure 6: Thermal spray environment (CaRPE survey)

Figure 7: Thermal spray dust exhaust equipment characteristics (CaRPE survey)

Figure 8: Personal respiratory protective equipment of workers and booth cleaning (CaRPE survey)

Figure 9: Achievement of emissions measurements (CaRPE survey)

Figure 10: Pictures of melted metal droplets and jets during a) powder atomization, b) thermal spray and c) selective laser melting processes

Figure 11: PM particles description

Table captions

Table 1: Questions of CaRPE survey for thermal spray companies

Table 2: Ducted and diffuse emissions

Table 3: Efficiencies, maximum gas flow and particle content of the main dust collectors (Brinkmann et al, 2016)

Table 4: Benefits and limitations of the main dust collectors (Brinkmann et al, 2016; Peukert et al., 2001; Hallé et al., 2015; and experience from the authors)

Declaration of Interest Statement

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Dear Editor:

You can find below the credit author statement:

G. Darut : ***Conceptualization, Methodology, Validation, Resources, Writing - Original Draft, Writing - Review & Editing, Visualization, Funding acquisition***

S. Dieu : ***Investigation, Writing - Review & Editing***

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Highlights

- High energy-based process using metal particles generate ultrafine particles
- A survey has been investigated on thermal spray French community
- Thermal spray industrials are not aware of nanoparticles emission of processes
- Waste gas treatment device must be chosen in relation with emission nature

Dear Editor:

It is a pleasure to send you the manuscript entitled " Emissions from metallic powder and high energy-based process - Thermal spraying, powder atomization and additive manufacturing – knowledge refresh".

High temperature processes related to metal powders (e.g. atomization, thermal spraying) lead to the production and release of metal particles, which are partly nano-sized. There is a lack of knowledge with respect to the properties of these emissions and with respect to their management (collection, confinement or treatments). This paper aims at bridging the current knowledge in thermal spraying activity with a literature review and a survey done for a french environmental project named CaRPE about French thermal spray industries habits regarding processes, emission control, workers protection, dust equipment, etc.

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Table 1: Questions of CaRPE survey for thermal spray companies

Company activity	•How many employees use thermal spraying processes? •How many different thermal spray processes are you equipped with? •How many thermal spray booths are you equipped with? •What is the annual order of magnitude regarding raw material for thermal spraying (powder, wire, etc.)? •Which processes are you equipped with? •What are the sprayed metal based materials used with each process?
Emissions and dust equipment	•What is the main work environment in the workshop? •What type of air capture are you equipped with? •What types of dust exhaust equipment are you equipped with? •Do you have suction over the powder feeder (suction arm, etc.)? •How efficient is the filter medium of your cartridge or bag dust collector?
Personal protection	•What personal respiratory protection equipment most thermal spray operators wear? •What is the efficiency class of respiratory protective equipment filters? •When must PPE be worn? •How often do you clean the thermal spray booths? •How do you clean the thermal spray booths?
Emission control	•Are aerosols or particle emissions measured? •Do you take measurements at the level of operators (sampler on workstation)? •Do you take ambient measurements? •Do you take measurements out at the dust collector exit?

Table 2: Ducted and diffuse emissions [1]

Ducted emissions	Diffuse emissions
• process emissions released through a ventilation pipe via the process equipment • gas flow from energy-providing units, such as process furnaces, steam boilers, combined heat and power units, gas turbines, and gas engines • waste gases from emission control equipment, such as filters, incinerators/oxidisers or adsorbers, likely to contain unabated pollutants or pollutants generated in the abated system • tail gases from reaction vessels and condensers • waste gases from catalyst regeneration • waste gases from solvent regeneration • waste gases from vents from storage and handling (transfers, loading and unloading) of products, raw materials and intermediate • waste gases from purge vents or preheating equipment, which are used only in start-up or shutdown operations • discharges from safety relief devices (e.g. safety vents, safety valves) • exhaust air from general ventilation systems • exhaust air from vents from captured diffuse sources, e.g. diffuse sources installed within a facility	• process emissions from the process equipment inherent in running the plant, released from a large surface or through openings • non-ducted emissions (e.g. 'working losses' and 'breathing losses', when not captured and ducted) from storage equipment and during handling operations (e.g. drum filling, trucks or containers) • uncommon emissions, resulting from operations other than routine processing of the facility including emissions during start-up or shutdown and during maintenance • secondary emissions resulting from thewaste handling or disposal (e.g. volatile material from sewers, waste water handling facilities or cooling water) • fugitive emissions (see Glossary), such as equipment leaks from pump and compressor seals, valves, flanges, connectors and others piping items, or other equipment items, such as drain or vent plugs or seals

Table 3: Efficiencies, maximum gas flow and particle content of the main dust collectors (Brinkmann et al, 2016)

	Abatement efficiency (%)	**Waste gas flow (Nm^3/h)**	**PM content (g/Nm^3)**
Settling chambers	10-90	100 – 100 000	No restriction
Cyclones	$PM_{>50}$ – 99 PM_{10} – 30-90 $PM_{2.5}$ – 0-40 PM_1 – 5	1 – 100 000	1 – 16 000
Electrostatic precipitator	99 $PM_{2.5}$ – 97-99.2 PM_1 – 97	1 800 – 2 000 000	1 - 110
Fibrous media	99 – 99.9	300 – 1 800 000	0.1 - 230
Absolute filter	99.999 $PM_{0.1}$ – 99.999 $PM_{0.01}$ – 99.99	100 - 300	1 - 30
Wet dust scrubber (spray tower)	PM_{10} – 70 -99	2 500 – 170 000	No restriction

Table 4: Benefits and limitations of the main dust collectors (Brinkmann et al, 2016; Peukert et al., 2001; Hallé et al., 2015; and experience from the authors)

	Benefits	Limitations
Settling chambers	Simple construction, no moving part hence low maintenance and low operating costs Very low pressure drop Suitable for higher temperatures Low investment costs Low energy consumption Can be applied to processes with large fluctuations, e.g. with high and low temperatures	Poor removal efficiency, especially for small particles (below 50 μm) Unsuitable for sticky particles Not suitable when the density difference between gas and particulates is small Relatively large equipment Decrease of efficiency for low concentration at the inlet
Cyclones	Simplicity of the installation Recovery of raw material No moving parts, hence few maintenance requirements and low operating costs Low investment and maintenance costs Dry collection and disposal, except for wet cyclones Relatively small space requirements Low consumption of energy Relatively low pressure drop High density of particle flows can be treated	Relatively low PM abatement efficiency, particularly below PM_{10}. In the current regulatory framework, it should be used solely as a pre dust-removal system The higher the efficiency the higher the pressure drop and the energy consumption Axial entry cyclones cannot be used with particles likely to cause excessive erosion or clogging of the vanes in the inlet Unable to handle sticky or tacky materials Emissions to waste water with wet cyclones Noise Regular cleaning necessary to avoid self-heating risk with accumulation of combustible dusts

Electrostatic precipitator	High abatement efficiency (> 97 %) even for small sized particles (high efficiency until 10 nm) and high concentration of particles (efficiency can be increased by adding fields or zones) Capacity of treatment of important inlet gas flows Low maintenance costs and possibility to work at temperatures higher than 300°C Low energy consumption Low-pressure drop, hence energy requirement tends to be low (in some applications, an induced or forced draft fan is needed to overcome system pressure drop) Possibility to work under vacuum Suitable for a wide range of temperatures, pressures and gas flows Dust can be removed dry, making reuse possible (for dry ESP) Partial removal of acid fumes (for wet ESP) Wet ESPs can abate sticky particles, mists and highly resistive or explosive dusts At a voltage of > 50 kV, abatement efficiency is independent of the residence time, enabling more compact manufacturing (for wet ESP)	High initial investment costs Ozone can be formed by the electrodes, which be a source of environmental pollution Less suited for processes with varying gas streams, temperatures or dust concentrations. However, it can be offset by automatic adjustments. Varying operational conditions is easy, if the installation is designed for the worst case situation. Re-entrainment can be a problem due to high gas velocities, poor rapping or poor gas flow Sensitive to maintenance and settings Relatively large equipment size Highly qualified staff is required Special cautions to protect staff from the high voltage (electrical hazards) Dry ESP must be avoided with combustible dust, as it generated dust explosion risks. Pre-combustion of the dust can be an option before ESP treatment. The abatement capacity depends on the electrical resistivity of dust particles (with dry ESPs) Dry ESPs not recommended for the removal of sticky or moist particles

		Corrosion near the top of the wires due to air leakage and acid condensation, which is also an issue with wet ESPs (although acid gases are also absorbed by the water) Wet ESP is adapted to combustible/ explosible dust provided that dust does not react with the liquid phase (e.g. some metallic powder that tend to produce hydrogen when in contact with water). Protection measures must be also implemented (explosion vent, earthing of the equipment to avoid electrostatic discharges, regular cleaning is also necessary to avoid the creation oof sparks between the electrodes). Also all electrical safety measures must be correctly implemented. Wet ESPs are relatively expensive and require post-treatment of sludge water
Fibrous media	In general, fabric filters provide high abatement efficiencies for coarse and fine particles Efficiency and pressure drop of continuously cleaned filters are relatively unaffected by large changes in inlet dust loads Dust is sorted dry without using consumables. The separated dust might be reused in the preceding process or recycled Residual emissions are virtually independent of the intake concentration Relatively simple operation	Fabric filters are not suitable for wet or sticky dusts because of the risk of filter clogging Heating the waste gas stream prevents condensation of fluid on the ceramic filters Static electricity may hinder the cake from being removed from the fabric Big size of the equipment Reverse air bag filter system requires numerous mechanical moving pieces which can be then source of failures. It then needs

	Reliability	regular maintenance. On the contrary air-pulse filters are much easier to maintain. Filters must be antistatic (not claimed as antistatic but truly antistatic) and correctly earthed to avoid electrostatic discharges that could ignite explosible dusts High clogging by ultrafine particles
Absolute filter	Abatement of submicron particles of fine dust is possible Very high abatement efficiency with very low residual emission Outlet air is very clean and can flow within the plant Modular structure Not sensitive to small fluctuations in the waste gas stream Relatively simple operation Usually not sensitive to corrosion problems	Care has to be taken with explosive hazards High maintenance and frequent filter replacement required Not suitable for the abatement of wet dust Not suitable for high dust loads (except if prefiltration is carried out) Glass fiber medium is not suitable for waste gases which contain alkalis High clogging by ultrafine particles
Wet dust scrubber	Can handle gas streams which contain flammable and explosive dusts with low risk Reasonable size of the equipment Can handle both gaseous and particulate pollutants Good efficiency of abatement for particles below 10 µm Possibility to collect sticky particles Provides cooling for hot gases Corrosive gases can be neutralized	Significant water usage and generation of waste water. The higher the efficiency of abatement, the higher the consumption of water and energy High maintenance costs due to corrosion and erosion issues Risk of plugging for treatment of high concentration of particles in the flow High pressure drops required for an efficient treatment

	Simultaneous removal of dust and inorganic compounds	Waste (or by-product if reused or recycled) collected wet Protection against freezing required Collected PM may be contaminated and/or not recycled Off-gas may require reheating to avoid visible plume It tends to minimize the risk of explosion or even eliminate the risk of fire and explosion, unless of course dust is reactive with the liquid phase such as some metallic dust that may form hydrogen in the presence of water.

Figure 1

Click here to access/download;Figure;figure1b.tiff

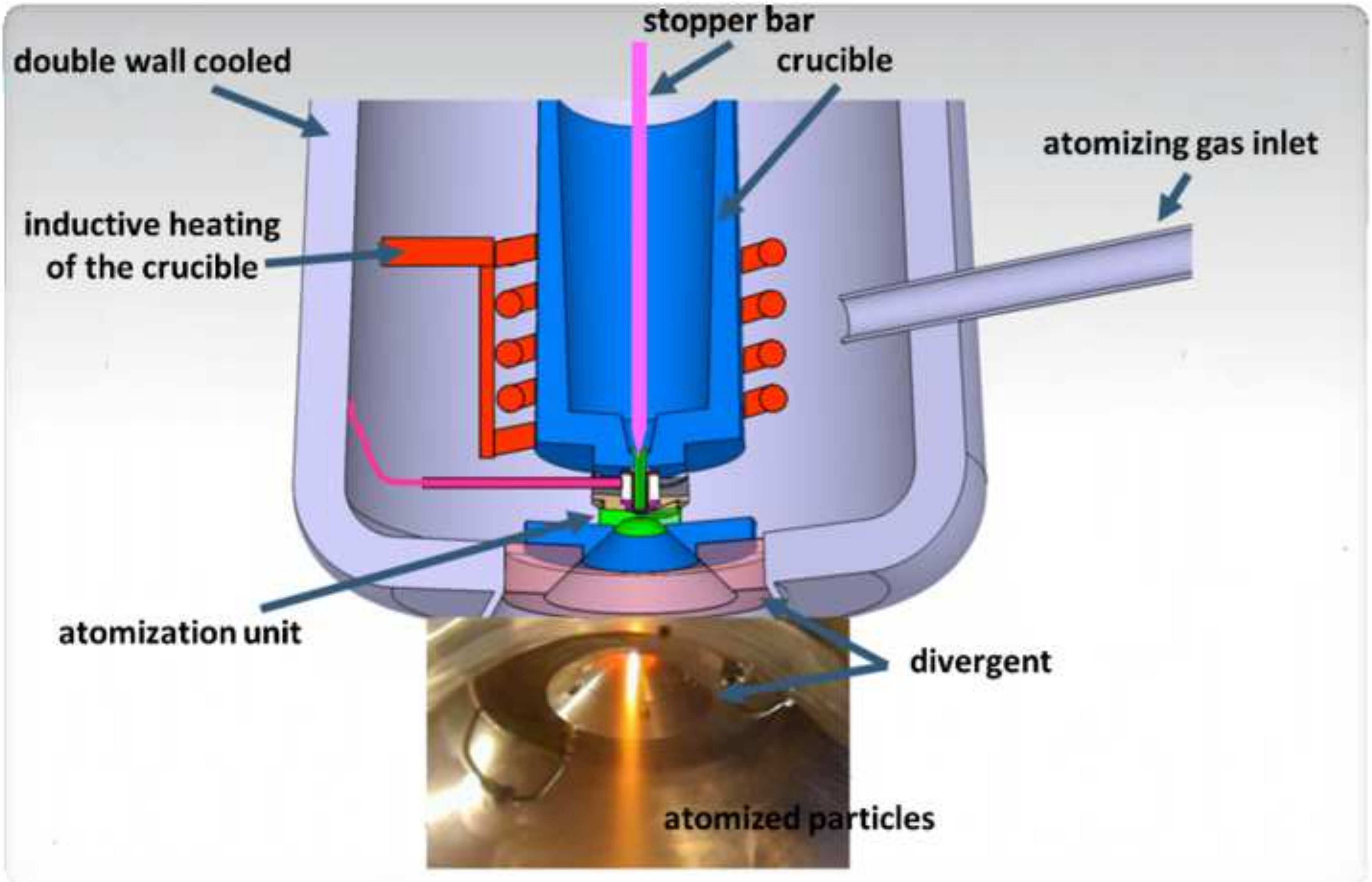


Figure 2

Click here to access/download;Figure;figure2b.tiff

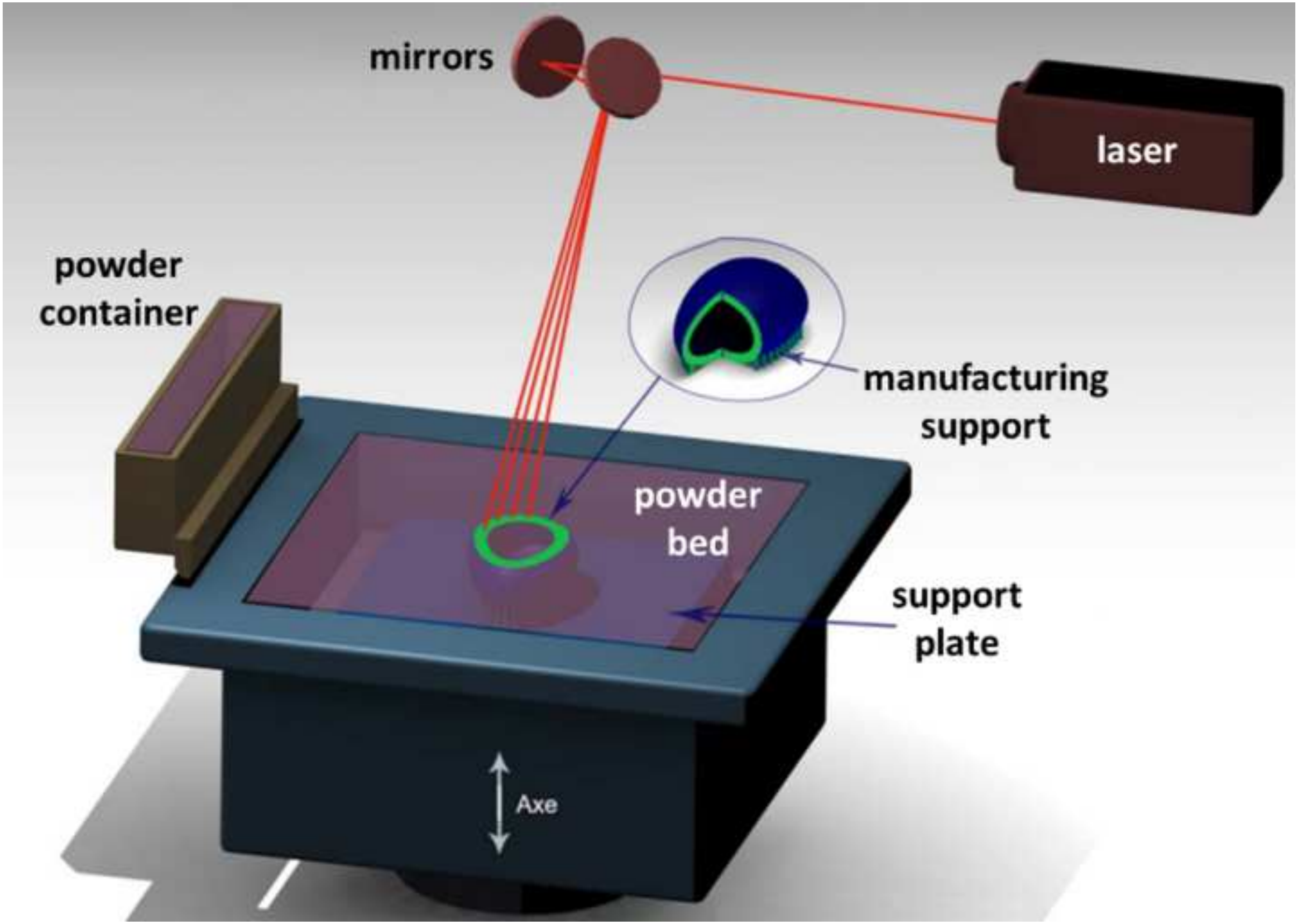


Figure 3

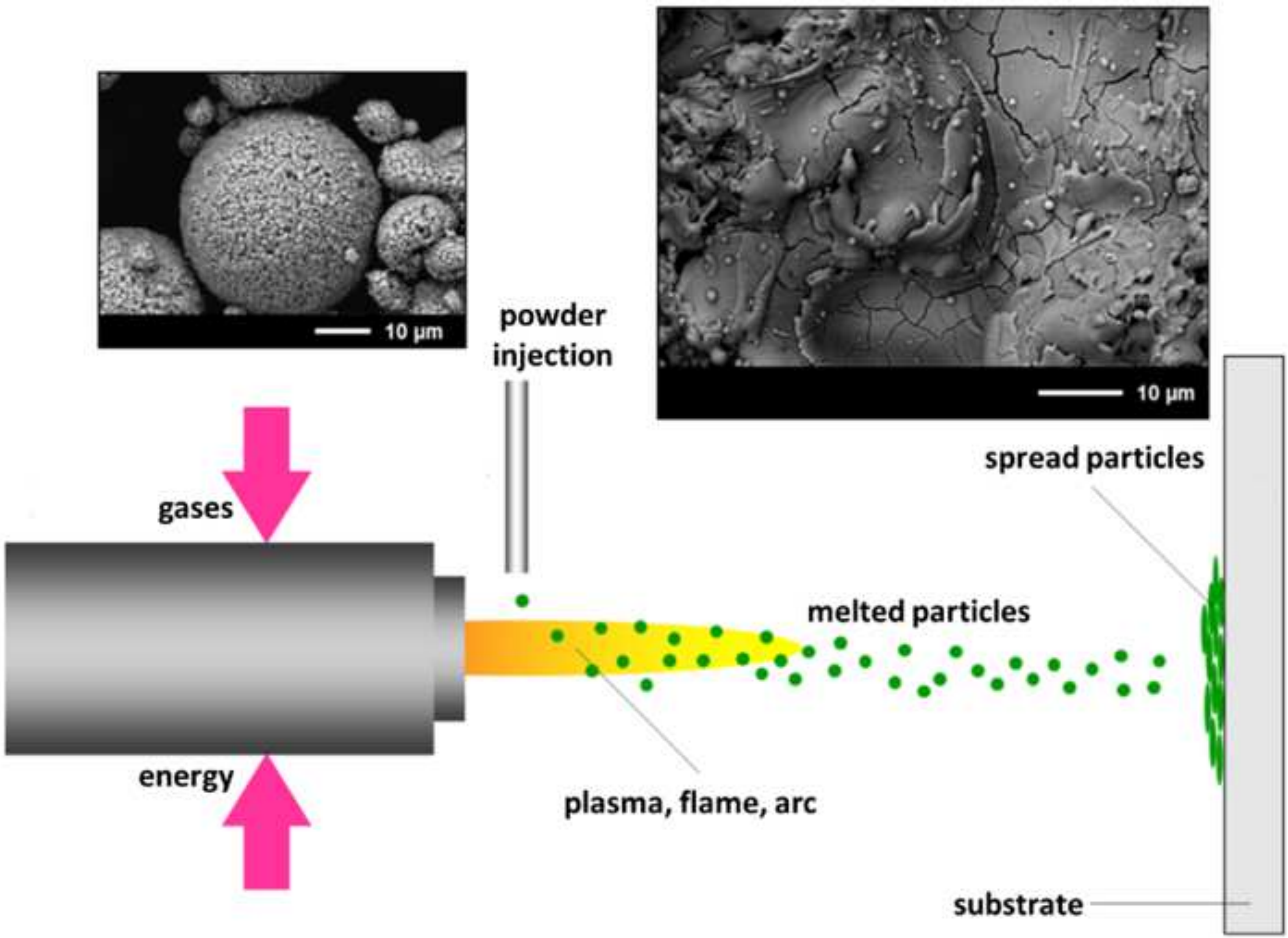
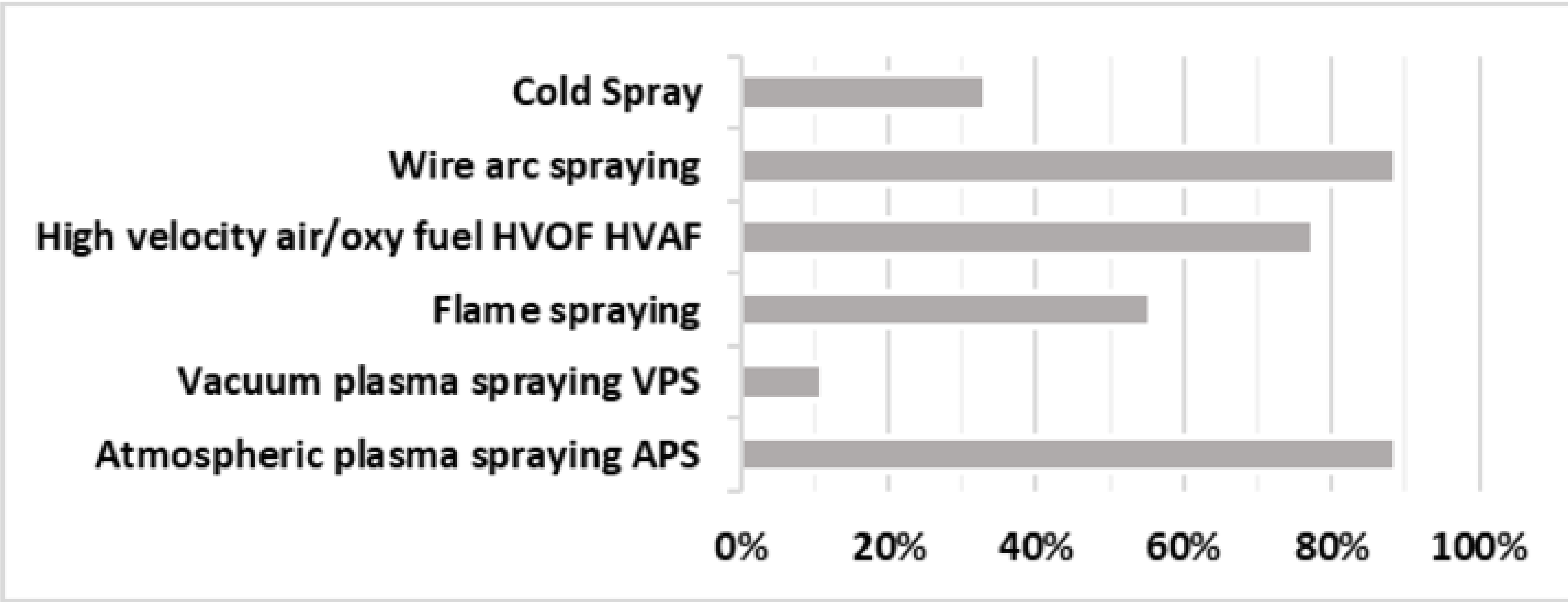

10 µm
10 µm
powder
injection
gases
energy
spread particles
melted particles
plasma, flame, arc
substrate

Figure 4



Cold Spray
Wire arc spraying
High velocity air/oxy fuel HVOF HVAF
Flame spraying
Vacuum plasma spraying VPS
Atmospheric plasma spraying APS
0%
20%
40%
60%
80%
100%

Figure 5

Click here to access/download;Figure;figure5.tiff

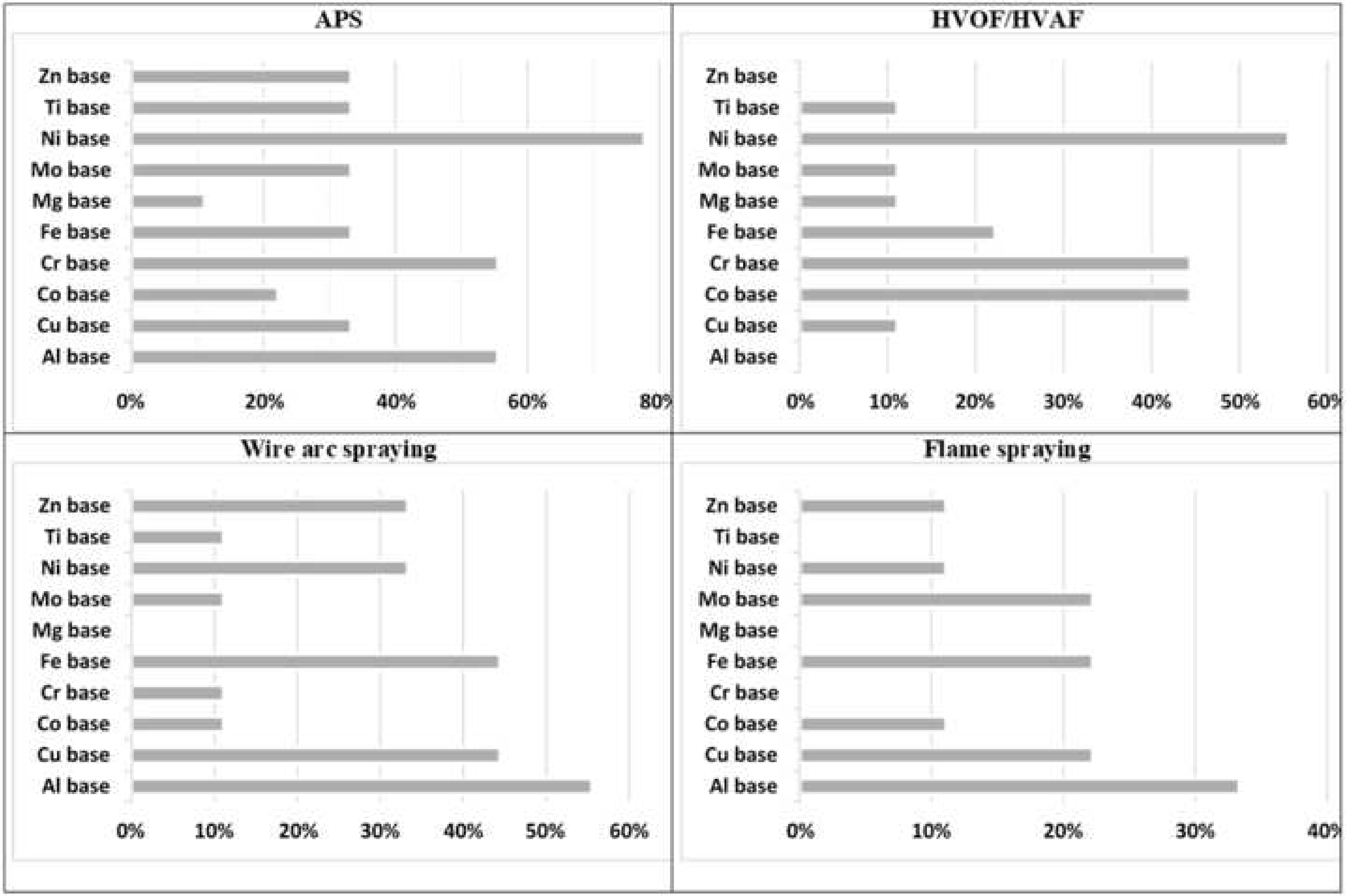


Figure 6 Click here to access/download;Figure;figure6.tiff

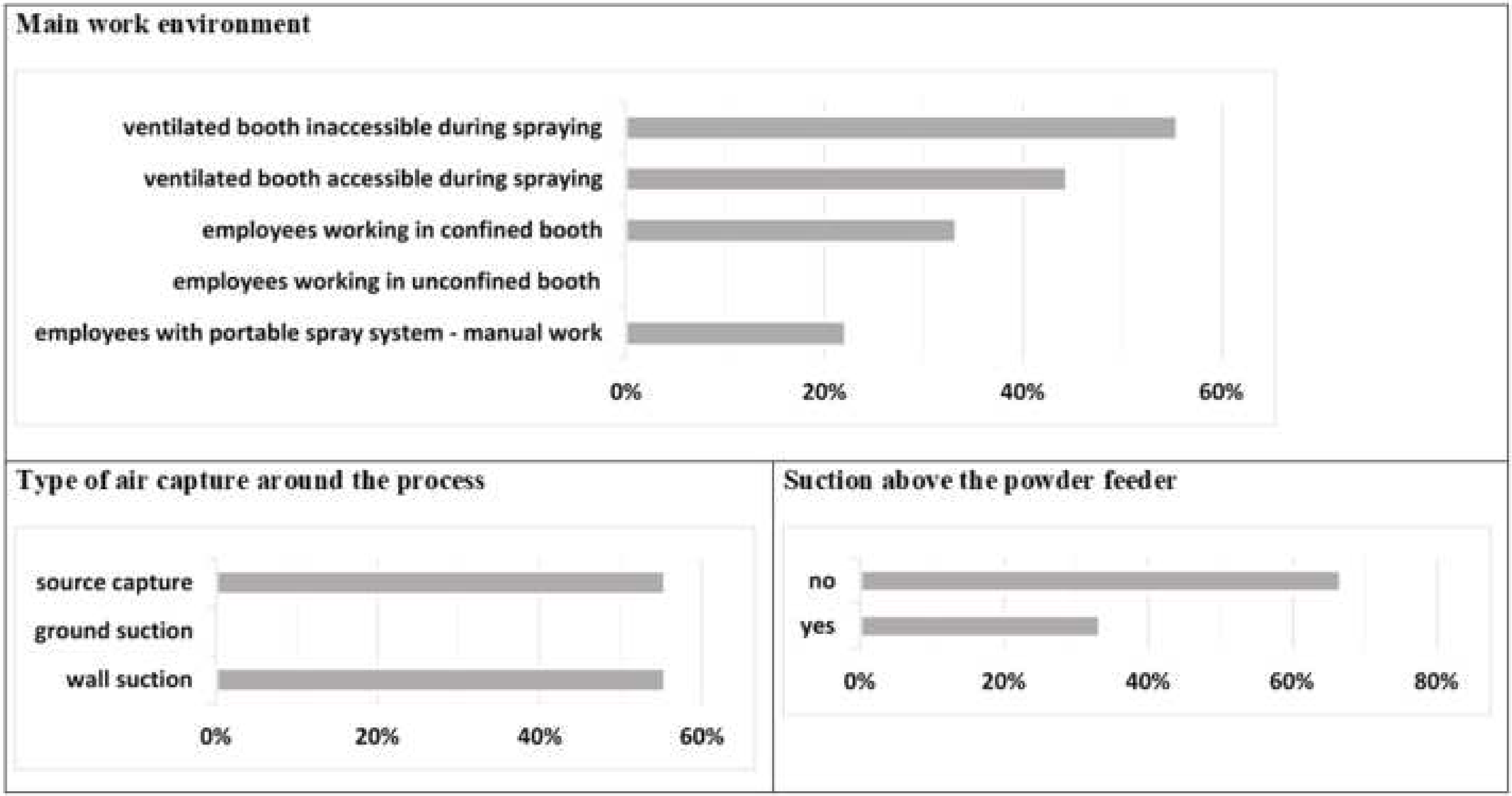
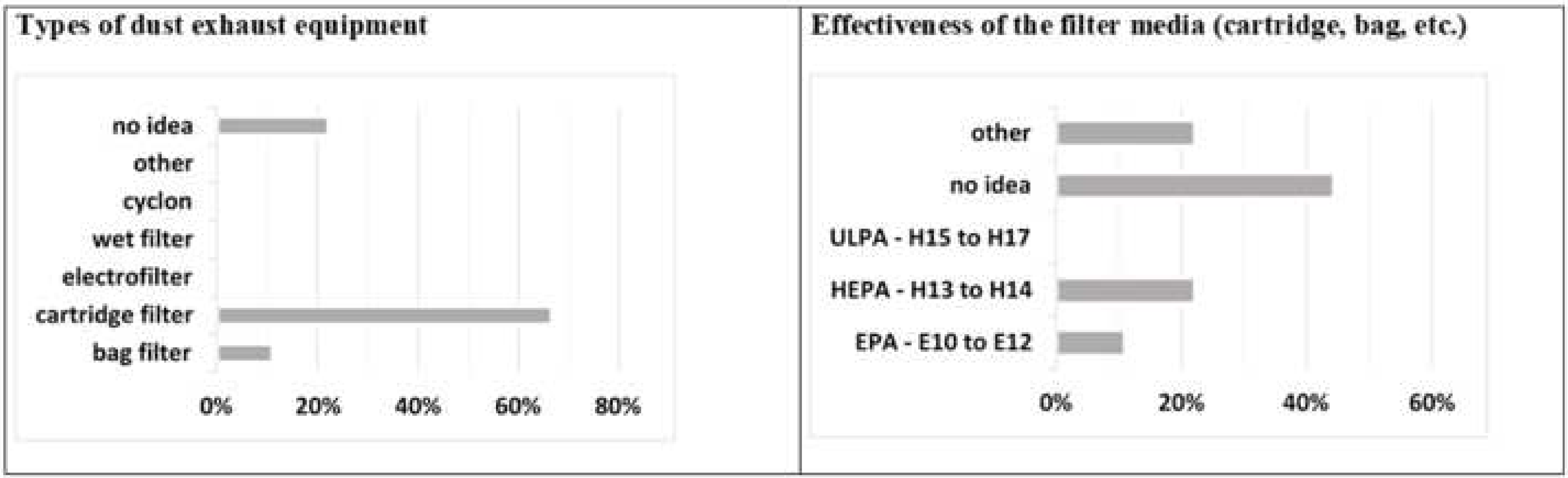


Figure 7



Types of dust exhaust equipment
no idea
other
cyclon
wet filter
electrofilter
cartridge filter
bag filter
0%
20%
40%
60%
80%
Effectiveness of the filter media (cartridge, bag, etc.)
other
no idea
ULPA - H15 to H17
HEPA - H13 to H14
EPA - E10 to E12
0%
20%
40%
60%

Figure 8

Click here to access/download;Figure;figure8.tiff

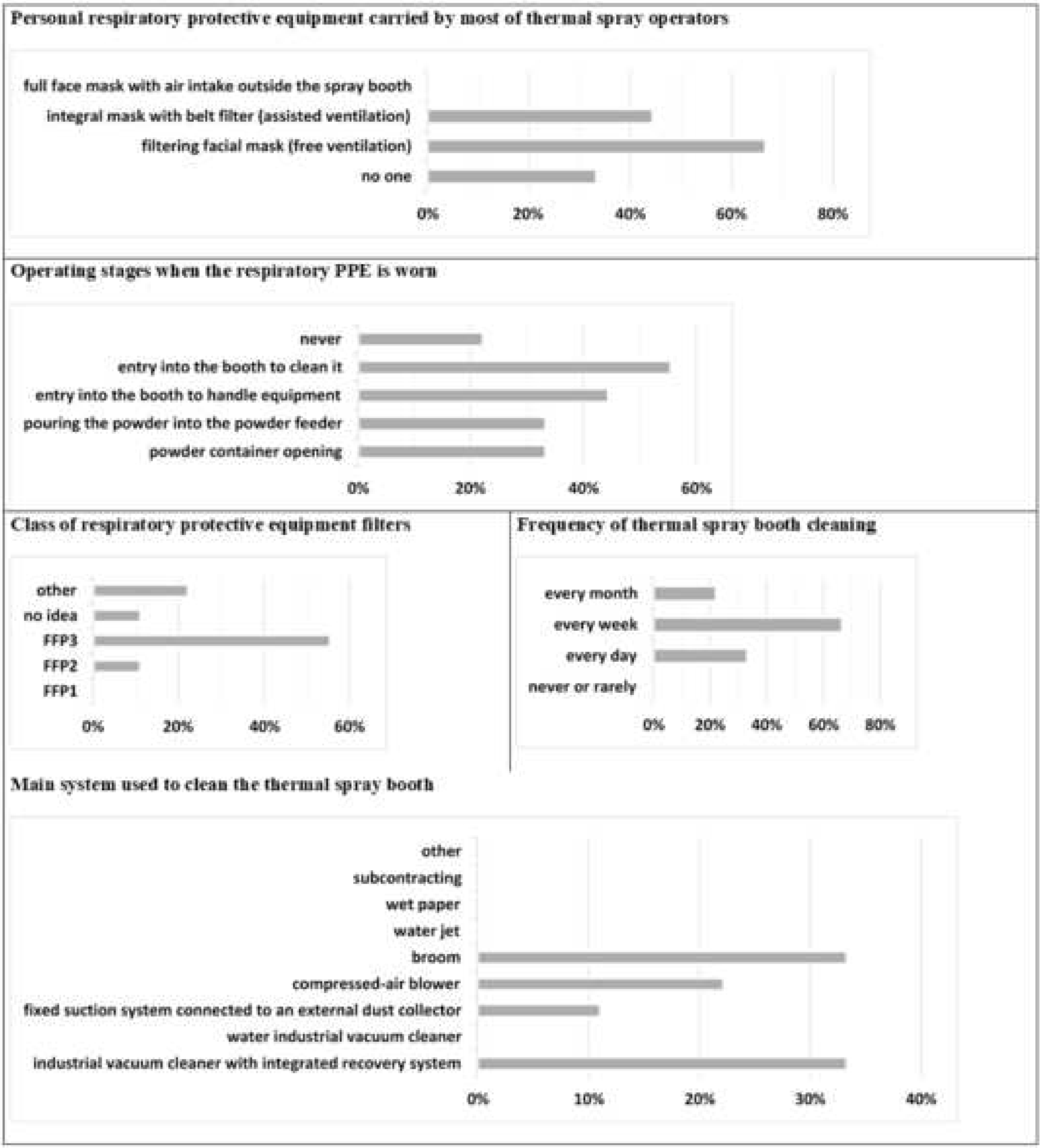


Figure 9

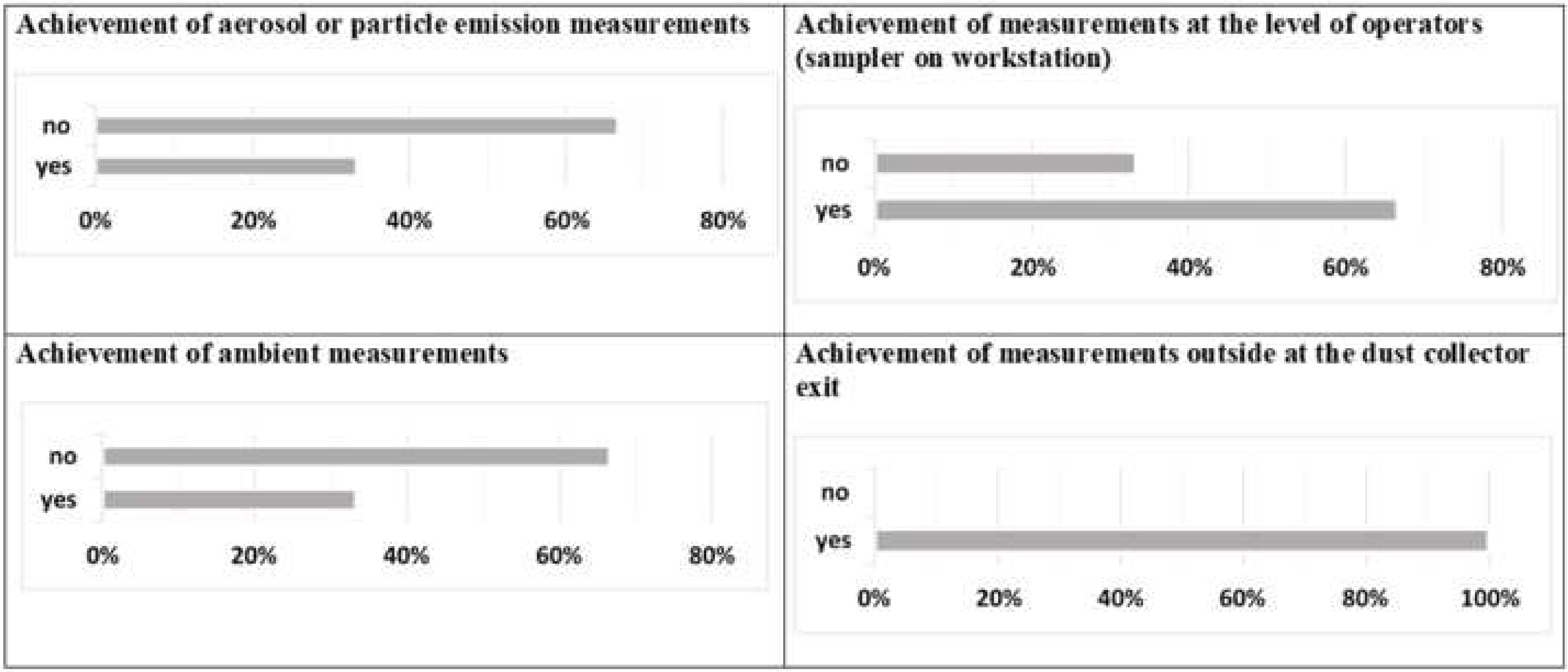
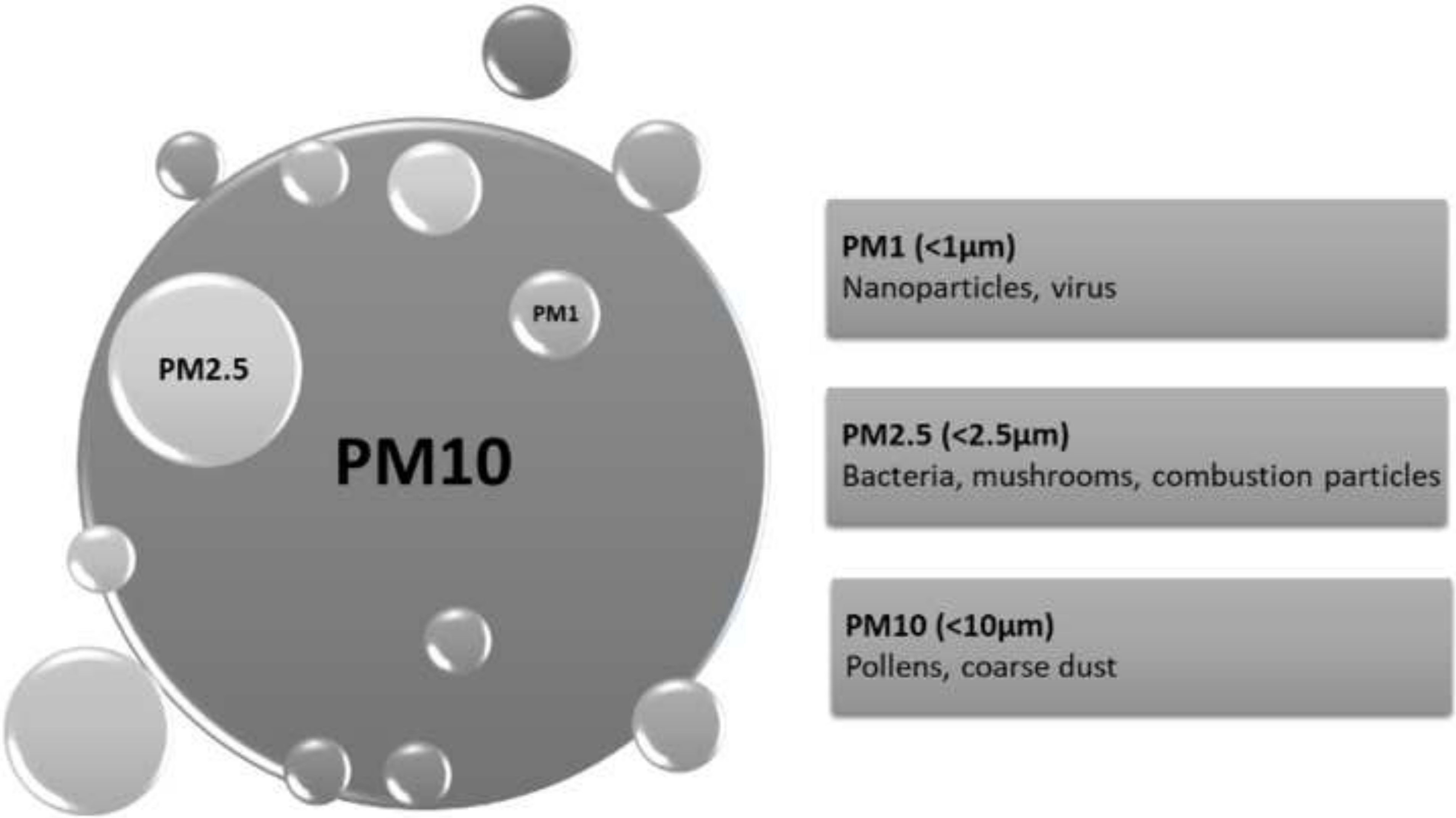

Achievement of aerosol or particle emission measurements
no
yes
0%
20%
40%
60%
80%
Achievement of measurements at the level of operators (sampler on workstation)
no
yes
0%
20%
40%
60%
80%
Achievement of ambient measurements
no
yes
0%
20%
40%
60%
80%
Achievement of measurements outside at the dust collector exit
no
yes
0%
20%
40%
60%
80%
100%

Figure 10

Click here to access/download;Figure;figure10.tiff

Figure 11


PM2.5
PM1
PM10
PM1 (<1µm)
Nanoparticles, virus
PM2.5 (<2.5µm)
Bacteria, mushrooms, combustion particles
PM10 (<10µm)
Pollens, coarse dust