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Inhalation exposure to hazardous substances during powder-bed processes

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Abstract

This work resumes first results concerning the identification of workers' inhalation exposure by means of workplace measurements in the field of additive manufacturing. In particular for powder-bed processes, risks caused by mixed exposures due to released particles and relevant chemical constituents or possible volatile compounds have to be evaluated. The workplace measurements are focused on processes in the automotive as well as the aviation and tool construction industry. The aim is to gain exposure data concerning the application of metal-containing powders and alloys as well as polymer powders in powder-bed processes and to derive instructions for good working practice.

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Keywords: additive manufacturing; powder-bed process; inhalation exposure; occupational safety

1. Introduction

Additive manufacturing processes have gained growing importance during the last years, as, for instance, a recent comprehensive information research by Kaierle et al. shows [1]. In particular, an intensified distribution of powder-bed based processes can be observed in industry. More and more, these technologies are integrated into series production of industrial components with higher complexity. Due to the wide range of procedures, it is now possible to process a large variety of high-tech materials. Instead of powders and solids, liquids with various physical and chemical properties can be used as well. However, there is a notable knowledge deficit concerning the risks resulting from inhalation exposure to hazardous substances released into the air at the workplace during powder-bed fusion and sintering processes, including pre- and post-processing activities like filling of raw material into the machine, component removal and further processing, component and machine cleaning etc. Looking at the raw materials actually applied in industrial additive manufacturing, the assessment yielded medium or high risks regarding the release and exposure to hazardous substances [1]. In case of powder-bed based processes, particulate raw materials are used which may contain or release a certain amount of potentially hazardous nanoparticles. This has to be considered apart from the risks connected with the chemical nature of the substances. An actual research project of the Institute for Occupational Safety and Health (IFA) of the German Social Accident Insurance (DGUV) evaluates risks resulting from the inhalation exposure to specific hazardous substances along the process chain during 3D printing with special regard to the materials used [2]. Amongst others, it has turned out that, in particular, manual post-processing of metal parts produced by 3D printing can result in increased exposures and, in specific cases, to the exceedance of occupational exposure limit (OEL) values. In addition, a working group of a German employers' liability insurance association plans to identify need for action with respect to occupational safety in the field of additive manufacturing, and an expert committee (no. 105.6) of the Association of German Engineers (VDI) actually elaborates a guideline that shall compose recommendations for laser-beam melting with metallic powders to reduce the risks of machine operators [3]. Moreover, the ad-hoc group "Safety Issues" of the International Organization for Standardization (ISO) shall

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propose safety-relevant standards to the Technical Committee (TC) 261 "Additive Manufacturing" of the ISO [3].

The aim of this contribution is to present first results of investigations performed to determine the inhalation exposure of workers to hazardous substances that are released into the air at the workplace during the industrial powder-bed based additive manufacturing processes regarded. In the first step, laser- and electron-beam melting processes with metallic powders are taken into account. The results will supplement the findings of the IFA project [2]. They will contribute to the generation of a comprehensive data base concerning powder-bed based processes, thus being able to elaborate guidelines and information leaflets and to provide adequate support for industrial users of additive manufacturing technologies.

2. Additive Manufacturing Process

In the industrial work areas considered here, three powder-bed fusion machines of different manufacturers, i.e. two fiber laser machines and one machine with electron-beam source, were used for additive manufacturing of high-tech metallic components from Inconel 718 and Ti 64 powders. These machines are program-controlled industrial standard systems with manual filling of the metal powders as well as manual removal of the components after completing the respective construction job. Transport to the sawing, deburring, grinding and polishing stations after the end of the construction job is performed by means of simple handcarts or hand pallet trucks. In fact, no special transport containers are used. The generally closed machines work continuously. They are flushed with argon as protective gas (in case of the laser machines) and exhausted constantly, or operated under vacuum (in case of electron-beam machines). Machine opening occurred only during setup and component removal or in case of failure or maintenance. The control of the laser or electron-beam source is done with an operating display placed outside the respective machine. As an example, the results of the measurements performed during the post-processing (grinding and polishing) of the components removed from the respective machine are displayed and explained here, because it was found that the corresponding exposure to hazardous substances was higher than the exposure resulting from the other process steps.

3. Measurements

In order to determine the workers´ exposure to hazardous substances, both, stationary and personal air sampling are performed simultaneously. According to TRGS 402 [4], time-weighted average (TWA) values, referred to a complete work shift, are determined and compared to the OEL values. The minimum sampling time to be realized depends on the limit of quantification (LOQ) of the applied measurement method. The instrumentation required to carry out the investigations adequately (sampling and measurement as well as calibration equipment) is available to the institutions LZH and BAuA.

On three consecutive days, work cycles repeated for 30 up to 320 minutes were taken into account using stationary and personal air sampling. The work cycles included removal, cleaning, sieving and process set-up. In addition, a direct-reading measurement of the particulate matter (PM) background concentration was carried out at the workplace during normal operation with the closed machine overnight (480 min). The corresponding results are not significant and tend to be in a low concentration range (0.14 mg/m³ inhalable particles and 0.063 mg/m³ respirable particles on average).

3.1. Measurement methods and technology

Generally, the workplace measurements carried out refer to the official German standards which define the conditions of correct sampling and analysis. When analyzing the laser-additive processing of Inconel 718 and Ti 64 powders as described in section 2, the measurement methods summarized in Table 1 and Table 2 were applied to determine the concentrations of the relevant hazardous substances in the workplace air (here: inhalable and respirable particle fraction as well as specific metals and their compounds). A detailed description of these methods and the corresponding sampling can be found in [5]. While the gravimetric evaluation was done by the LZH, the chemical standard analyses of the metals and their compounds listed in Table 2 were performed by an accredited laboratory (ProChem GmbH, Hildesheim, Germany).

Table 1. Measurement methods and IFA key codes for particulate matter [5].

Parameter	Method	Key code
Inhalable particles	Plane filter[1]: gravimetric evaluation	IFA 6068
Respirable particles	Plane filter[1]: gravimetric evaluation	IFA 7284

Table 2. Measurement methods and IFA key codes for metals and their compounds [5].

Parameter	Method	Key code
Nickel, cobalt, titanium, vanadium	Plane filter[1]: gravimetric evaluation, acid digestion[2], AAS[3] graphite tube	Following IFA 8095
Chromium	Plane filter[1]: gravimetric evaluation, acid digestion[2], AAS[3] graphite tube	IFA 6645
Iron	Plane filter[1]: gravimetric evaluation, acid digestion[2], ICP-MS[4]	Following IFA 6310
Aluminum	Plane filter[1]: gravimetric evaluation, acid digestion[2], AAS[3] with flame	IFA 6060

The relative LOQ value for the gravimetric analysis of the particle mass concentration was derived from the uncertainty of weighing 10 blank nitrocellulose plane filters (± 0.18 mg) and the sampling volume at a flow rate of 10 l/min (see also [6]). According to the relevant OEL values, LOQ values corresponding to a high accuracy of the measurement results could be reached for sampling times longer than 180 minutes.

Up to four adjustable gas samplers, type DESAGA GS 312 (Sarstedt AG & Co. KG, Nümbrecht, Germany), were used simultaneously for stationary sampling of the relevant PM released during the different steps of the additive manufacturing process. The samplers provide adjustable flow rates up

[1] Plane filter made from cellulose nitrate, pore diameter 8 µm.
[2] Acid digestion according to IFA with HNO_3/HCl at a ratio of 2:1 (v/v).
[3] Atomic absorption spectrometry.
[4] Inductively coupled plasma mass spectrometry.

to 12 l/min (here, a value of 10 l/min was set). In addition, two gas samplers, type SG 10-2 (GSA Messgerätebau GmbH, Ratingen, Germany), were used to perform the personal air sampling of both, respirable and inhalable particle fraction. These samplers provide adjustable flow rates up to 10 l/min. For stationary and personal sampling of airborne particles, a personal sampling system for hazardous substances compliant with the IFA requirements [5] (GSA Messgerätebau GmbH, Ratingen, Germany) was used. Both, a head for sampling of the respirable particle fraction ("Feinstaub-Probenahme" – FSP) and a head for sampling of the inhalable particle fraction ("Gesamtstaub-Probenahme" – GSP) were applied. They are designed for a flow rate of 10 l/min.

To monitor the relevant particle concentrations in the air at the workplace online, a DustTrak™ DRX Aerosol Monitor 8533 (TSI GmbH, Aachen, Germany) was used. This device can measure size-segregated mass fraction concentrations corresponding to PM 1, PM 2.5, PM 4 (respirable particle fraction), PM 10[5] and total PM size fractions simultaneously and log the data as a function of time for subsequent offline evaluation. The operating principle of the instrument is based on laser photometry, measuring the light scattering due to the particles captured by partial volume flow extraction. To achieve mass fraction measurements, particle cloud (total area of scattered light) and single particle detection are combined.

The PIMEX method (PIcture Mixed EXposure [8]) refers to the synchronous recording and visualization of workloads of employees in real time. The workflow is filmed with a video camera. The occurring exposures (such as particles, solvents etc.) are recorded synchronously with the video using different direct-reading measuring devices. This information is available at any time and can be used for further analysis. The possibility of directly linking exposure profiles with the employee's current activity reveals instructive connections between the work process, the prevailing stress as well as the specific demands and measures against unfavorable situations.

3.2. Measurement strategy

According to [4], the strategy of workplace measurements to be performed in the course of a risk assessment comprises several steps. Prior to a specific measurement, information about the process, the related process steps and the materials used as well as the individual activities carried out by the employee are collected at the different workplaces involved. In principle, all possible substances must be taken into account upon planning the measurement. Depending on the release behavior of the hazardous substances, their quantity and their toxicity, it may be sufficient if the measurement is restricted to the relevant substances. Their selection is comprehensibly justified in the minutes of the on-site inspection of the individual company. The following list shows the course of action for the investigations described here:

- Consideration of all working steps relevant for the additive manufacturing process (pre- and post-processing, actual manufacturing process, cleaning and maintenance)
- Representative sampling (personal, stationary)
- Measurement at several measuring points during a work step (complete duration)
- Adaptation to the specific conditions in each company (the strategy may change in the course of the project)
- Determination of raw materials used (materials used for the manufacturing process including all ingredients taking into account the safety data sheets)
- Selection of validated measurement and analysis methods (parameters: respirable and inhalable particle fraction as well as their constituents and possibly crucial decomposition products)
- The LOQ of the measurement method is decisive for the sampling duration. So far, a minimum duration of 180 min for the inhalable and respirable particle fraction to be investigated (use of the SG-10-2 sampling pump at a flow rate of 10 l/min) has proven to be expedient.
- Integration of the PIMEX Imaging System and the DustTrak™ DRX Aerosol Monitor

The results of the workplace measurements must describe the exposure during the shift representatively. Shift average values representing the time-averaged concentrations of the hazardous substances in the workplace air as well as short-term exposure values for activities with increased exposure are used for this purpose. The decision is made depending on the situation encountered in the work area. A suitable measuring method with appropriate measuring points and times depending on the details of the production procedure is chosen correspondingly.

4. First Measurement Results

The temporal progression of the particle concentration can be used to draw conclusions on individual activities of the machine operator, as can be seen in the example shown in Fig. 1. On the whole, the graph for the mass concentration of the inhalable particles, recorded with the DustTrak™ DRX (stationary sampling) during manufacturing with one of the fiber laser machines is inconspicuous and the concentration is at a low, non-relevant level on average. This is valid for all three powder-bed based additive manufacturing procedures considered here. However, two broad peaks in Fig. 1 can be assigned to specific activities of the operator (see the arrows in the diagram): the first peak indicates the machine opening, whereas the second, even broader peak denotes a part of the cleaning process (sweeping), while the machine is still closed, and the subsequent opening of the hatch at the front.

The pie charts (see Fig. 2) of the detailed analysis of the inhalable and respirable particle fraction, derived for the experiment regarded in Fig. 1 as well, show that in the respirable fraction, a higher percentage of the particles can be assigned to specific metals resulting from the raw material. Obviously, the workshop background is more present in the inhalable fraction which is indicated as the unassigned particle portion.

[5] The respective number refers to the aerodynamic particle diameter in [µm] at which the weighting function, describing the particle size shares incorporated into the corresponding PM value, decreases to 50% [7].

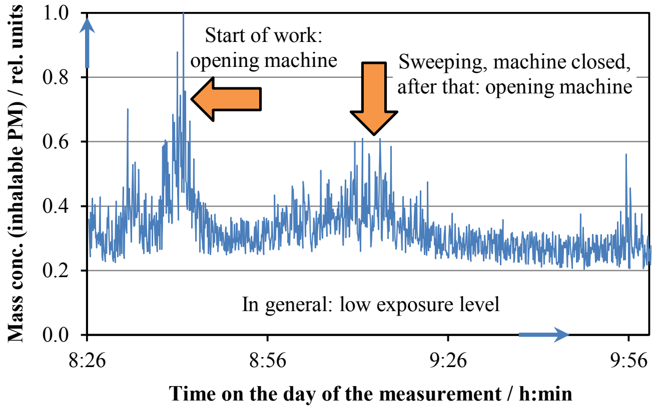
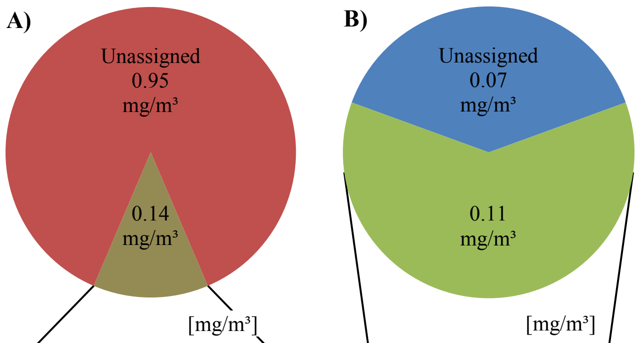


Fig. 1. Qualitative temporal progression of inhalable PM in the course of the usual routine job, stationary logging using the TSI DustTrak™ DRX. Mass concentration (conc.) given in relative (rel.) units, referred to the maximal concentration value recorded during the period displayed.



A)

Nickel	1.25E-02
Cobalt	< 5.20E-04
Chromium*	3.54E-03
Iron	1.00E-02
Titanium	1.15E-02
Aluminum	< 1.04E-01
Vanadium	< 1.04E-03

B)

Nickel	5.80E-04
Cobalt	< 5.20E-04
Chromium*	< 5.20E-04
Iron	< 5.10E-03
Titanium	1.56E-03
Aluminum	< 1.04E-01
Vanadium	< 1.04E-03

Fig. 2. Detailed analysis (for the relevant metal components) of the inhalable (A) and respirable (B) particle fraction.

5. Discussion of Protective Measures

Generally, an assessment of the work area is carried out in accordance with section 4 of the GefStoffV [9]. According to §10 of this ordinance, special protective measures required for activities with hazardous substances that are carcinogenic, mutagenic or toxic for reproduction (category 1A and 1B) have to be taken, if the release of such substances into the air at the workplace cannot be excluded. In fact, this applies to the powder-bed processes investigated here. Since the additive manufacturing systems are not opened unless loading and unloading of the workpieces, filling of the raw material or cleaning is required, this exposure may fall under the category of peak limitation. A final decision on the protective measures which are strictly necessary, can only be taken if appropriate workplace measurements according to TRGS 402 [4] are performed, using analytical methods with sufficiently long sampling durations (> 180 min) which fulfill the requirements of the European Standard EN 482 [10]. These measurements have to yield results with respect to substance-specific loads.

According to TRGS 910 [11] and TRGS 561 [12], acceptable and tolerable concentrations are given for substances with an exposure-risk relationship (ERR). Taking into account the protective measures already realized at the workplaces related with the powder-bed processes investigated here, the results of the workplace measurements showed that the tolerable and acceptable concentrations are complied with. Regarding the hazardous substances with OEL values according to TRGS 900 [13] that were analyzed, the protective measures that are already realized at the workplaces regarded here are sufficient in accordance with TRGS 402 [4] as well.

The analyses showed that in case of the powder-bed processes considered in this contribution, compliance with the assessment standards is ensured and the protective measures are sufficient. This includes the pre- and post-processing activities, what has to be documented in the course of the risk assessment to be performed before starting the production of the metallic workpieces. Thus, additional protective measures are not necessary. However, effectiveness checks according to TRGS 402 [4] are recommended at annual intervals. If no changes occur during the activities considered, it is sufficient to check and document the effectiveness by means of regular inspections, incorporating visual inspections of machine surfaces and the ground to identify powder sedimentation, the verification of suction power and proper function of the air conditioning units as well as employee interviews, if required.

The validity of these statements for the examined work areas exclusively refers to the parameters of the processes that were performed during the measurements and to the materials used therein. In case of significant variations of the parameter sets, the kind and amount of raw materials or the existing protective measures, such as the exhaust ventilation, a re-assessment of possible inhalation exposures is required.

6. Conclusions

The investigations performed in the course of the first sampling and measurement campaign show that in case of the powder-bed based additive manufacturing processes considered here, compliance with the relevant rules and standards is ensured and the protective measures already realized are sufficient. Thus, additional protective measures are not required at the moment, provided that the process conditions (raw material powder, process gas, laser output power or electron-beam energy etc.) are not changed significantly.

So far, relatively few workplace measurement campaigns have been carried out in this context. Of course, a series of further campaigns in other industrial companies is planned in order to generate a comprehensive data base, also taking into account powder-bed processes with polymeric raw materials (laser sintering processes). In the end, the results shall help to elaborate standardized working procedures and EMKG control guidance sheets[6] for additive manufacturing processes.

[6] The BAuA's control guidance sheets in accordance with the EMKG (German abbreviation for "Easy-to-use workplace control scheme for hazardous substances") concept implement the requirements of the GefStoffV [9] and the body of technical regulations.

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