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Inhalation exposure to metals during additive processes (3D printing)

R. Beisser, M. Buxtrup, D. Fendler, L. Hohenberger, V. Kazda, Y. von Mering, H. Niemann, K. Pitzke, R. Weiss

Abstract

Systems for additive manufacturing such as laser sintering and laser beam melting systems have undergone a huge innovative leap through to small-series production in the last few years. So far there have been only very few publications on inhalation exposure to hazardous substances during these processes. For this reason the expert committee “Raw Materials and Chemical Industry”, Hazardous Substances Section, of the German Social Accident Insurance (DGUV) together with its Institute for Occupational Safety and Health (IFA) and the German social accident insurance institutions initiated a measurement programme in this field. The publication presents measured data on laser deposition welding and laser beam melting with alloyed steels and nickel-, aluminium-, titanium- and copper-based alloys. Under the current state of technology, only the construction process proper is automated, while the work steps during the pre- and post-processes are performed manually or semi-automatically. As a result of the associated variations in working methods with major effects on the degree of inhalation exposure, the measured values show a broad spread. From these measurement findings, it therefore proofs difficult to derive measures tailored to additive manufacturing applications.

Inhalative Exposition gegenüber Metallen bei additiven Verfahren (3D-Druck)

Zusammenfassung

Anlagen zur additiven Fertigung wie Lasersinteranlagen oder Laserstrahl-Schweißanlagen haben in den letzten Jahren einen großen Innovationssprung hin zur Kleinserienfertigung erfahren. Zur inhalativen Exposition gegenüber Gefahrstoffen bei diesen Verfahren gibt es zurzeit nur wenige Veröffentlichungen. Deshalb hat der Fachbereich Rohstoffe und chemische Industrie, Sachgebiet Gefahrstoffe, der Deutschen Gesetzlichen Unfallversicherung (DGUV) zusammen mit dem Institut für Arbeitsschutz der DGUV (IFA) und den Unfallversicherungsträgern (UVT) ein Messprogramm für

diesen Bereich initiiert. Vorgestellt werden Messdaten zum Laserauftragsschweißen und Laserstrahlschmelzen mit legierten Stählen, Nickelbasis-, Aluminium-, Titan- und Kupferbasislegierungen. Beim derzeitigen Stand der Technik ist in der Regel nur der eigentliche Bauprozess automatisiert. Die Arbeitsschritte während des Prä- und Postprozesses erfolgen manuell oder halbautomatisiert. Durch die damit verbundene individuelle Arbeitsweise mit starkem Einfluss auf die Höhe der inhalativen Exposition ergeben sich starke Streuungen der Messwerte. Die Ableitung maßgeschneiderter Maßnahmen zur Anwendung bei additiven Fertigungsverfahren anhand der Messergebnisse gestaltet sich somit schwierig.

1 Introduction

3D printing has been a big talking point for some time now, with the term "3D printing" being used synonymously for additive manufacturing processes in general. In additive manufacturing processes, a component is produced through the layer-by-layer addition of material. Additive manufacturing processes are differentiated according to process and are described in greater detail in the guideline VDI 3405. This publication is concerned solely with laser beam melting and laser deposition welding. The materials employed in these processes are various powder metal alloys that are welded together in layers by means of a laser. Widely used, for example, are stainless steels and nickel-, aluminium-, titanium- and cobalt-based alloys.

The conditions under which 3D printers are used can vary greatly according to the application. Such machines can be operated in anything from showrooms and small laboratories to large industrial shops, for example. They can also be operated in rooms without mechanical ventilation or in rooms with as many as eight air changes per hour. To assist enterprises with their assessment of the inhalation risk during additive manufacturing processes, the Raw Materials and Chemical Industry Committee, Hazardous Substances Section, of the German Social Accident Insurance (DGUV) together with its Institute for Occupational Safety and Health (IFA) and the German social accident insurance institutions have initiated the "Exposure during Additive Manufacturing Processes (3D Printers)" measurement programme. This paper presents the measurement findings on inhalation exposure during laser beam melting and laser deposition welding.

2 Description of the processes

In the laser beam melting of metals from the powder bed and in laser deposition welding, metal powder is melted layer-by-layer by a focused laser beam to produce solid components. Depending on the process, the powder is supplied by either a coater or a powder nozzle. **Figure 1** shows the process chain for the two processes.

In the course of the measurement programme, powder alloyed steels, nickel- and copper-based powders (**Table 1**), titanium powder and aluminium powder were used. The details of their compositions were taken from the technical data sheets. The titanium powder used is composed of 5.5 to 6.5% aluminium, 3.5 to 4.5% vanadium and 89.0 to 91.0% titanium; the aluminium powder of 87 to 91% aluminium and 9.0 to 11.0% silicon; and the copper-based powder of unknown quantities of copper, zinc and nickel.

The powder sizes range from about 20 to 60 µm.

Figure 1:
Typical process chain for laser beam melting and laser deposition welding (italics).
The other work steps are identical for both processes.

Pre- and manufacturing processes		
Replenishing powder	Setting up machine/ preparing first layer	Laser-based manufacturing process
Replenishing powder	*Laser-based manufacturing process*	

↓

Post process			
Separating component from platform	Removing powder from component	Grinding	Screening remaining powder and preparing it for next manufacturing process
Separating component from platform		*Grinding*	

Further work steps (for both processes)	
Full cleaning	Powder analysis

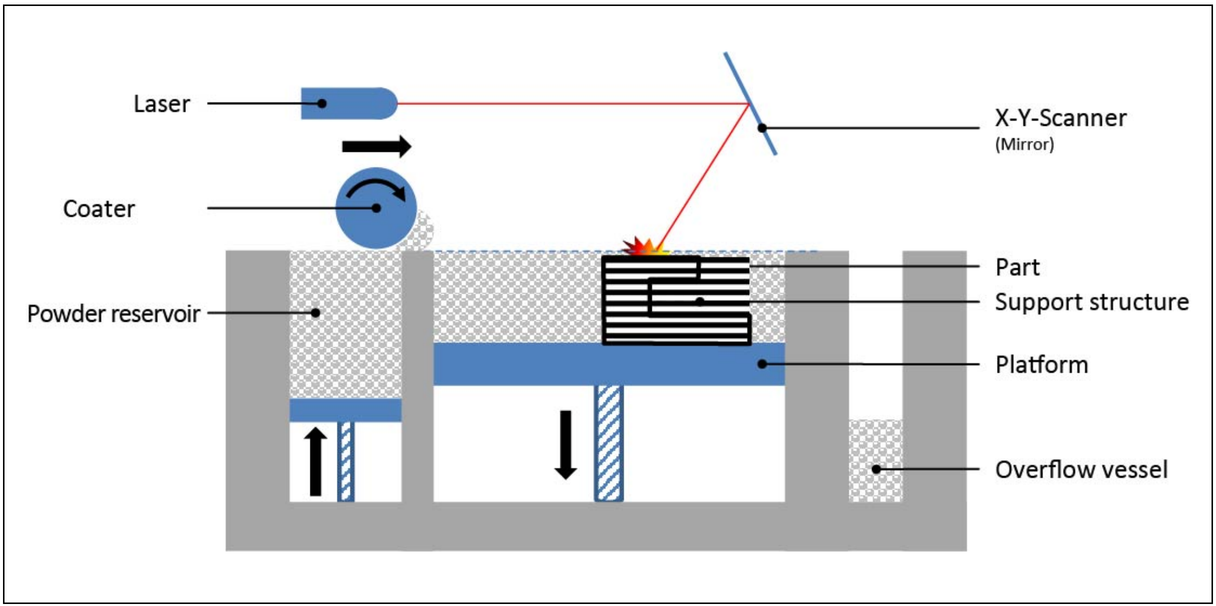
Tabelle 1:
Contents of alloyed steels (nos. 1.4404, 1.4548, 1.2709) and of nickel-based powder
(nos. 2.4668 and 2.4856).

Material number	**Components in %**					
	Iron	**Chromium**	**Nickel**	**Cobalt**	**Manganese**	**Molybdenum**
1.4404	Remainder	16.7	10.7	<0.9	<2	2.0 to 2.5
1.4548	Remainder	15.00 to 17.50	3.00 to 5.00	--	0 to 1.00	--
1.2709	Remainder	≤0.25	17.0 to 19.0	8.50 to 10.0	≤0.15	4.50 to 5.20
2.4668	Remainder	17.0 to 21.0	50.0 to 55.0	≤1.00	≤0.35	2.80 to 3.30
2.4856	≤5.0	20.0 to 23.0	≥58	≤1.0	≤0.5	≤8.0 to 10.0

2.1 Laser beam melting

Laser beam melting is a powder-based process (**Figure 2**), well-known as laser forming, Selective Laser Melting (SLM®), LaserCUSING® and Direct Metal-Laser Sintering (DMLS®). So that material is always available for the next layer, the coater has to apply a thin film of powder roughly 15 to 500 µm thick from the powder reservoir to the base plate. With a laser, the powder layer is fully melted in the desired places and forms the first material layer after solidification. The coater then makes the next film of powder available, which is laser-melted as the next layer. This cycle is repeated until all the layers of the component have been generated. The entire process takes place in an inert gas atmosphere and can take anything from several hours to days, depending on the component. After the manufacturing process, excess powder is removed from the component by blasting with glass beads or by brushing, for example. The component is then separated from the base plate and – if desired – ground and painted. Excess powder is screened and reprocessed for further manufacturing processes. Cleaning the machine is another of the work steps. The intensity of cleaning depends on whether a powder change or preparation of the next production cycle is next. In addition, this can be followed by various other work steps, such as powder analysis for its flow behaviour or composition.

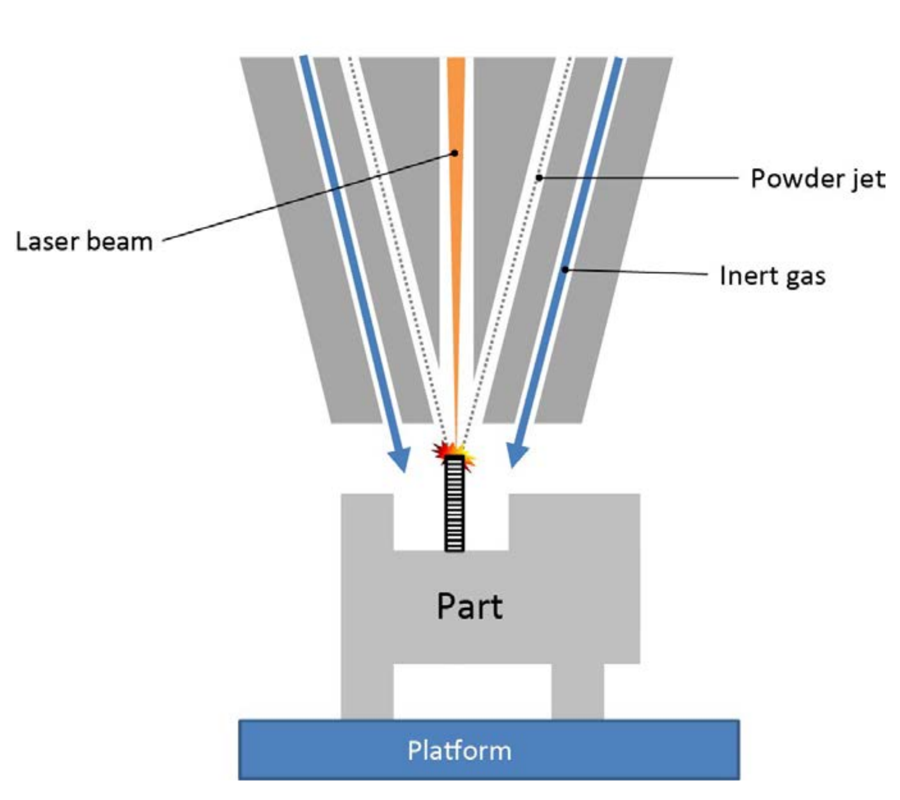
Figure 2:
Schematic illustration of laser beam melting [1].



2.2 Laser deposition welding

Unlike laser beam melting, this process does without a powder bed and instead the material is supplied coaxially with an inert gas during the manufacturing process (**Figure 3**). Like during laser beam melting, the material is liquefied by a laser. The laser and nozzle move layer by layer over the surface until the component is fully generated. Powder removal as practised during laser beam melting is omitted with this process, although the component, if desired, is also removed from the production platform. This is followed by other work steps, such as post-treating the welds.

Figure 3:
Schematic illustration of laser deposition welding.



3 Methods

3.1 Scope of the MGU measurement programme

The “Exposure during Additive Manufacturing Processes (3D Printers)” measurement programme is based on a uniform measurement strategy with the systematic collection of operating and exposure data [2]. The primary goal is to obtain valid and utilisable measured data on the inhalation exposure of employees to hazardous substances during the application of additive manufacturing processes.

The measurement study is being performed by IFA and the Measurement Services of the social accident insurance institutions. Overall, the additive manufacture of metal components by laser beam melting and laser deposition welding has so far been investigated in twelve enterprises. The exposure data are documented in IFA’s MEGA exposure database [3].

3.2 Measurement strategy

A large number of hazardous substances can be released, depending on the metal primary material employed and the treatment process. To ensure uniform substance identification, a substance list was therefore drawn up on the basis of safety data sheets to itemise the most commonly used materials, their main contents and possible reaction products. Standard IFA collection methods were employed for the hazardous substance measurements in the production shops. The sample carriers were subsequently evaluated in the IFA laboratory. The measurement and analysis methods are described in greater detail in Section 3.3.

Since the primary materials are available in powder form, the respirable and inhalable dust fractions were measured in all cases. Further individual metals and their compounds (chromium and its compounds, chromium(VI) compounds, nickel and its compounds, etc.) were also measured. The individual substances were identified on the basis of the above-mentioned substance list. In addition to these obligatory measurements, the number concentrations of ultra-fine particles were measured at certain additive manufacturing machines with directly indicating measuring systems. These were supplemented with reference measurements in the ambient air. The measurements were performed during different production processes and work steps.

The manufacturing process proper takes place in closed machines and takes several hours. On laser beam melting machines, the production chamber is additionally flooded with inert gas (e.g. nitrogen) to create an inert gas atmosphere. Once the manufacturing process has started, employees do not usually stand at the machine. During production, stationary measurements were therefore performed at the production machine itself without actual employee exposure.

After the manufacturing process, the workpieces are removed from the machine and the excess powder is removed. During the post-process, such as the cleaning of the machine, the treatment of the powder in special screening devices and mechanical post-treatment (e.g. grinding and blasting), high dust exposure can be expected. During such activities, personal hazardous substance measurements took place in the shop conditions existing on site. The employee exposure measured under these conditions was assessed in accordance with the Technical Rule for Hazardous Substances (TRGS) 402 “Identification and assessment of the risks from activities involving hazardous substances: inhalation exposure” [4].

Figure 4 shows the cleaning of the handling chamber of a Selective Laser Melting machine with an industrial vacuum cleaner, with measurements performed on the person (left). The manufacturing chamber was then removed from the machine with lifting gear (right).

Figure 4:
Left: Cleaning of the handling chamber of a Selective Laser Melting machine with an industrial vacuum cleaner. Right: Manufacturing chamber being removed from the machine with lifting gear.

3.3 Analysis of metals and their compounds

Airborne dust particles were sampled with various sampling systems according to the dust fraction being collected and the hazardous substance being measured. For the sampling of metals and their compounds in the respirable and inhalable fractions, IFA's particulate or total dust sampling systems, FSP-10 or GSP-10 [5; 6], were used with a sampling time of at least two hours and a flow rate of 10 l/min. The metal-laden dusts were collected on cellulose nitrate filters (pore width 8.0 µm, with a test certificate on metal contents, e.g. Sartorius, 11301-37-N) with a diameter of 37 mm. In some cases, the respirable and inhalable fractions were determined gravimetrically before the quantitative analysis of the metals and their compounds.

The concentrations of the metals and their inorganic compounds were determined quantitatively by ICP mass spectrometry (ICP MS) or total reflection X-ray fluorescence spectrometry (TXRF) in multi-element analysis.

In the analysis of air samples by ICP MS, the former were broken down, diluted and analysed using the standard acid decomposing agent for the total metal content using the process of the German Research Foundation (DFG) [7].

For X-ray fluorescence analysis, the samples were processed as filter dispersions with acetone and subsequently applied to quartz plates.

Measured values below the quantification limit were documented with their respective individual quantification limits. This depends above all on the analysis method and sampled air volume (flow rate and sampling duration). The processes are suitable for measurements conforming to TRGS 402 [4] and satisfy the requirements of DIN EN 482 [8] and DIN EN 13890 [9].

The following metals and their compounds were quantitatively determined in the context of the project: aluminium, chromium, cobalt, iron, copper, manganese, nickel and titanium.

Chromium(VI) compounds were sampled in the inhalable fraction on 37 mm quartz fibre filters (e.g. Munktell, MK 360) using the GSP-10 sampling head with a flow rate of 10 l/min. The chromium(VI) compounds were released from the filter with a mixture of sodium hydroxide and sodium carbonate. UV spectrometry was performed after acidification with sulphuric acid/phosphoric acid and derivatisation with diphenyl carbazide at a measurement wavelength of 540 nm [10]. The method is specific to chromium(VI).

4 Results

In the further consideration of the results, the distinction between laser beam melting and laser deposition welding is disregarded, as the process steps of the two techniques barely differ (Figure 1). However, during the pre- and post-processes in the enterprises studied, the working methods for one and the same work step are in some cases very different owing to differences in the shop conditions. These range from encapsulated and partially dust-extracted/encapsulated to insufficiently or non-extracted work steps. Furthermore, the open handling of the powder does not always conform to the rules for dust-free operations [11]. The measured values show a broad spread as a consequence.

The manufacturing process in all machines took place in an inert gas atmosphere and the process air was internally recirculated.

In terms of workplace health and safety, the inhalation exposure assessment of the use of the metal powders investigated to date in additive manufacturing processes varies.

4.1 Aluminium-based alloys

A total of 21 measurements were carried out for aluminium-based metals (**Table 2**). Depending on the composition of the aluminium materials, the measurements covered in some cases a variety of hazardous substances in addition to aluminium and its compounds.

Table 2:
Hazardous substance concentrations in the workplace air from the processing of aluminium.

Material: Aluminium			**Process step**			
Hazardous substance	**Limit value in mg/m³**		**Pre-process**	**Manufacturing process**	**Post-process**	**Powder analysis/full cleaning**
Respirable dust	**1.25 (OEL)**	Number of values	2	9	5	2
		Measured value (mg/m³)	<0.22	<0.21	<0.24	<0.25
Inhalable dust	**10 (OEL)**	Number of values	3	11	5	2
		Measured value (mg/m³)	2 values <0.04 0.92	5 values <0.04 0.05 to 0.89	2 values <0.21 0.07 to 0.39	<0.31/0.72
Aluminium and compounds (R)		Number of values	3	9	3	2
		Measured value (mg/m³)	<0.00075/ 0.0017/ 0.049	5 values <0.083 0.0017 to 0.014	<0.00045/ 0.0044/ 0.0045	0.045/0.018
Aluminium and compounds (I)	**-**	Number of values	2	10	4	2
		Measured value (mg/m³)	0.0063/0.47	1 value <0.0095 0.0008 bis 0.2	0.0076 to 0.17	0.079/0.49
Ultrafine particles	**-**	Number of values	-	4	-	-
		Measured value (1/cm³)	-	$2.1 \cdot 10^3$ to $1.4 \cdot 10^4$	-	-
		Ambient air reference value (1/cm³)		$8.6 \cdot 10^3$ to $1.7 \cdot 10^4$		

R = respirable dust fraction, OEL = Occupational Exposure Level to TRGS 900 [12], I = inhalable dust fraction

When aluminium-based alloys were used for laser beam melting and laser deposition welding, the general dust limit values for the respirable and inhalable dust fractions were complied with in all cases, and the measured values for the respirable dust fraction were always below the detection limit. For aluminium and its compounds, there is no substance-specific limit value. The number of ultra-fine particles at a maximum of 5.2×10^3 particles/cm^3 was lower than the ambient air reference value.

All work steps during the pre-process, such as powder replenishment and setting up the production platform, were performed without measurement at source. During the pre-process no respirable dust fraction was detected. For the inhalable dust fraction two of the three measured values are below the detection limit. The measured value above the detection limit is below the OEL. The concentration for aluminium and its compounds in the respirable dust in the workplace air is below the quantification limit for one of the three measured values. The other two measured values are 0.0017 mg/m^3 und 0.049 mg/m^3. In the inhalable dust slightly more aluminium and its compounds was detected (Table 2).

The manufacturing process took place in all cases in an inert gas atmosphere, with the process air being internally recirculated. Nevertheless, it was possible on a few occasions to detect inhalable dust and aluminium and its compounds in the respirable and inhalable dust during the manufacturing process. A possible explanation is that some machines, owing to their age or intensity of maintenance, no longer close tightly and are operated in any case at slight overpressure. Another explanation could be that the leakage rates vary according to machine manufacturer and type. The post-process and other work steps such as powder analysis and full cleaning for a change of material were performed in some cases with and in some cases without encapsulation. In addition, the processing of the powder by screening, detaching the component from the platform and removing powder from the component (Figure 1) were performed in some cases with the metal powder exposed. The hazardous substance concentrations measured during these process steps strongly reflect the various technical activities and individual working methods. It is obvious here that measurements were performed in the shop conditions existing on site. For instance, the values for aluminium and its compounds in the inhalable dust range from 0.0076 to 0.17 mg/m^3 for the four measurements. The machines were also cleaned without additional dust extraction and, with a value of 072 mg/m^3 for inhalable dust and a value of 0.49 mg/m^3 for aluminium and its compounds in the inhalable dust fraction, showed the highest exposure of all. By contrast, powder analysis performed in most cases with only a few grams of powder yielded much lower values.

4.2 Alloyed steel

16 measurements were performed at machines processing alloyed steels (**Table 3**). The measure-ments covered different hazardous substances according to the composition of the steels, as was the case with aluminium-based metals. Neither respirable dust nor chromium(VI) compounds were detected at any of the process steps. For the metals that were detected, all the acceptance and tolerance concentrations were observed along with the OELs. The number of ultra-fine particles at a maximum of 5.1×10^4 particles/cm^3 was of a magnitude similar to the ambient air reference value.

Table 3:
Hazardous substance concentrations in the workplace air from the processing of alloyed steels.

Material: Alloyed steel			**Process step**		
Hazardous substance	**Limit value in mg/m³**		**Pre- and manufacturing process**	**Post-process**	**Powder analysis/Full cleaning/ Bystander**
Respirable dust	**1.25 (OEL)**	Number of values	4	7	2
		Measured value (mg/m³)	<0.25	<0.26	<0.33
Inhalable dust	**10 (OEL)**	Number of values	4	7	2
		Measured value (mg/m³)	<0.25	4 values <0.17 0.35 to 2.87	<0.31/5.32
Iron and compounds (I)		Number of values	4	4	3
		Measured value (mg/m³)	<0.00082/0.0015 bis 0.052	0.0053 bis 0.37	1.3/0.015/0.0011
Iron and compounds (R)		Number of values	5	4	3
		Measured value (mg/m³)	2 values <0.0012 0.0024/0.0094	0.0014 to 0.033	2 values <0.0021 0.0062
Chromium and compounds (I)	**2 (OEL)**	Number of values	6	6	3
		Measured value (mg/m³)	1 value <0.000078/ 0.00029 to 0.011	0.0011 to 0.1	0.00019/0.28/ 0.00019
Chromium (VI) (I)	**0.001 (AssC)**	Number of values	6	6	2
		Measured value (mg/m³)	<0.00027	<0.00028	<0.00036
Nickel and compounds (R)	**0.006 (OEL/AC/TC)*)**	Number of values	5	7	2
		Measured value (mg/m³)	3 values <0.00016 0.00022/ 0.00073	1 value <0.00015/ 0.00024 to 0.0059	<0.00025
Cobalt and compounds (R)	**0.0005 (AC) 0.005 (TC)**	Number of values	1	2	-
		Measured value (mg/m³)	<0.00016	0.0013/ 0.0016	-

Table 3: continued

Material: Alloyed steel			Process step		
Hazardous substance	**Limit value in mg/m³**		**Pre- and manufacturing process**	**Post-process**	**Powder analysis/Full cleaning/ Bystander**
Manganese and inorganic compounds (I)	**0.2 (OEL)**	Number of values	3	4	-
		Measured value (mg/m³)	0.00047/ 0.00053	0.0047	-
Ultrafine particles	**-**	Number of values	4	2	-
		Measured value (1/cm³)	$2.9 \cdot 10^4$ to $4.6 \cdot 10^4$	$1.4\ 10^4$ to $5.1 \cdot 10^4$	-
		Ambient air reference value (1/cm³)	$1.6 \cdot 10^4$ to $2.3 \cdot 10^4$	$7.7 \cdot 10^3$ to $3.7 \cdot 10^4$	

I = Inhalable dust fraction, OEL = Occupational Exposure Level to TRGS 900 [12], AssC = Assessment Criterion to TRGS 561 [13], R = Respirable dust fraction

*) Nickel metal is subject to an OEL. An acceptance and tolerance concentration (AC, TC) has been derived for carcinogenic nickel compounds.

Owing to the brevity of the work steps, it was not possible to distinguish between the pre- and manufacturing processes in the measurements presented in the following (**Tables 4** to **6**), as analysis of some of the metals contained in the alloy calls for a sampling time of more than two hours. For the pre- and manufacturing processes, the measured values for inhalable dust were below the detection limit. For iron and its compounds, the main component of the steels employed, the measured values were 0.0094 mg/m^3 maximum in the respirable fraction and 0.052 mg/m^3 maximum in the inhalable fraction. Nickel and its compounds – the third- and fourth-largest components in the metal powders employed, according to the manufacturer – achieve values of 0.00073 mg/m^3 maximum.

Of the work steps during the post-process and also others such as cleaning, some were performed with dust extraction or encapsulation and some were not, depending on shop conditions. This yields a broad spread in the measured values for these work steps. Overall, the measured values are generally higher than during manufacture. The values for iron and its compounds in the inhalable dust fraction, for example, range from 0.0053 to 1.3 mg/m^3. For nickel and its compounds, the concentrations range from below the quantification limit almost to the acceptance/tolerance concentration. This clearly demonstrates the effect on exposure levels of low-dust working methods, effective collection and properly adjusted mechanical ventilation.

Table 4:
Hazardous substance concentrations in the workplace air from the processing of nickel-based alloys.

Material: Nickel-based alloys			**Process step**		
Hazardous substance	**Limit value in mg/m³**		**Pre- and manufacturing process**	**Post-process**	**Analysis**
Respirable dust	**1.25 (OEL)**	Number of values	5	2	
		Measured value (mg/m³)	4 values <0.04 0.09	<0.26/0.32	
Inhalable dust	**10 (OEL)**	Number of values	5	1	1
		Measured value (mg/m³)	1 value <0.02 0.5 to 0.89	1.64	<0.04
Nickel and compounds (R)	**0.006 (OEL/AC/TC)*⁾**	Number of values	4	2	-
		Measured value (mg/m³)	1 value <0.00019 0.0003 to 0.012	0.018/0.019	-
Nickel and compounds (I)		Number of values	4	1	1
		Measured value (mg/m³)	0.00069 to 0.28	0.6	0.009
Cobalt and compounds (R)	**0.0005 (AC) 0.005 (TC)**	Number of values	3	2	1
		Measured value (mg/m³)	<0.00027	<0.00016/0.0002	0.000061
Manganese and inorganic compounds (I)	**0.2 (OEL)**	Number of values	3	1	-
		Measured value (mg/m³)	0.00011 to 0.0009	0.0026	-
Manganese and inorganic compounds (R)	**0.02 (OEL)**	Number of values	3	2	-
		Measured value (mg/m³)	<0.00027/ 0.000066/ 0.00009	<0.00016/0.0013	-
Chromium and compounds (I)	**2 (OEL)**	Number of values	3	1	1
		Measured value (mg/m³)	0.0026 to 0.1	0.21	0.0033
Cr(VI) (I)	**0.001 (AssC)**	Number of values	4	2	1
		Measured value (mg/m³)	<0.0006	<0.00027	<0.00027

I = Inhalable dust fraction, OEL = Occupational Exposure Limit to TRGS 900 [12], AssC= Assessment criterion to TRGS 561 [13], R = Respirable dust fraction

*⁾ Nickel metal is subject to an OEL. An acceptance and tolerance concentration (AC, TC) has been derived for carcinogenic nickel compounds.

Table 5:
Hazardous substance concentrations in the workplace air from the processing of titanium alloys.

Material: Titanium-based alloys			**Process step**	
Hazardous substance	**Limit value in mg/m³**		**Pre- and manufacturing prozess**	**Post process**
Respirable dust	**1.25 (OEL)**	Number of values	-	1
		Measured value (mg/m³)	-	<0.67
Inhalable dust	**10 (OEL)**	Number of values	1	-
		Measured value (mg/m³)	<0.06	-
Titanium and compounds (I)	**10 (LIL)**	Number of values	1	1
		Measured value (mg/m³)	0.0063	0.028

OEL = Occupational Exposure Limit (TRGS 900), LIL = Lowest International Limit value listed in the GESTIS list of international limit values for chemical substances

Table 6:
Hazardous substance concentrations in the workplace air from the processing of copper alloys.

Material: Copper-based alloys			**Process step**	
Hazardous substance	**Limit value in mg/m³**		**Pre- and manufacturing process**	**Post process**
Respirable dust (mg/m³)	**1.25 (OEL)**	Number of values	2	1
		Measured value (mg/m³)	<0.12/0.16	<0.33
Inhalable dust (mg/m³)	**10 (OEL)**	Number of values	2	1
		Measured value (mg/m³)	<0.13/0.33	3.13
Copper and compounds (R) (mg/m³)	**0.01 (MWC)**	Number of values	2	1
		Measured value (mg/m³)	0.0016/0.03	0.091
Nickel and compounds (R) (mg/m³)	**0.006 (OEL/AC/TC)*⁾**	Number of values	2	1
		Measured value (mg/m³)	<0.00057/0.0017	0.0014
Nickel and compounds (I) (mg/m³)		Number of values	2	1
		Measured value (mg/m³)	0.0023/0.02	0.0014

OEL = Occupational Exposure Limit (TRGS 900), MWC = Maximum Workplace Concentration (MAK) from the list of the DFG-MAK Commission

*⁾ Nickel metal is subject to an OEL. An acceptance and tolerance concentration (AC, TC) has been derived for carcinogenic nickel compounds.

4.3 Nickel-based alloys

On machines processing nickel-based alloys, eight measurements were carried out. In terms of inhalation exposure, these alloys are the most critical. For activities with carcinogenic nickel compounds or activities in which these arise, an acceptance and tolerance concentration of 0.006 mg/m³ in the respirable fraction is applied as the assessment criterion [13]. The powders described in this section always contained at least 50% nickel, which is possibly the reason why certain measurement results are above the acceptance and tolerance concentration. In none of the work steps chromium(VI) compounds were detected, although chromium was listed as an alloying component of the metal powders. The number of ultra-fine particles at 1.4 x 10^4 particles/cm^3 maximum was below the ambient air reference value.

Again because of the brevity of the work steps, it was not possible to distinguish between the pre- and manufacturing processes for nickel-based alloys. Although all the investigated work steps were performed encapsulated, the values vary a great deal. The four measured values for nickel and its compounds in the respirable dust fraction range from below the quantification limit to the twofold transgression of the acceptance/tolerance concentration. This suggests that the capture and encapsulation methods adopted were in some cases not sufficiently effective.

For the post-processes, the measured values were somewhat higher overall, as the work steps took place without effective capture devices. The acceptance/tolerance concentration for nickel and its compounds in the respirable dust fraction at 0.018 und 0.019 mg/m³ is exceeded. The acceptance concentration for cobalt and its compounds according to TRGS 561 and the assessment criteria for manganese and its compounds, chromium and its compounds and chromium(VI) compounds are complied with. However, cobalt and its compounds and manganese and its compounds were both detected in one of two measurements.

4.4 Other metal alloys

Results were obtained not only with metal powders based on aluminium, alloyed steels and nickel undergoing laser beam melting and laser deposition welding, but also with other alloys. For these applications only few measurement results are currently available, although these are to be presented here briefly for the sake of completeness.

An investigated machine processing titanium-based materials operated mainly in its open state, and only the screening and manufacturing processes were performed encapsulated. The OELs for respirable and inhalable dusts were complied with in this case (Table 5). For titanium and its compounds there is no substance-specific OEL, so reference was made to the lowest international limit value (LIL), which was also complied with.

The measurement programme also included a machine in which copper-based materials were processed by laser beam melting. No mechanical ventilation was installed in the machine's manufacturing chamber. Furthermore, the machine had been modified, which could explain why a significant quantity of process gases escaped from the machine into the environment during operation. This is indicated by an elevated respirable dust value compared to the other measurements in Tables 2 to 6. For one of two measured values, the assessment criterion (DFG maximum workplace concentration (MAK) value) for copper was exceeded during the pre- and manufacturing processes (Table 6). The value for nickel and its compounds in the respirable dust fraction was complied with. In the post-process work steps, work was performed for an extended period with open powder and in some cases without low-dust procedures – the value obtained here for copper and its compounds of 0.091 mg/m³ is a little higher still than in the pre- and manufacturing processes.

5 Protective measures and summary

Summing up, it can be said for the current state of the measurement programme that on the machines for laser beam melting and laser deposition welding investigated so far, no chromium(VI) compounds were detected in the workplace air when materials containing chromium were processed. In machines processing metal powders based on alloyed steels, and aluminium and titanium alloys, the assessment criteria were complied with. One reason for this is that the machines are usually operated with encapsulation or dust extraction in order to achieve the required product quality.

During the processing of nickel-based alloys, the results show that the measures implemented on the machines investigated to date are not yet sufficient. When such materials are processed, each work step is to be provided with hazardous substance capture devices, preferably directly at source. Before nickel-based alloys are processed, possible alternative materials should be considered (substitution).

Independently of the alloy employed, low-dust procedures must always be adopted [11; 14]. If this is ensured, respiratory protection is not necessary during steps in which powder and carcinogenic metals are not processed in their open state. When processing alloys of carcinogenic metals and their compounds, not only the minimisation requirement of the Hazardous Substances Ordinance, but also TRGS 910 [15] and the new version of TRGS 561 [13] are to be observed if these metals and their compounds have been detected in the air. As a basic principle when processing powder alloys in combination with hot surfaces, for example, fire and explosion risks are to be taken into account.

When working at the machines described, all employees must wear work and protective clothing. The work clothing is to be stored separately from street clothing and is to be cleaned by the employer to prevent adhering substances being carried over into the outside world. Furthermore, the valid occupational safety and health regulations are to be observed.

In this publication, the data so far available from the measurement programme have been evaluated for laser beam melting and laser deposition welding. A statistical evaluation is not yet possible owing to insufficient data. The strong spread in the measured values presented here shows that, as expected, individual working methods, installed capture systems and the ventilation situation in the enterprises concerned have a major effect on exposure. At present, many work steps in process preparation (pre-process) and post-treatment (post-process) are still performed manually. Growing automation of these processes as well will have a further effect on future exposure levels in the investigated work areas of additive manufacturing processes.

For this reason and as a database for the planned issuing of recommendations for the risk assessment of the German Social Accident Insurance Institutions, the measurement programme is being continued as an aid to entrepreneurs for risk assessment.

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Dr rer. nat. Renate Beisser, Dr rer. nat. Yvonne von Mering, Dipl.-Chem. Katrin Pitzke, Institute for Occupational Safety and Health of the German Social Accident Insurance (IFA), Sankt Augustin.

Martin Buxtrup, Dipl.-Ing. Ludger Hohenberger, German Social Accident Insurance Institution for the public sector in North-Rhine/Westphalia (UK NRW), Münster.

Dipl.-Ing. Dirk Fendler, German Social Accident Insurance Institution for the energy, textile, electrical and media products sectors (BG ETEM), Cologne.

Dipl.-Wirtsch.-Ing. Valentin Kazda, German Social Accident Insurance Institution for the energy, textile, electrical and media products sectors (BG ETEM), Wiesbaden.

Dr Heike Niemann, German Social Accident Insurance Institution for the public sector in Schleswig-Holstein and Hamburg, Hamburg.

Dipl.-Ing. (FH) Roman Weiss, German Social Accident Insurance Institution for the woodworking and metalworking industries (BGHM), Mainz.