Picosecond and Femtosecond Laser Machining May Cause Health Risks Related to Nanoparticle Emission

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It is well known that nanoparticles are generated as by-products during ultrashort-pulsed laser ablation. Airborne nanoparticulate matter is well known as potential health risk when workers are exposed during operation of laser machinery. In order to provide safety-related statements on nanoparticles generated during laser micromachining, we studied the particle size distribution during picosecond (ps) and femtosecond (fs) laser ablation. At the same pulse energy, fs pulses release similar share of nanoparticles (>80%) in the aerosol fraction, with fs compared to ps generating a far higher share 7 nm sized particles during machining of metals (steel, brass) and ceramics (zirconia). These nanoparticles sampled at the workplace have the same chemical composition than the ablated material (iron-chromium-nickel alloy, yttria-doped zirconia). A quantitative risk assessment is carried and compared with indicators of toxicological effects of inhaled nanoparticles. The surface equivalent of the nanoparticles dispersed in the air of the workplace is not likely to exceed the surface dose which cause inflammatory response in animal lung. But within one 8 h shift, the background level is exceeded by a factor of 20 so that efficient fume extraction is strongly recommended for safe operation during fs and pf laser micromachining even in research laboratories.

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1. Introduction

It is well known that the fume produced during pulsed laser ablation, for example during the structuring of ceramic micromolds, contains a significant nanoparticulate share [1-6]. Results on the influence of laser parameters on the particle size distributions using fs laser pulses have already been presented [7, 8]. The mass rate and relative concentration of nanoparticle emission is influenced by the laser parameters as well, including pulse duration and pulse overlap [9], and may rise to 99% of the total particulate emission for shorter laser pulses [4]. Currently there are only few data on the parameters influencing the generation of nanoparticles during ultrashort pulsed laser ablation even if the release of these inhalable particles may constitute a strong health risk.

Clearly, the potential health risk will rise with increasing personal exposure levels; and these levels will depend on a variety of parameters including air exchange and workplace conditions. Personal exposure levels are usually described by the mass rate, although toxicological studies indicate that the adverse health effects of nanoparticles deposited to the lung depend on their number concentration and specific surface area. For example, instillation of different ultrafine particles indicates a surface area threshold dose for acute lung inflammation in mice [10] and that nanoparticle surface areas (or its related number counts) should be considered for inhalation toxicology discussion more likely than the inhaled particle mass.

In consequence, we investigated the particulate emissions during femtosecond and picosecond laser micromachining and studies the particle sizes and particle number frequencies released from the respective process. In order derive recommendations for laser users, we investigated the typical range of applied laser parameters and materials (steel, brass, zirconia) more likely than working under artificial ideal conditions. Based on these findings, the acquired emission rates of airborne particles with a size smaller than 100 nm are used for calculation of nanoparticle surface emission rates. The comparison of these emission rates with thresholds of inflammatory response and calculation of virtual workplace concentrations shall help to determine the overall health risk level.

2. Experimental

The experimental setup is shown in Fig. 1. A constant volume flow of 10 l/min is used to capture the fumes released above the workpiece within the half-open laser ablation chamber. The aerodynamic particle size is acquired using en electrical online low-pressure cascade impactor (ELPI, Dekati, Finland). This device determines the particle size distribution in the range of 7 nm to 4 μm once per second. More details on the setup can be found elsewhere [7].

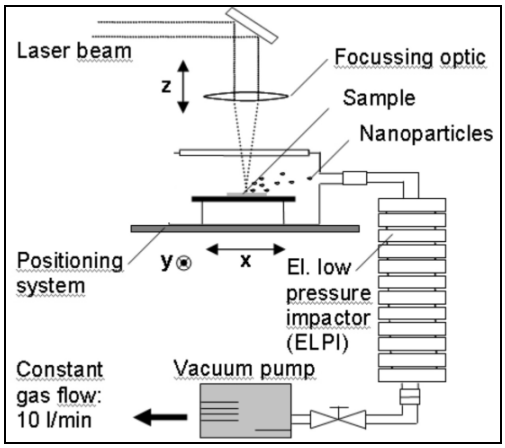

Fig.1 Experimental setup and principle of aerosol sampling using cascade impaction

3. Results

Most amplified femtosecond lasers have lower repetition rates than picosecond lasers have different because of the different laser concepts. In consequence, it is impossible to realize same average laser power and pulse energy at the same time. Since it is known that the pulse energy may strongly affects the particle size [4,9], same pulse energies were used for comparison of the size distributions.

Fig. 2 shows the particle size distribution of particle emission during the laser ablation of steel, zirconia and brass using an ultrashort pulsed (fs) laser. The curves display a monomodal distribution with a share of nanoparticles in the particulate matter of more than 80% for all three materials. The frequency maximum is located at 50nm with a share of approximately 35%. There is a significant amount in the frequency of nanoparticles with an ultrafine aerodynamic diameter of 7 nm (brass: 16%, steel: 10%, Zirconia 6%).

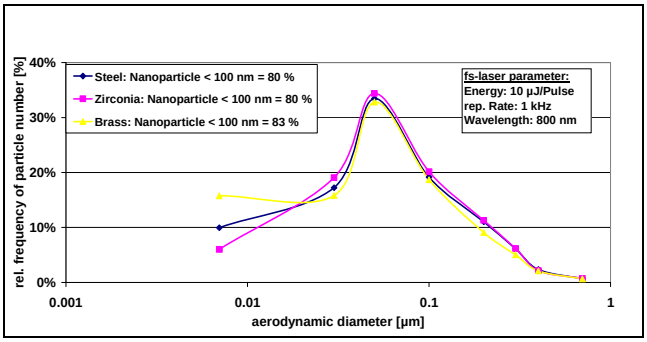

Fig.2 Particle size distribution during fs-laser ablation (10µJ) of steel, brass and zirconia

less amount of the 7 nm particle fraction and a higher share of 50 nm sized particles are emitted. This is in agreement with previous studies on pulse duration effects on the particle size, where longer laser-matter-interaction time regimes (continuous wave and ns compared to fs) caused a shift of the particle size distribution to bigger values [7].

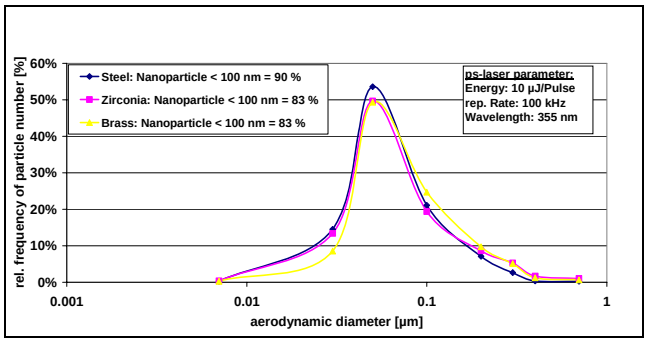

Fig.3 Particle size distribution during ps-laser ablation (10µJ) of steel, brass and zirconia

If only the nanoparticulate fraction (which are particles smaller than 100 nm) is considered, the results show that at the same pulse energy of 10µJ the amount of nanoparticles generate from fs and ps laser processing are in the same order of magnitude (2-3 * 10^6 particles per second).

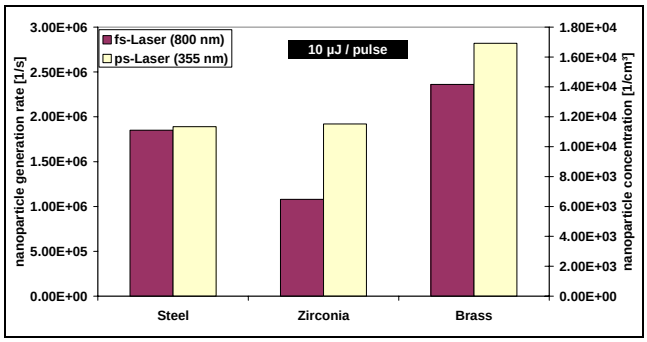

Fig.4 Nanoparticle number concentration (< 100 nm) and generation rate during fs- and ps-laser ablation of steel, zirconia and brass

Because a summary parameter is considered in Fig. 4, the difference in the emission rates of the 7 nm particles is averaged with the different share of 50 nm particles. If particles with sizes from 7 to 100 nm are compared, no significant differences are observed in dependence from the type of laser and processed materials steel, zirconia and brass.

It has to be pointed out that the laser ablation has been carried out at the same pulse energy but at 100 times higher laser power for the picosecond laser having far higher repetition rate (100 kHz) compared to the fs laser (1 kHz).

Within the laser power range of 0.01-0.5 Watt (fs) or 0.5-2 W (ps), tab. 1 shows a summary of the measured results for both laser systems and three different materials processed. Nanoparticles generated during ultrashort pulsed laser machining have been found to be mainly spherical, so that their nanoparticle surface area equivalent given in Tab. 1 is calculated based on the measured particle size distribution.

Tab.1 Nanoparticle number emission rates and its particle surface equivalent for the typical range of laser parameters during ps and fs laser micromachining.
Materials: steel, brass, zirconia

Laser	femtosecond	picosecond	
Wavelength	800	355	nm
Pulse Energy	10 – 500	5 – 20	µJ
Power	0.01 – 0.5	0.5 – 2	W
Repetition Rate	1	100	kHz
Nanoparticle Number Emission Rate	1.1 – 8.0	0.9 – 2.8	10^6/s
Nanoparticle Surface Emission Equivalent (Brass)	2.4 – 2.9	1.2 – 4.6	10^{-4} cm²/s

Despite the particle emission rate, the particle composition is an important factor for the determination of the health risks during exposure to these particles and their possible inhalation. In the case of ablating stainless steel it would make a difference if the nanoparticulate fraction contains still the highly toxic chromium originating from the machined iron-chromium-nickel alloy.

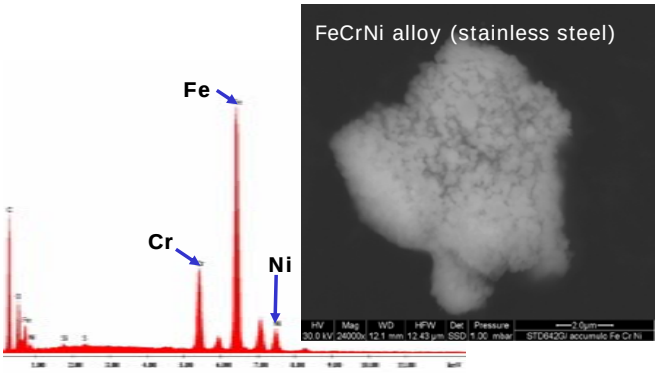

Fig.5 Chemical composition and morphology of representative nanoparticle aggregate sampled at the laser machining workplace during fs laser ablation of stainless steel. Left: electron dispersive X-ray analysis. Right: transmission electron microscope image

Using Energy Dispersive X-ray analysis (EDS by EDAX , USA) and scanning electron microscopy (Field Emission Gun Environmental Scanning Electron microscopy, FEG Quanta, Fei Company, the Netherlands), the chemical composition and morphology of nanoparticles sampled at the laser machining workplace during fs laser ablation of Zirconia and stainless steel is studied. The results for stainless steel and yttria oxide stabilised zirconium dioxide (Y-TZP Zirconia) are shown in Fig. 5 and 6. The EDX spectra clearly show that the nanoparticles released during ultrashort-pulsed laser ablation still contain the chemical elements of which the processed bulk material is made of. This is an important finding since it means that Threshold Limit Values (TLV) given in standards and regulations are applicable referring to the respective substances.

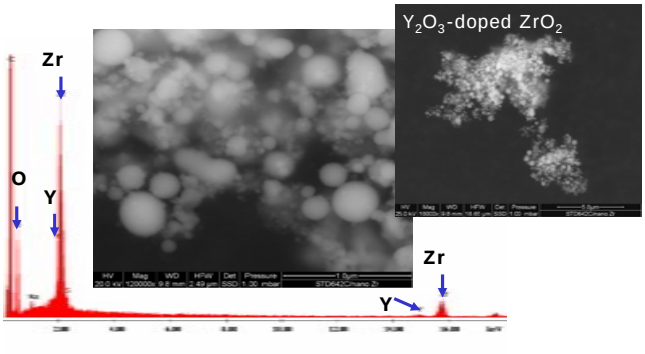

Fig.6a Chemical composition and morphology of representative nanoparticle aggregate sampled at the laser machining workplace during fs laser ablation of yttria-stabilized zirconia. Left: electron dispersive X-ray analysis. Right: transmission electron microscope image

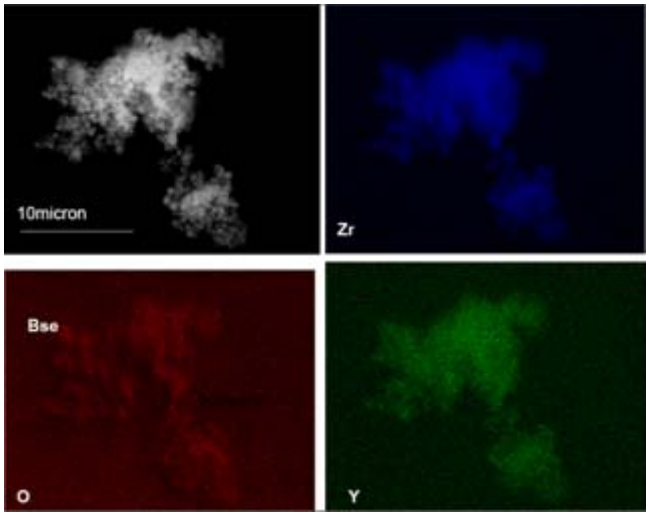

Fig.6b Chemical composition of representative nanoparticle aggregate sampled at the laser machining workplace during fs laser ablation of yttria-stabilized zirconia analysed in the TEM by electron energy loss spectroscopy.

4. Risk assessment

In view of the relatively high fraction of nanoparticles in the fume produced during laser ablation, safety-related statements regarding exposure levels are required, particularly for occupational safety. To provide quantitative statements, a simple geometric model from former studies [7] is used which is summarized in figure 7.

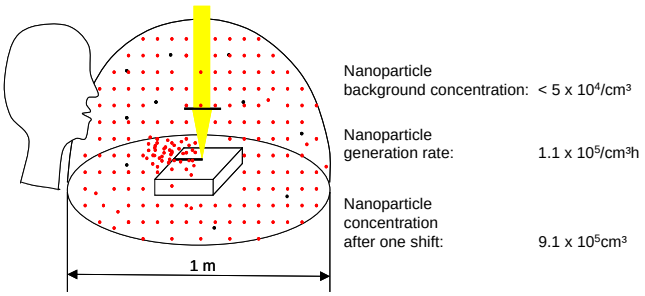

Fig.7 Geometric model for the assessment of the exposure levels of nanoparticles during fs-laser ablation of brass (500µJ, 1 kHz at 800 nm)

The model compares the potential nanoparticle exposure level to the background exposure level (1 - 5 x 10^4 cm^3) for a person (the laser operator) within 0.5 m distance from the laser ablation process. Taking a worst case scenario (processing brass, fs-pulsed with 500µJ/pulse), a nanoparticle generation rate of 8 x 10^6 s^{-1} for fs laser ablation and 3 x 10^6 s^{-1} for ps-laser ablation was measured. The results of the simplified calculation is that the rate of increase in nanoparticle concentration, assuming that all released nanoparticles are contained within a 0.5 m radius hemisphere is in the range of the background level after 1 minute, rising to up to 20 times the background level after an 8 hour shift of continuous fs-laser operation (500 µJ, 1 kHz). For ps-laser ablation, the amount of laser generated nanoparticle concentration within the model hemisphere is calculated in dependence of the laser power (pulse energy 5-20µJ at 100 kHz). Fig.7 shows that the nanoparticle concentration (based on particle number measurements) increases by a factor of 3 when the laser power is increased by a factor of 4. Obviously, higher laser power (pulse energy) leads to higher emission rates, but to a lower share of nanoparticles within the aerosol fraction. At higher power, higher concentrations of clusters are ejected from the material. At higher concentrations, the probability of coalescence and agglomeration leading to particle growth is higher, so that over all a higher ablation rate but lower share of small particles are detected at the ELPI..

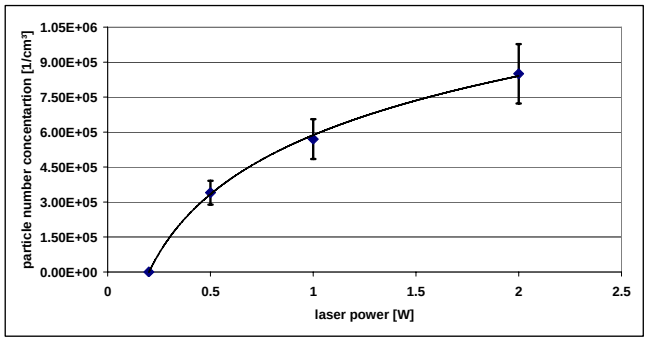

Fig.8 Particle number concentration (in a 1 meter diameter hemisphere) during ps-laser ablation of steel as function of laser power

After one shift, the concentration level close to the operator reaches 10^5 - 10^6 nanoparticles per cm^3. In detail, this amounts to 9.1 x 10^5 for fs-laser machining at 0.5 W and 3.2 - 8.5 x 10^5 for ps-laser machining with 0.5 - 2 W laser power.

In the investigated range, picosecond laser micromachining releases less nanoparticles than femtosecond laser machining if working at the same power (0.5 W), but still in the same order of magnitude.

At 2 W ps-laser power, the nanoparticles emission rates are the comparable to those from 0.5 watt femtosecond laser machining. In the following, we consider the data from 500 µJ (0.5 W) fs-laser machining as reference.

5. Comparison with toxicological data

At the example of processing brass (worst-case) it can be calculated that the specific surface area of the nanoparticles generated during ultrashort-pulsed laser ablation is 1 cm^2/h or 8 cm^2 per shift. In consideration of lung clearance rates (50%-93%) and typical deposition rates (50% in the alveoli region for particles < 100 nm) [10-12] we assume a surface area of the minimum biopersistent share of nanoparticles in the lung of about 2 cm^2 per working day.

Toxicological studies have determined that the threshold value of inflammatory responses where below the threshold of 20-200 cm^2/cm^2 (nanoparticle surface per lung surface) lung there is no reaction in rats and the threshold of pulmonary inflammation is 10 cm^2 per g lung tissue [10,11,12].

Comparing these data to the results of our simplified model it appears that the amount of released nanoparticles is negligible in terms of toxicological thresholds for a one hour process. Even if the comparison of the animal model with human lung should be considered with care since different inflammatory mechanisms take place, it could contribute to a first estimation of the risk level. For the human lung having a total mass of about 1,300 g in adults, the inflammatory threshold for rats (the threshold relevant to human lung is still undefined) is equivalent to 13.000 cm^2 nanoparticle surface. Considering that 2 cm^2 per day is the biopersistent surface equivalent, 6.500 days of inhalation of 100% of the nanoparticle emissions would be required during ultrashort-pulsed laser operation at 0.5-2 W laser power.

If high-power ps-laser systems available today with an output power up to 50 W are considered and the nanoparticle emission rate would correlate linear with power, still 1 year (260 working days) of inhalation is required in theory to exceed a nanoparticle surface dose which is equivalent to the biopersistent fraction causing inflammatory response in rats.

Tab.2 Emission Mass rates, Theshold Limit Value at workplace (TLV), Nominal Hygienic Air Requirement Limit Value (NHL) and required Air Exchange Rate in a 50 m^3 laser lab. Calculations for the typical range of laser parameters during ps and fs laser micromachining of steel, brass, zirconia

	Emission Mass Rate m_E [mg/h]	**TLV [mg/m³]**	**NHL [m³/h]** (= m_E/TLV)	**Air Exchange Rate [1/h]** (=NHL/50m³)
Femtosecond-Laser (10-500 µJ; 0.01-0.5 W)				
Brass	10 – 100	20	0.5 – 5	0.01 – 0.1
Steel	10 – 100	1	10 – 100	0.2 – 2
Zirconia	~30	1	33	0.7
Picosecond-Laser (5-20 µJ; 0.5-2 W)				
Brass	10 – 50	20	0.5 – 2.5	0.01 – 0.05
Steel	10 – 50	1	10 - 50	0.2 – 1
Zirconia	50-100	1	50-100	1-2

Despite the number and surface of nanoparticulate emissions, the aerosol emission mass rate has to be consid-

ered for safety-related statements. The range of particulate emission mass rates (m_E) are compared to the threshold limit values (TLV) at the workplace (example: Germany) in Tab. 2. Dividing m_E by the respective TLV gives a value for the volume flow of clean air that would have to be continuously fed to the emission source to dilute the emissions so that the TLV is not reached. This value is called the Nominal Hygienic Air Requirement Limit Value (NHL) and can be used to calculate the required air exchange rate for a given workplace. At the example of typical laser lab with a volume of 50 m³, this rate is smaller than $2h^{-1}$, meaning that the air in the room has to be exchanged with clean air 2 times per hour. This requirement can be easily fulfilled with standard ventilation systems, even if air exchange is costly, especially in climate rooms. Of course, if a share of the emissions are captured (e.g. 90%) close to its source, far lower air exchange rates ($0.2\ h^{-1}$) are required, saving costs.

Finally, it has to be pointed out that there are still no data available on toxicological effects of inhaled laser generated nanoparticles, especially their long-term adverse health. Therefore, whilst recognising that there are currently no international or even national guidelines on precautions mandatory during pulsed laser ablation, the authors recommend full closing of the laser machine and efficient fume extraction, in particular during ultrashort laser ablation.

6. Conclusions

Nanoparticles can the found in pathologic tissues and are known to cause adverse health effects [14]. These effects are even worse if the aerosols are inhaled by persons having respiratory or heart disease. It has been shown that the mortality of these persons increases by 2.7 % (0.8-8%) per 10 µg/cm³ increase of concentration of fine particles [15].

But the generation of nanoparticle cannot be avoided during laser ablation, especially ultrashort-pulsed laser ablation which releases a higher share of nanoparticles than ns-pulsed or cw laser ablation. generation during laser processing depends strongly on the used parameters (pulse energy, wavelength etc.).

Comparing the nanoparticle emission rates and its nanoparticle surface equivalent for ps- and fs-laser micromachining of steel, brass and Zirconia with inflammatory thresholds, one may conclude that these thresholds are not likely to be exceeded in standard operation. By calculation, it would take more than 6.500 working days to exceed this threshold during laser operation at 0.5-2W. Even with ultrashort-pulsed high-power lasers available today, 260 working days are required to exceed this theoretical threshold of inflammation.

Even if the mechanisms of nanoparticle toxicity are not fully understood, a main factor seems to be the effective surface area (besides solubility, reactivity). Despite these findings, threshold limit values TLVs are given only for the mass concentration of particles, not related to the number or surface of the contaminants. Even if there are still more data required on nanoparticulate emissions during ultrashort-pulsed laser machining, we have estimated the required air exchange rates in a 50 m³ laser lab to be less than $2h^{-1}$.which can easily be realized by available ventilation systems. The cost of ventilation can be drastically minimized if the emissions are captured at its source.

In addition, we have shown for the first time that the nanoparticles released during ultrashort-pulsed laser machining may have the same chemical composition than the ablated material (e.g. Iron-Chromium-Nickel alloy). Since these alloys may be higher soluble and reactive than its less reactive counterparts like elemental oxides, toxicity studies on these laser generated particles should be carried out in the next future in vitro and in vivo.

In consequence, a safe operation of ultrashort-pulsed laser machinery is possible, in particular if the risks are known and released fumes are considered with care.

Due to geometric limitations of the experimental setup in research labs, add-on fume extraction systems are often the only acceptable emission capturement technique. Such state-of-the-art fume extraction technologies are capable to capture more than 90% of the fumes to the machinery. Even better, full housing of the laser machinery would prevent the release of nanoparticle to the workplace. The latter should be obligatory during industrial ultrashort-.pulsed laser machining.

Finally, one has to consider the release of the fumes to the environment. Often, the question arises if standard waste gas filtration techniques are adequate to filter airborne nanoparticles. In our case, it is advantageous that the filtration efficiency is lowest in the meso-scale (300 nm), bigger or smaller particles are filtered with higher efficiency. At bigger sizes the impaction efficiency is higher and at smaller particle sizes, diffusion effects rise [16]. In consequence, filtering nanoparticles (particulate matter < 100 nm) can be realized by state-of-the-art filters, like high efficiency particulate air (HEPA) filters.

Acknowledgments

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