Laser micro sintering of SiO$_2$ with an NIR-Laser

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ABSTRACT

Many materials have already been investigated for laser micro sintering. Nearly all technical metals can be processed with this rapid prototyping technology. A new field of investigation is the sintering of ceramics.

For industrial and also for medical, especially dental, application silicon dioxide is a multiply applicable material. One of its interesting features is that the properties of the resulting material can be varied between ceramic on the one and vitreous on the other side, depending on the extent of crystalline or amorphous character of the nano-scale structure. A special problem with laser micro sintering of ceramics is the poor absorption of Nd:YAG laser radiation by most of the materials. Besides that, laser micro sintering of ceramics, in contrary to the process with metals, is not merely a series of aggregational transitions.

A solution for the micro part generation of SiO$_2$ is reported. Typical laser sintering results from this material are presented. Material specific behaviors during laser micro sintering are discussed.

Keywords: laser micro sintering, fused silica, powder

1. INTRODUCTION

1.1 Laser micro sintering – mechanism and preferable beam source

In the year 2002 laser micro sintering, a modification of selective laser sintering, was developed by Laserinstitut Mittelsachsen e.V.$^1,2$. Following its successful application to generate metal micro parts, the technology is presently carried forward to process non-metal materials. The current area of interest has been the group of oxide and non-oxide ceramics especially those of practical concern.

In 2006 the successful fabrication by laser micro sintering was reported of bodies with a high structural resolution from a ceramic blend of alumina and silica. The sintering of the material is accomplished through laser radiation in a pulsed wave regime. Wavelengths of the employed lasers are in the near infrared, in the visible or in the near UV spectral range$^3$.

Since 2005, SiC, a typical non-oxide ceramic material was processed with the ends of highly resolved thermo-stable and abrasion resistant micro-bodies. Recently the first specimens with high accuracy were generated from silicon blended SiC as well as from the technically pure material$^4$.

According to a detailed report on the possible mechanism of laser micro sintering$^5$ in the case of metal powders, the mechanism relies on the condensation and fusion of the heated material upon the impact of short and intensive laser pulses (pulses from a $q$-switched laser). The process is supported by a rapidly expanding plasma and/or vapor bulb arising from each impact. The suitable wavelength range for laser micro sintering has been the near infrared (NIR) region since Nd:YAG lasers are available in high diversity, and there is no difficulty to acquire a beam source that yields the optimum parameters for any process. Additionally, metals absorb the NIR-radiation to a sufficient extent.

This is different in the case of ceramic materials: As typical for dielectrics, direct absorption of NIR-radiation is not possible. Either radiation with higher quantum energy is required or an intensity of the beam that provides a sufficiently high probability of two-photon excitation events. Furthermore, in contrast to metals, dissociation of the material has to be dealt with in the course of the process, in the case of SiC even without the transition through a liquid phase$^6$.

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1.2 Laser micro sintering of silicon monoxide

The application of silicon monoxide (SiO) offers the chance to generate ceramic or vitreous silica micro parts with an NIR-laser. Preliminary experiments showed that the material absorbs radiation of the respective spectral range sufficiently for laser processing. There are obviously two known modifications of solid SiO, the graphite-like type and another one that is usually referred as amorphous SiO. The latter one was used for the laser sintering experiments described in the following chapters. Various suggestions have been made on the real nature of this material6-11.

The expected reaction as a result of laser irradiation is oxidation and fusion (1); but also disproportioning (2) will take place.

\[
2\text{SiO} + O_2 \rightarrow 2\text{SiO}_2 \quad \text{(1)}
\]
\[
2\text{SiO} \rightarrow \text{SiO}_2 + \text{Si} \quad \text{(2)}
\]

Although the oxidation reaction would be the most favorable for a generative technique, its probability is limited because of the relatively short process time laser micro sintering that will allow only partial rearrangement of the solid structure.

Because of the reactive nature of the generative process laser micro sintering of SiO could be the first example of highly resolved selective laser reaction sintering.

2. EXPERIMENTAL

2.1 Experimental setup

The beam of an Nd:YAG laser (λ=1064nm) operated in mono-mode with a maximum power of 20 Watt is directed onto the mirror of a galvanometer scanner (Fig.1). An acousto-optical modulator positioned in the optical path between the laser and the scanner works as a fast on/off switch for the beam. The galvanometer scanner allows for the rapid navigation of the beam, which is focused by a plane field (F-theta) lens. For most of the experiments, a lens with a relatively short focal length of 100mm was preferred, because the achievable focus diameter provided sufficient intensity of the incident radiation. With a 100mm lens 1064nm radiation can be focused onto a spot with a radius below 20µm, depending on the diameter \(w_0\) of the unfocused beam and the \(M^2\) factor of the laser. The focused beam irradiates selectively the powder coating on the probe according to the cross section of the expected product. If the chamber is operated under a defined atmosphere the lid is closed and the laser beam enters via a window.

![Fig. 1: Schematic of the experimental setup](image1)

![Fig. 2: Schematic of sinter chamber](image2)
The powder is coated onto the probe via one or more cylindrical blades which are moving with a circular type of motion across the coating platform (Fig.2) depositing a new layer on the substrate whenever a coating cylinder traverses the probe. The cylinder blades are swung by levers that are attached to the axels of the coating drives. During a lengthy sintering procedure these coating blades are refilled with powder at certain intervals through cut-outs in the coating platform via their respective powder pistons. In the type of sinter chamber described in Fig. 2 the cut-out for the probe piston is positioned in the centre of the coating stage. The positioning drive of this piston has a denoted accuracy of 0.1µm. The profile of the ‘edge’ of the cylinder blade is shaped according to the specific needs of the powder materials.

For processes that require vacuum and defined reaction atmospheres, the chamber can be evacuated by a combination of two vacuum pumps. A sliding vane rotary pump produces a fine vacuum. To attain high vacuum a downstream turbo molecular pump is activated. The achievable vacuum is $10^{-5}$mbar.

### 2.2 Powder specification

The applied powder material (Patinal) was purchased from Merck KGaA (Darmstadt, Germany), it is of the type demoted as amorphous SiO, has a reddish brown colour and consists of <45µm grains. SEM views are shown in Fig. 3.

![SEM views of the applied silicon monoxide powder](Image)

Fig. 3: The applied silicon monoxide powder (Patinal, Merck). The particle diameters vary between 50µm and below 2µm. The grains seem to be not agglomerated.

The material properties of the SiO-powder according to the producer’s information are compared with the respective figures for SiO$_2$ in Tab. 1.

<table>
<thead>
<tr>
<th>Properties</th>
<th>SiO (20 °C)</th>
<th>SiO$_2$ (20 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>2.13 g/cm$^3$</td>
<td>2.32 g/cm$^3$</td>
</tr>
<tr>
<td>Molar mass</td>
<td>44.09 g/mol</td>
<td>60.08 g/mol</td>
</tr>
<tr>
<td>Melting temperature</td>
<td>1702 °C</td>
<td>1723 °C</td>
</tr>
<tr>
<td>Vaporization temperature</td>
<td>1880 °C</td>
<td>2230 °C</td>
</tr>
</tbody>
</table>

### 2.3 Laser sinter regime

The specimens were sintered in steps of 1µm thick sinter layers. As a beam source a 20W fibre laser (1064nm) was operated in mono-mode. The powder was irradiated with q-switched pulses at a repetition frequency of 80kHz. The beam is focused with a 100mm lens yielding a waist diameter of 30µm. Some probes were oven sintered at 1600°C in an additional final step. The following results have been obtained from experiments under environmental atmosphere to allow for oxidation during laser and oven sintering.
3. RESULTS

3.1 Assessment of the sintered compound

With the described laser regime cylindrical specimens with a diameter of 3mm (Fig. 4 a) were generated by line-wise scanning the laser beam across the powder layer. The cores of the cylinders seem to be, at least partially, oxidized. It is detectable, that the mantle consists of an attachment of only partially solidified powder (Fig. 4 b) that has never been irradiated by the laser beam. This attachment is not easily removable. Parts of the powder attachments even exist after cleaning in hydrofluoric acid (Fig. 4 c). The acid treatment allows a view upon the internal structure of the sintered part. The material of the specimens seems to be fused mainly horizontally with few and weak interconnections between the layers. Also, darker areas are observable and can be an evidence for insufficient oxidation of the silicon monoxide material. Investigations about the pressure strength on specimens like this show that the resulting density of the parts is very low. The pressure strength is about 40MPa compared to 1000MPa of the bulk material.

3.2 Partition sintering and oven treatment

Better results were achieved by using a sinter regime that stepwise heats small partitions of the powder bed over a defined time. This strategy allows controllable heating and simultaneous fusion of the powder in the respective volumes. A specimen generated by this regime is shown in Fig. 5a. The mentioned regime of sintering the powder layer by successively fusing defined partitions of the material is clearly visible. During an additional oven process the specimen brightens considerably (Fig. 5b). Also the cut-ins between the separately sintered subunits that are still visible after laser sintering are smoothed. The pressure strength increases and reaches 300MPa after the heat treatment. Fig. 6 shows SEM views of two specimens’ microstructure before and after the oven treatment. It is observable that there are no significant differences in the microstructures except for a conversion of
crystalline into amorphous components during oven sintering. Obviously the fine crystalline particles have been fused with the amorphous material.

In order to avoid the oven treatment, assays were made to increase the amount of amorphous material already in the laser sinter process by successively raising the average power of the radiation up to as far as 14W. Fig. 7 shows a specimen produced with these parameters. Amorphous morphology was obtained but the resolution and the accuracy decreased considerably. The material consists of solidified bubbles (Fig. 7b) and the obtained body shows low pressure strength.

3.3 Generation of highly resolved micro parts

The sintering assays showed that there are two possible ways for laser micro sintering of SiO to obtain bodies with highly resolved geometries. The first way is to choose a strategy that yields completely oxidized specimens (Fig. 8). These show a high resolution and accuracy but a relatively poor density. A view at the surface shows that the sintered layer consists of solidified material as well as decomposition products (Fig. 8). Also the typical brown attachment of partially solidified powder is detectable along the outline. The second way is to irradiate the powder with a low fluence (energy per area). By this way only weakly solidified specimens are obtained, although with a detectably higher density than the aforementioned type. The density and pressure strength is further increased by a following heat treatment (Fig. 8b). These micro parts show very fine geometric details and are much denser. Presently these properties are obtained at the expense of the fidelity due to the considerable shrinkage (in the order of 10%) during the oven process.
4. DISCUSSION

4.1 Background considerations of the sinter reaction

According to eqs. (1) and (2) during laser processing of SiO two principle reaction paths are conceivable: disproportioning and oxidation. There exist no reports no reports if SiO₂ is produced by reaction of environmental oxygen with Si (subsequent to disproportioning of SiO) or if SiO is oxidized directly by environmental oxygen. Both cases are conceivable during a laser sintering process. Recent findings¹² support the assumption, that oxidation of the solid material regards the reaction of the decomposition product i.e. silicon. It is generally accepted that when heated above 900°C disproportioning of SiO takes place at a rate that after ten seconds 80% of the material is transformed. Other researchers mention a reaction time in the order of hours for the completion of disproportioning¹¹ though this is obviously a period the material needs to reach final modifications of the products Si and SiO₂. In the same temperature range the vapor pressure of SiO is around 1.3Pa which means that at the onset of disproportioning also noticeable evaporation of molecular SiO will start. This should be the specie that is directly oxidized in an oxygen containing environment, meaning that it has to re-precipitate to contribute to the solid body.

From the above consideration based on current knowledge, it is evident that the discussion of the results has to be kept close to a phenomenological description, to avoid over interpretation.

4.2 Comprehensive survey of the sinter results

Line-wise laser sintering of SiO results in a body with a very low density and poor pressure strength. Optical appearance and evaluation of ESEM views suggest that the resulting compound consists of silica, silicon and un-decomposed silicon monoxide. The generated structures are clearly brighter due to a fine crystalline texture. Additionally, under the microscopic view an amorphous like texture is observable. Principally the same material composition is obtained when the sintering strategy is altered so that the laser irradiates small volume partitions of the powder, allowing simultaneous heating and fusion of the respective material in each of the entities.

Considerable gain in density and can pressure strength be achieved by a final oven sintering process. ESEM views show that the amorphous entities within the body fuse together. It also can be assumed that one of the effects of the oven treatment is a higher degree of segregation of silicon and silica in the compound fraction that consists of disproportioned SiO. Assays to accomplish the fusion of amorphous phases already in the laser sinter process resulted in a glassy but porous and brittle consistence of the sintered body. Presently oven treatment seems to be indispensable.

4.3 Compromises for high geometric resolution

The highest geometric resolutions are achieved with a laser micro sintering regime, that yields a very brittle body with a, nevertheless, fair relative density. During the following oven sintering process density and firmness of the part is enhanced considerably. Shrinkage of around 10%, however, deteriorates the process fidelity.

4.4 Reaction sintering in the absence of oxygen

After the above presented results the question arose if the solidification of SiO powder is also possible by mere disproportioning of silicon monoxide.

First preliminary laser sinter experiments in the absence of oxygen yielded a solid body of a relatively high firmness. As only little information regarding material properties and no analytical results of this compound are available yet, contemplations on the type of reaction or the composition of the resulting solid would be premature. Presently Figs. 9 show photographs of a fracture surface of a laser sintered specimen.
5. SUMMARY AND OUTLOOK

From SiO powder micro-parts with a high geometric resolution can be generated. Presently, due to the need of an additional oven sintering process, the fidelity of the technique does not suffice yet the requirements of precision micro-production. Presumptions that the character of the process is “reaction sintering” could be verified by the experimental observations, although the exact nature of the material conversion is still unclear.

The latest experiments have shown that reaction sintered solid bodies from SiO with better material qualities can possibly be obtained in oxygen free or oxygen reduced environment. The composition of the compound has not been defined yet. Only the results of preliminary assays are available presently at the moment. Therefore research activities in the immediate future will deal with the potential of this reaction regime.

6. APPRECIATIONS

The presented experiments have been conducted in the course of the project, ‘INNOPROFILE – Rapid Microtooling mit laserbasierten Verfahren’ funded by the German ‘Bundesministerium für Bildung und Forschung’ respectively.

Fig. 10: a) High density sintered material under inert atmosphere. b) Material sintered under environmental atmosphere.
REFERENCES