

PROCESSING OF SILICON CARBIDE BY LASER MICRO SINTERING

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Abstract

Silicon carbide – a solid with covalent bonds - is conventionally synthesized via the Acheson process. Usually solid bodies of silicon carbide with definite shapes are generated from the grained material via hot isostatic pressing or liquid phase sintering. Both processes are conducted under well-controlled temperature regimes. Applying the freeform fabrication technique “Laser Micro Sintering” poses a big challenge to experimental skill due to the non-equilibrium conditions that are characteristic features of laser material processing.

Successive layers SiC layers with a thickness of 1µm were processed with coherent radiation of 1064 nm. The specific behavior of two different silicon carbide powders - one of them blended with additives - are reported along with interpretational approaches.

Introduction

In the year 2002 selective laser micro sintering was developed by the Laserinstitut Mittelsachsen e.V. [1]. It is a modification of selective laser sintering and has been successfully employed, since, to generate metal micro parts. As part of the proliferation, the technology is presently carried forward to process non-metal materials. The current area of interest is the group of oxide and non-oxide ceramics especially those of practical concern.

Because of its hardness as well as its heat and corrosion resistance silicon carbide is still of high importance in modern tool making. Except for wafer production, where single crystalline samples are generated by CVD-processes, technical silicon carbide up to now is synthesized via the Acheson process. This has not principally changed since its implementation in 1892. From the lumpy or grainy solid thus gained, the generation of shaped SiC tools cannot be accomplished by conventional sintering of the pure material as it lacks a liquid phase under ambient pressure. Therefore shaped bodies for mechanical engineering purposes – especially when high structural resolution and density are requested - are generated from silicon carbide powders, that contain additives such as boron carbide, silicon, and aluminum silicate. Additionally those processes are often completed with adjacent infiltration or nitridation.

There is a number of reports on multi-step techniques for selective laser sintering of silicon carbide bodies [1-5]. The aim of the presented research is the direct generation of SiC micro parts. The method of choice is laser micro sintering although difficulties have been expected because of the lack of a liquid phase. As observed from laser micro sintering of metals, the process evidently needs a transitional closely localized melt pool [6].

Experimental setup

The beam of an Nd:YAG laser ($\lambda=1064\text{nm}$) operated in mono-mode with a maximum power of 4 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 56mm was preferred, because the achievable focus diameter provided sufficient intensity of the incident radiation. With a 56mm lens 1064nm radiation can be focused onto a spot with a radius below $7\mu\text{m}$, 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 laser beam enters via a window in the lid.

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 $0.1\mu\text{m}$. 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 definite 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 1×10^{-5} mbar.

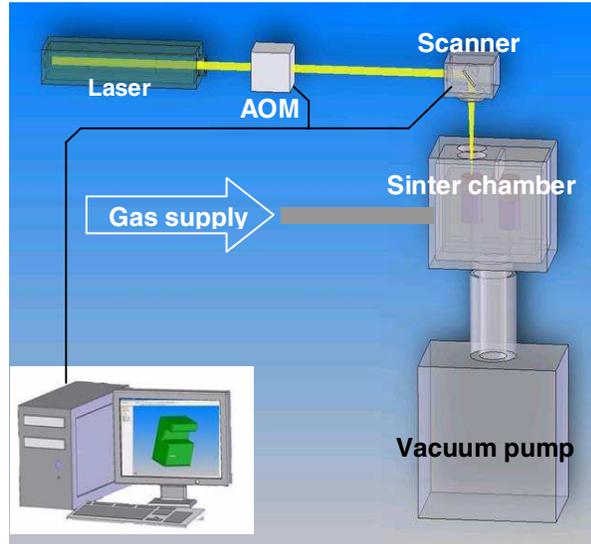


Fig. 1: Schematic of the experimental setup

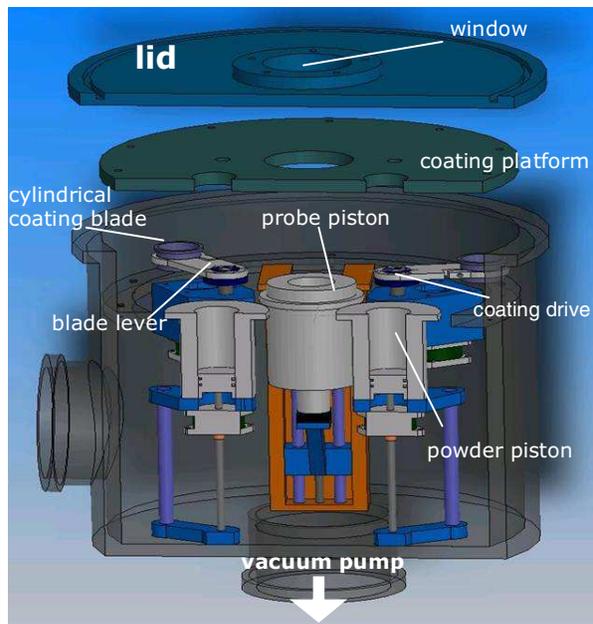


Fig. 2: Schematic of sinter chamber

Experimental

The results of direct selective laser sintering of SiC have been gained from experiments with silicon blended SiC ('SiSiC') containing an additional 8% of carbon and with technically pure SiC. The additional content of carbon in the silicon blended powder was supposed to yield information on the chance of secondary SiC formation. Anticipating a possibly poorer temperature and wear resistance of the products, assays were also conducted with technical grade SiC.

To attain the possibly highest structural resolution SiSiC was sintered with laser micro sintering regimes i.e. employing q-switched laser pulses. This was considered conceivable as silicon – unlike SiC - can acquire liquid state under environmental pressure.

SiSiC: Fig. 3 shows an arrangement of cubes with an edge length of 1mm that were generated with varying laser powers and degrees of defocusing. The respective specimen's

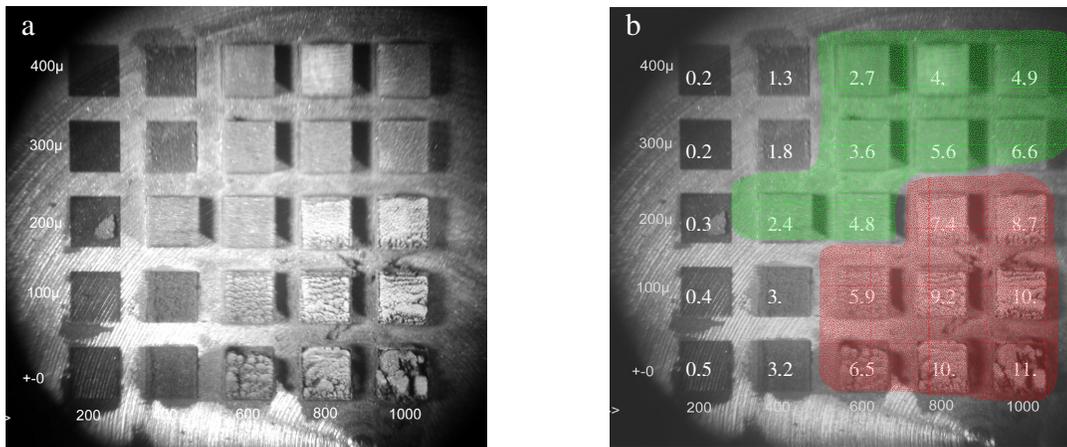


Fig. 3: a) Cubes with an edge length of 1mm from SiSiC powder sintered under ambient conditions with varying focal positions (bottom row at powder level, top row 400μm above) and laser powers (left column 0.8W, right column: 4W); b) Intensity ranges in 10^7 W/cm^2 for undisturbed sintering (green), oxidation of the material (red), and sinter failures (uncoloured).

cross sections were pulsed in a pattern of parallel lines with a constant hatch of 5μm. Constant laser powers were applied for each column – the denotations of 200-1000 for the respective columns correspond to laser powers of between 0.8 and 4.0W. At 4W the half width of the pulses was 325ns at a pulse repetition rate of 30kHz. For the specimens in the bottom row the focus was positioned on the surface of the powder coating. The focus for each of the other rows was aligned 100μm higher above the powder surface than for its bottom neighbor (see notation on the left edge of the photographs). The pulse intensities (denotation on each specimen in Fig. 3b) were calculated as a function of the respective degree of defocusing and of the applied laser power according to equations 1 and 2 for a waist radius of $\omega_0=10,5\mu\text{m}$.

$$(Eq. 1) \quad \text{Intensity : } I = \frac{P_{\max}}{A} = \frac{P_{AV}}{\tau_H \cdot f_P \cdot A} = \frac{P_{AV}}{\tau_H \cdot f_P \cdot \pi \cdot \omega_z^2}$$

$$(Eq. 2) \quad \text{Beam waist(z): } \omega_z = \omega_0 \sqrt{1 + \left(\frac{z}{z_R}\right)^2} = \omega_0 \sqrt{1 + \left(\frac{\lambda \cdot z}{\pi \cdot \omega_0^2}\right)^2}$$

Above an intensity of 7 W/cm^2 - corresponding to the red zone in Fig. 3b - considerable disintegration of the solid can be observed [Fig 4a]. In some cases with a high degree of destruction the sintered products consist completely of loosely attached oxide particles like the displayed specimen. This one had been processed with an intensity of $11 \cdot 10^7 \text{ W/cm}^2$. Sintering without or with just slight oxidation is feasible with parameters of the green zone [Fig. 4b]. This cube was generated with an intensity of $5.6 \cdot 10^7 \text{ W/cm}^2$. As a rule, below an intensity of $3 \cdot 10^7 \text{ W/cm}^2$ solidification of the powder cannot be

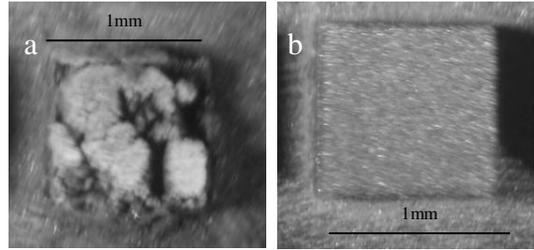


Fig. 4 a) Decomposed and oxidized product due to excessive intensity **b)** firmly sintered body

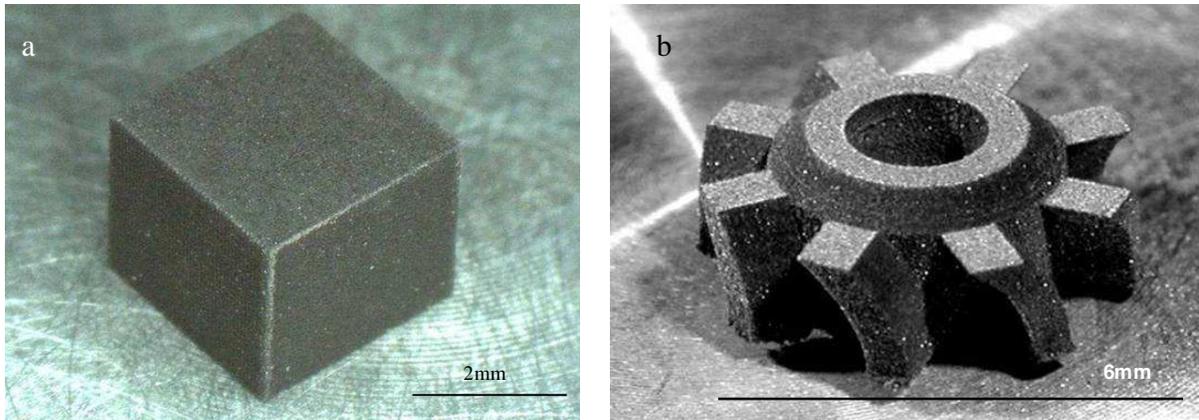


Fig. 5 a) high definition cube consist of SiSiC **b)** micro-turbine of SiSiC

achieved with q-switched pulses.

With the acquired optimum parameters samples were generated from the described SiSiC powder. The cube and the miniature gear wheel [Fig. 5] show high structural resolution and fidelity. The cube has an edge length of 3mm. The gear wheel is 6mm in overall diameter, the blades have a gauge of 0,5mm. The material composition determined by x-ray diffraction is listed in Tab. 1: and compared with the composition of the powder. Fig. 6 is a cross section view of an equally sintered body from the same SiSiC material

Tab. 1: a) The components of the applied Powder **b)** portions for the sintered body

	a) powder	b) sintered body
Si	41%	63%
SiC	50,8%	37%
3C	0%	5%
15R	?	5%
4H	?	7,6%
6H	?	19,8%
C	8,2%	?

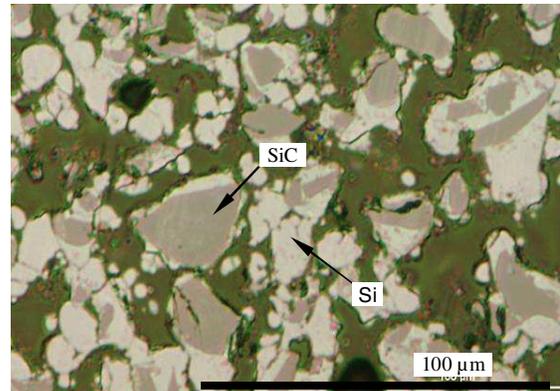


Fig. 6: Cross section view of a sintered body from SiSiC powder; green areas: resin matrix.

Technical SiC: For the assays, an SiC powder (technical notation C15) was applied with a mean grain size of $0.6\mu\text{m}$, ranging from $0.1\mu\text{m}$ to $2\mu\text{m}$ [Fig. 7a]. Due to the wide grain size distribution the material revealed good coating behavior. Powders with a nearly even grain size like the one of type F800 [Fig. 7b] did not yield coherent coatings.

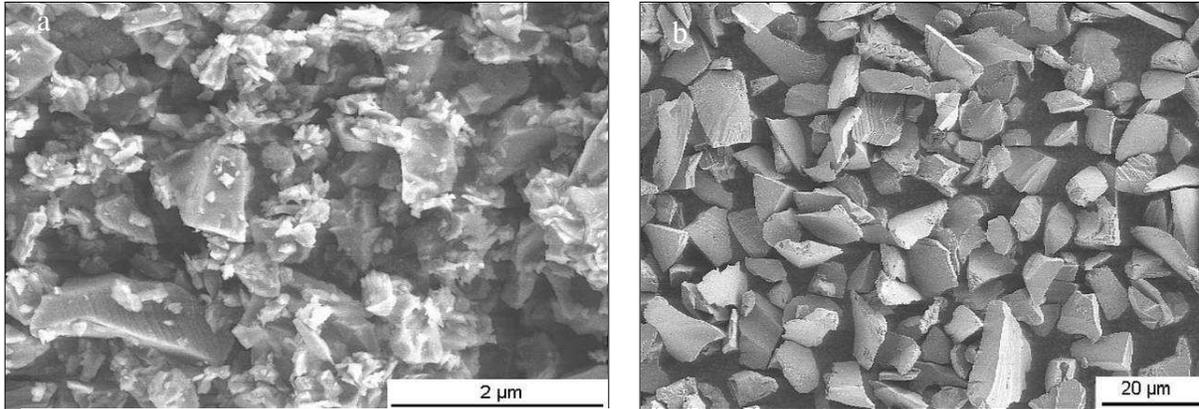


Fig. 7: *a)* SiC powder (Type C15) that was applied for the experiments. *b)* SiC powder (Type F800) poorly suited for the process, mainly because of its uniform grain size.

The first assays revealed the inapplicability of the q-switched laser regime for the selective sintering of technical pure SiC. As the high pulse peak intensities usually caused disintegration of the material, the further experiments were conducted with continuous (cw) laser radiation. Under employment of cw radiation there is an increased chance of oxidation as will be discussed below (chapter 'discussion'). Therefore the processes were performed under an inert gas atmosphere.

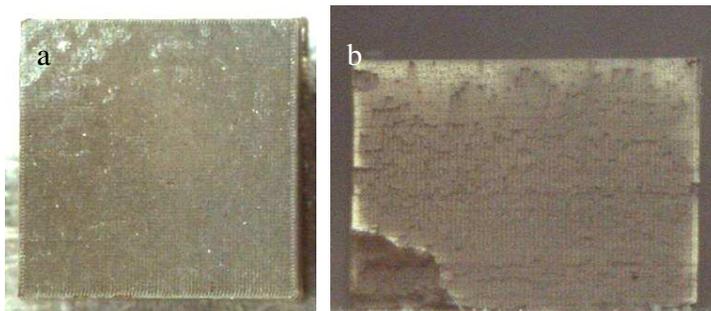


Fig. 8: *a)* Solid structure generated from SiC powder under an inert shield gas. The nature of the bright tarnish has not been identified yet. *b)* Side view: incidental failures occur frequently

At an energy input (fluence) of 0.4 J/mm^2 for a sinter layer with a thickness of $1\mu\text{m}$, solid bodies were generated. As a comparison, the fluence for the generation of specimens from SiSiC-powder described above was 0.3 J/mm^2 . The bodies presented in Fig. 8 are $3\text{x}3\text{x}2\text{mm}$ square columns. Although sintered under oxygen free shield gas, a white tarnish is visible at the edges. [Fig. 8b]. Frequently the fusion of a sinter layer is only fragmentary and the resulting empty

patches are - if at all - repaired only very slowly by successive and limited adjoining of the following layer material to the rim of the defect, like in the generation of an undercut.

Fig. 9 presents a part from SiC powder, which had been generated with undercuts of a 63° angle. The maximum feasible angle of undercut has not been determined yet. More information about the consistency of the sintered solid is expected from the upcoming results of x-ray studies.

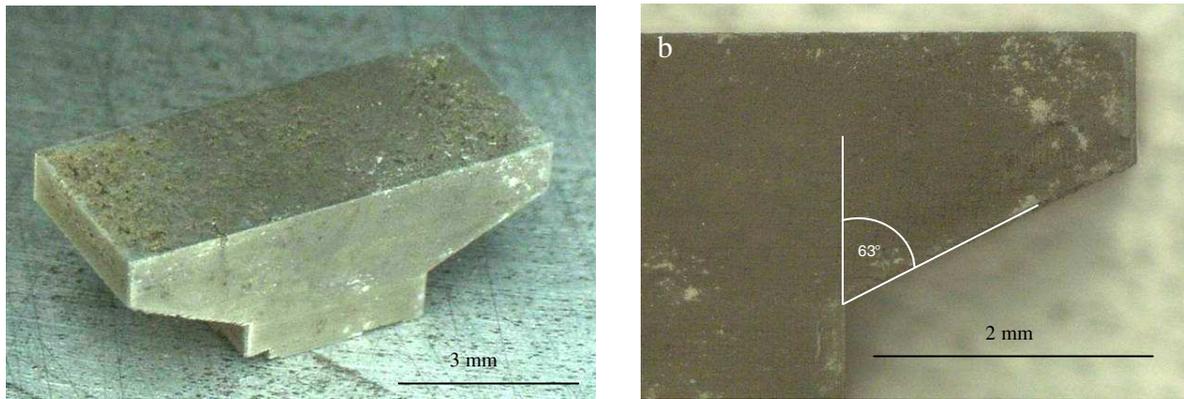


Fig. 9: a) Overhanging structure of pure SiC b) Magnification of the overhanging part

Discussion

SiSiC: From table 1 the higher silicon content after sintering gives evidence that dissociation of SiC without recombination must have occurred. Formation of secondary SiC from silicon and the carbon additive can not be proved. Interestingly, however, some β -modification SiC (type 3C) was formed in the course of the reaction. The cross section view of the sintered SiSiC-Probe [Fig. 6] reveals the morphology of the generated material. SiC-grains (brown areas) are embedded in a matrix of silicon (bright areas) that is functioning like a ‘glue’ that provides for the necessary firmness of the composite.

SiSiC can be laser sintered under normal atmosphere with regimes that are characteristic for laser micro sintering although parameters have to be chosen carefully to avoid oxidation. The prevention of oxidation can be explained with a shield effect of the vapor/plasma plume produced by a q-switched pulse. Among others, one of the

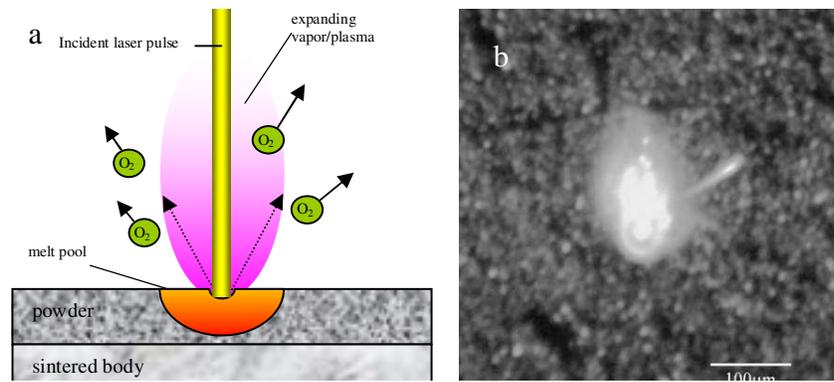


Fig. 10: a) Shield effect of the plasma plume b) Plasma plume of a single laser pulse on a metal powder layer

hypothesized effects of each q-switched pulse is the rapid eruption of an overheated melt pool, which leads to a recoil onto the remaining solid and molten material condensing it and accelerating it towards the substrate material. This effect is required for selective laser sintering of very loosely packed powders. Otherwise the liquid volumes, which are limited in size because of the intended high resolution, will contract into discrete spherical droplets, that are poorly or not at all attached to the substrate structure or the adjacent material in the layer [7].

In the early stage of laser micro sintering the process was conducted exclusively under a special oxygen-free atmosphere to avoid oxidation of the powder and the sintered body. More recent developments [8] revealed that under specific conditions oxidation is essentially suppressed during the impact of an intense and short laser pulse due to the expanding plasma or

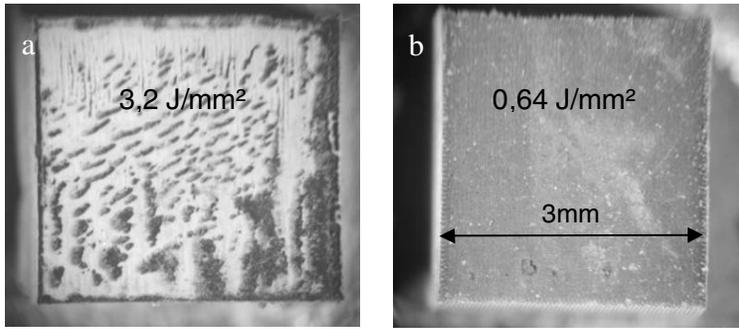


Fig. 11: Surfaces of cubes sintered with different fluences from SiSiC powder

that the thermal energy in the processed material has to be drained by sufficient heat flux and radiation before oxygen has access to the surface. Fig. 11 shows two SiSiC specimens sintered with different fluences. For the generation of both cubes the same pulse parameters were used. The difference is a factor of 5 in pulse density or 'fluence' (energy per unit area). The sample processed with the higher fluence is visibly oxidized whereas the surface of the other probe is virtually free of oxide. It can be concluded that at otherwise constant parameters and material properties a critical limit of the fluence should not be transgressed in order to avoid oxidation. Additionally by variation of the pulse parameters, the shielding effect of the pulses [Fig. 10] can be modified. Continuous (cw) laser radiation will not provide a sufficient shield effect, as the occurring intensities are too low, additionally rapid cooling is delayed as the powder is exposed to the radiation for a longer time.

These findings can be exploited for the generation of a laminated ceramic body consisting of alternating oxide and non-oxide layers, without interruption of the process chain.

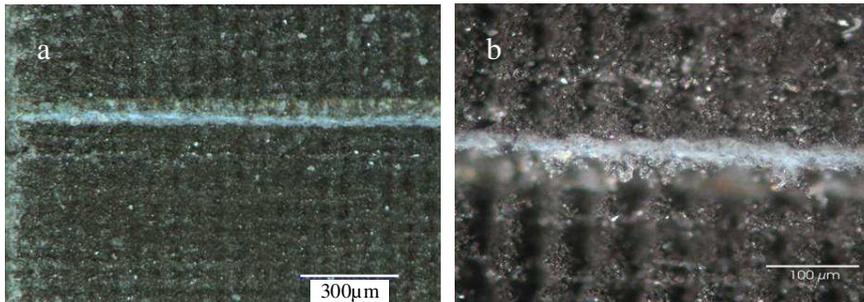


Fig. 12: An inlaying oxide layer that was generated by changing the laser regime from q-switched to continuous wave for a few layers during sintering SiSiC

the dynamics of energy uptake, heat flux, heat radiation and a balance of the dissociated and sintered material along with the respective heat of reaction. Furthermore, the consistency of the powder layer has considerable influence upon the depth of impact as well as the general sinter behavior of the powder. Presently experiments are conducted with these ends.

For the pulsed laser sintering of SiSiC the following mechanism is suggested: Silicon has a considerably higher absorption coefficient for 1064nm (the applied radiation) than SiC. By absorption of the pulse some of the silicon is evaporated and causes the above mentioned vapor/plasma plume with its shield effect, while the rest of the silicon remains liquid. After solidification it acts as a matrix to bind the SiC crystals, which remain unaltered to

vapor plume [Fig. 10]. The adjacent convection and diffusion of oxygen makes this phase the critical one for oxidation [7]. The findings in the experiments corroborate the interpretation that after a laser treatment, which went along with a plasma plume, subsequent oxidation occurs preferentially when there is enough heat left in the oxygen accessible surface zone of the solid. Thus, it becomes evident

Fig. 12 shows the result of selective changes between a q-switched and a continuous wave regime in order to generate an oxide zone (white) in between two segments of non-corrosively sintered SiC material. A quantitative model of these processes will require precise information on

a noticeable extend. This hypothesis is consistent with the subsequently described observation during sintering of the unblended SiC material (see below).

Technical SiC: When the unblended ('technical') SiC was treated under normal atmosphere with the same q-switched regime as for the previous material, the only recognizable effect was the disintegration of the material. At a sufficiently reduced intensity, oxidation was detected at the spots of incidence [Fig. 13a,b]. In accordance with the above explanation for the sintering mechanism of SiSiC it can be concluded that, lacking a second component in the

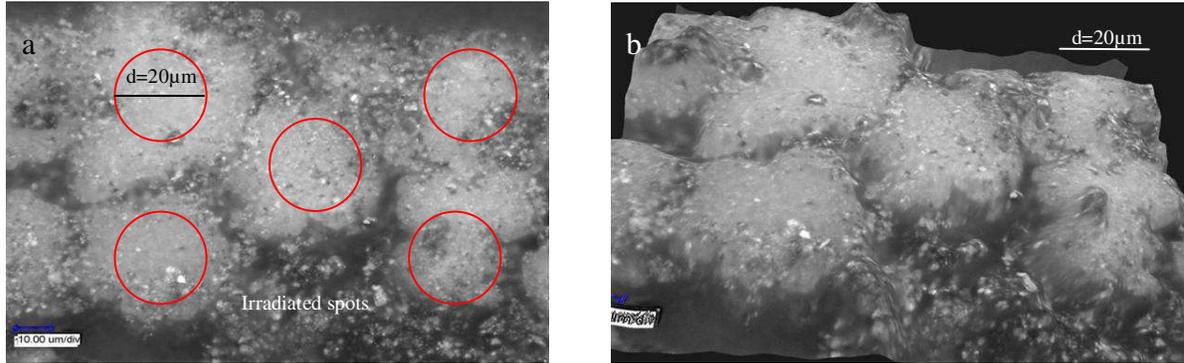


Fig. 13: a) Oxidation products of SiC after treatment with weak intensity pulses b) 3D-view of the spots

powder, the radiation is absorbed at high intensities by the SiC itself with subsequent dissociation. If the speed of ablation is small enough, so that dissociated material remains on the spot, it is oxidized. Because of the low stability of unblended SiC at higher intensities, a regime with continuous radiation (with intensities below the dissociation threshold) and an inert process atmosphere was chosen for the assays.

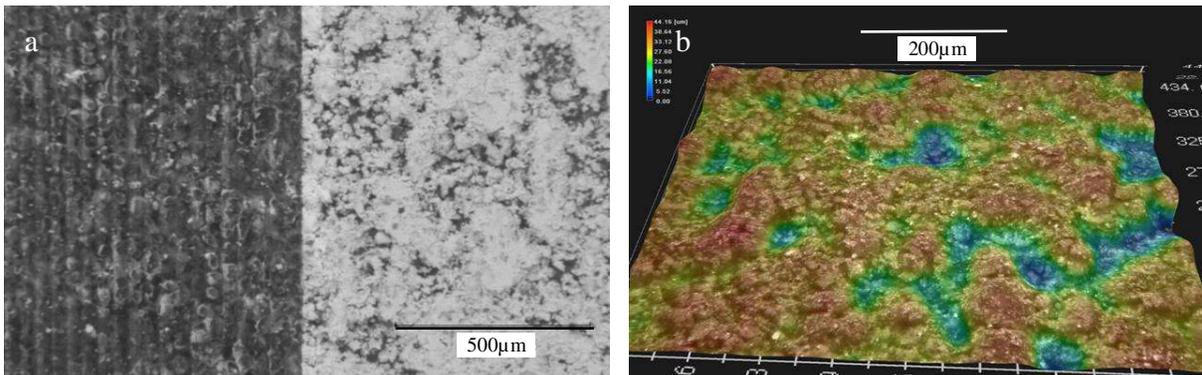


Fig. 14: a) powder coating(right) and sinter result (left) b) 3D-View of sintered layer with insufficient powder coating

Homogeneous and thin powder coatings are crucial for selective laser sintering of unblended SiC. Layers with a too low packing and too high thickness yield defects in the respective sinter layer. The powder layer should not exceed 5µm in thickness. The right half of Fig. 14a shows a typical incomplete powder coating. The corresponding sinter layer on the left half displays the defects that arise from incomplete coating. The colour coded 3D-presentation [Fig. 14b] depicts more explicitly the gaps due to inhomogeneous coating. Requirement for the healing of the defects is an almost perfect coating of the following layers. The initiation of the sinter reaction seems to be dependent on thermal activation. As the powder itself - because of its poor absorption and its low density - does not take up sufficient energy from the radiation, the start

of the process relies on the heat transfer from the absorbing underlying material. This is considered a reason for the necessary limitation of the powder layer thickness, as the radiation has to penetrate the powder without considerable scattering. Additionally the underlying solid should absorb the radiation to a sufficient extent, which could be the case if the already sintered material not only contained SiC but also its dissociation products - especially silicon. This explanation complies with the following theoretical consideration: The smallest possible band gap of SiC (3C-SiC) is 2.416eV [9], the incident wavelength (1064nm) merely/ carries a quantum energy of 1,17eV. As direct single photon excitation of SiC is impossible, the material has to be activated indirectly. For the very first layer of an object, the substrate has the role to absorb and transfer heat to the SiC powder. The following layers are produced on top or in the immediate vicinity of already sintered material, which according to the above considerations contains also silicon from the dissociation concomitant with the sintering process. This silicon content could possibly absorb enough of the incident energy to activate the surrounding grains of the incumbent powder layer. This cycle is interrupted if the layer is too thick to permit sufficient unscattered penetration of the beam to the solid body.

Conclusion and outlook

The results demonstrate the successful laser micro sintering of blended and pure SiC powders. It is possible to generate directly precise micro bodies from SiSiC powder. The content of silicon remaining in the body after the process is still a drawback, as the material properties of silicon are not desired in an SiC-part. The future endeavors aim at considerable reduction of the silicon portion in the sintered body. Laser micro sintering of pure SiC powder posed a bigger challenge to the control of the laser sintering process. Bodies can be generated with a pleasingly high resolution although only simple geometries have been realized yet. In the near future, the theoretical model of laser sintering of non-oxide ceramics has to be more specified, based on qualitative and quantitative investigations and analyses of the products. After improvement of the powder packing noticeably easier initiation and control of the process is expected. Anticipating these upgrades to be achieved, micro sintered SiC parts will be implemented as functional components in industrial tools.

Appreciations

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References

- [1] Jakubenas, K.; Marcus, H.L. 1995, 'Silicon Carbide from Laser Pyrolysis of Polycarbosilane', *J. Am. Chem. Soc.*, vol. 78, no. 8, pp. 2263-2266.
- [2] Stierlen, P.; Schanz, P.; Eyrer, P., 1998, 'SiSiC – Low Process-Shrinkage – High Temperature for the Laser Sinter Process', in D. L. Bourell et al. (eds), *The Proceedings of the 9th Annual SFF Symposium*, 198, pp. 581-588.
- [3] Löschau, W.; Lenk, R.; Scharek, S.; Teichgräber, M.; Nowotny, S.; Richter, C, 1998, 'Prototyping of Complex – Shaped Parts and Tools of Si/SiC Ceramics by Selective Laser Sintering', in *Ceramics: Getting into the 2000`s*, 9th Cimtech-World Ceramics Congress, 1998, Florence, vol B, pp. 567-573.
- [4] Sindelair, R.; Niebling, F.; Buhler, P.; Greill, P.; Geiger, M. 2001, 'Selective Laser Sintering of Pre-ceramic Polymers', in M. Geiger & A. Otto (eds), *Laser Assisted Netshape Engineering 3*, Proceedings of the 3rd LANE 2001, August 28-31 2001, Erlangen, Germany, Bamberg-Meisenbach, ISBN 3-87525-154-7, pp. 447-458.
- [5] Evans, R.A.; Bourell, D.L.; Beaman, J.J.; Campbell, M.I. 2005, 'Rapid manufacturing of silicon carbide composites', *Rapid Prototyping Journal*, Jan. 2005, vol. 11, no. 1, pp. 37-40.
- [6] Regenfuss, P.; Hartwig, L.; Klötzer, S.; Ebert, R.; Brabant, Th.; Petsch, T.; Exner, H.; 2005, 'Industrial freeform generation of microtools by laser micro sintering', *Rapid Prototyping Journal*, Jan. 2005, vol. 11, no. 1, pp. 18-25(8)
- [7] Regenfuss, P.; Streek, A.; Hartwig, L.; Klötzer, S.; Brabant, Th.; Horn, M.; Ebert, R.; Exner, H.; 2006, 'Principles of Laser Micro Sintering', *Solid Freeform Fabrication Symposium Proceedings 2006*, submitted.
- [8] Regenfuss, P.; Streek, A.; Hartwig, L.; Klötzer, S.; Maaz, A.; Ebert, R.; Exner, H. 2005, 'Advancements in Laser Micro Sintering', in E. Beyer et. al (eds) *Proceedings of the Third International WLT-Conference on Lasers in Manufacturing*, Munich, Germany June 13-16 2005, ATV-Verlag GmbH, ISBN 3-00-016-402-2, pp. 685-688.
- [9] Humphreys, R.G.; Bimberg, D.; Choyke, W.J. 1981, 'Wavelength modulated absorption in silicon carbide', *Solid State Commun.* 39,163-167.