

Principles of Laser Micro Sintering

P. Regenfass*, A. Streek*, L. Hartwig*, S. Klötzer*, Th. Brabant*, M. Horn*,
R. Ebert*, H. Exner*

Laserinstitut Mittelsachsen e.V. / Hochschule Mittweida, Mittweida (Germany)
peter.regenfass@htwm.de

Keywords: laser micro sintering, plasma plume, shield effect, q-switched pulses, ceramics
Reviewed, accepted September 14, 2006

Abstract

Laser Micro Sintering was introduced to the international community of freeform fabrication engineers in 2003 and has since been employed for a variety of applications. It owes its unique features to certain effects of q-switched pulses that formerly had been considered detrimental in selective laser sintering. Besides sub-micrometer sized powders also materials with grain sizes of 1-10 micrometers can be sintered. Surface and morphology of the product are influenced by grain size and process environment. First results have been achieved with processing ceramic materials.

A comprehensive overview of the process and the features is given supported by experimental evidence. Routes of further development are indicated.

Introduction

The development of the laser micro sintering technique – a modification of selective laser sintering resulted from the endeavors to improve the resolution of direct metal selective laser sintering down to the 10 μ m dimension. Compliant with the state of the art [1] the contemporary approaches in the early period implied strict control of the atmosphere and use of very finely grained powder. But it was not until the development of a technique, which employed q-switched pulses and a special coating procedure, that functional micro parts with a structural resolution of 30 μ m could be generated from the respective powders [2]. Very soon it turned out that the side effects of those pulses not only led to a higher resolution but also could be exploited to generate virtually tension free parts.

Meanwhile the technique has been employed to the sintering of metal powders with larger grains, some of which can be processed under normal atmosphere also due to specific effects of the q-switched laser pulses; and even oxide ceramics have been processed successfully. The sintering of non-oxide ceramics with this method is presently under investigation.

In the following, the specific features and effects of q-switched laser pulses upon the powder materials are described and interpreted. The presented experiments were performed on the sinter machines reported in earlier publications [4-8] and modifications thereof.

Laser Micro Sintering of sub- μ m Metal Powders

The first attempts on the way to laser micro sintering were made with continuous ('cw') 1064nm laser radiation. Sub- μ m powder was supposed to be heated and fused very selectively by scanning the surface of a thin coating with a narrow laser spot of ca. 14 μ m, which was the ideal case for the employed optical arrangement. The assay turned out unsuccessful as molten powder contracted to discrete spherical droplets with little or no attachment to the substrate [Fig. 1a]. Especially at very low pressures, the material sublimated rapidly leaving a gap in the powder bed and only a few solidified droplets on the fringes of the laser track [Fig. 1b,c].

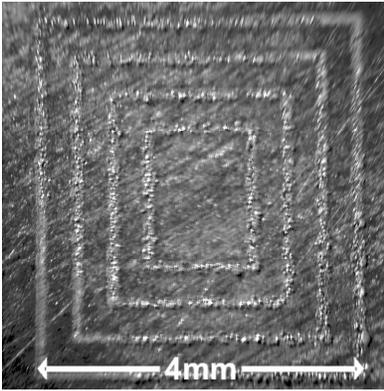


Fig. 1a: Square lines of solitary spherical tungsten droplets from 0.3 μ m powder under oxygen-free shield gas with cw laser radiation.

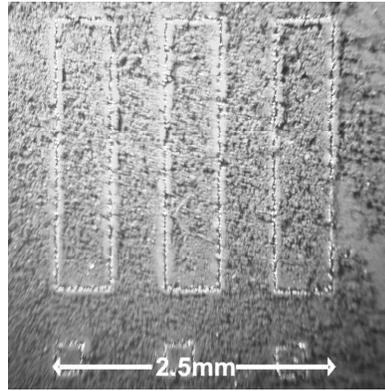


Fig. 1b: Gaps in the powder bed after processing tungsten powder with cw laser radiation in vacuum.

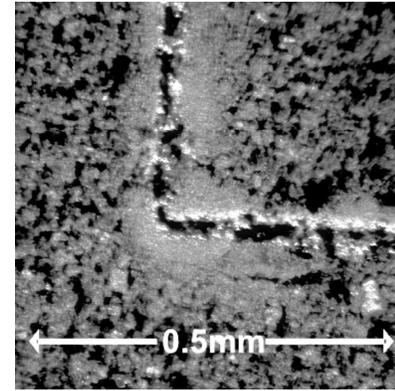


Fig. 1c: Blow-up view of the gap resulting from sublimation; the picture reveals a few droplets at the fringes.

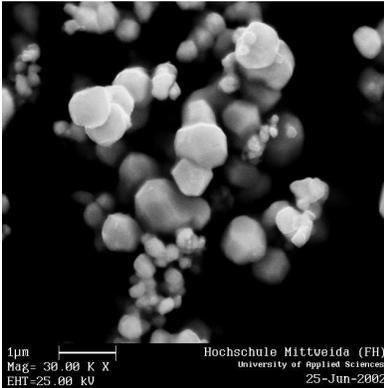


Fig. 2a: Tungsten grains in a loose and voluminous accumulation.

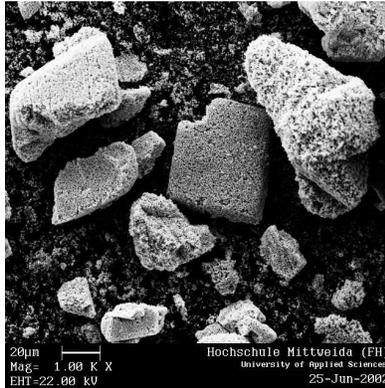


Fig. 2b: Agglomerates in sub- μ m grained tungsten powder.

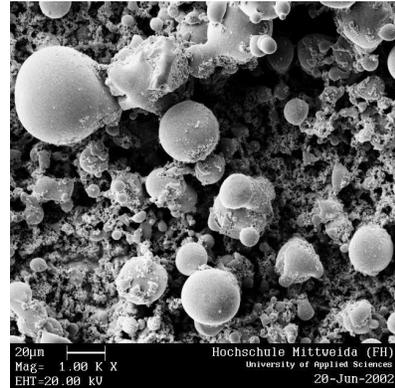


Fig. 2c: Spherical droplets after irradiation of sub- μ m tungsten with a cw-laser beam.

The cause for the problems was detected to be of a twofold nature:

1. Sub- μ m powders usually show a very voluminous consistency rather than sedimenting into a dense packing, as gravitational forces succumb to the inter particle forces [2,3]. In the case of a sub- μ m tungsten powder the loose arrangement of polyhedral single grains [Fig. 2a] and the agglomeration of the grains into almost regular lumps with preferred tetragonal angles [Fig. 2b] can be observed. Fig. 2c gives a good idea how these discrete lumps turn into solitary melt spheres when heated with moderate intensities i.e. not exceeding the boiling temperature of the liquid.
2. If the process atmosphere is below the vapor pressure of the metal at its melting point or a pressure even slightly above, the recoil of the sublimation or of the boiling that is caused by irradiation with only moderate intensities might not be sufficient to allow for enough residual liquid material as would be needed for fusion into a solid structure. Estimations of the critical process pressure can be made by use of the commonly known equation of Clausius and Clapeyron.

Employment of q-switched pulses proved to be the way out of these difficulties. When operated in the q-switched mode the employed laser yielded a 200 times higher intensity and four times the fluency compared to the cw-mode. Effects were observed that could be interpreted as a tightly located depth of impact by each laser pulse and/or a flattening effect upon the molten material.

Figs. 3 show isometric views of a very crumbly sintered volume from tungsten powder that had been irradiated by q-switched pulses with insufficient parameters. They are elevated side views of a predominantly poorly sintered body. Nonetheless the q-switched pulse effects are well visible. The top surface contains spots of fused metal that

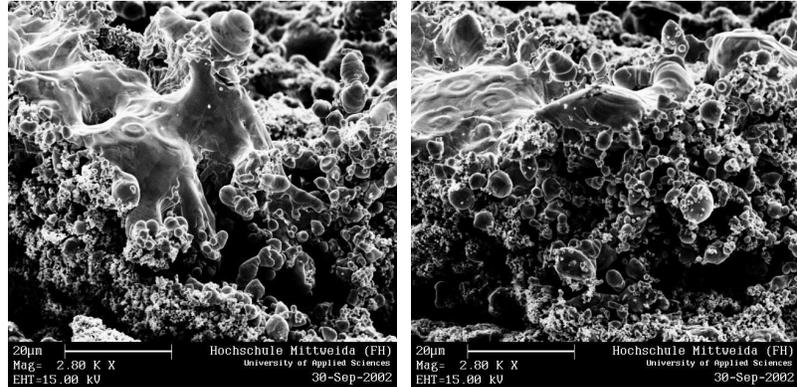
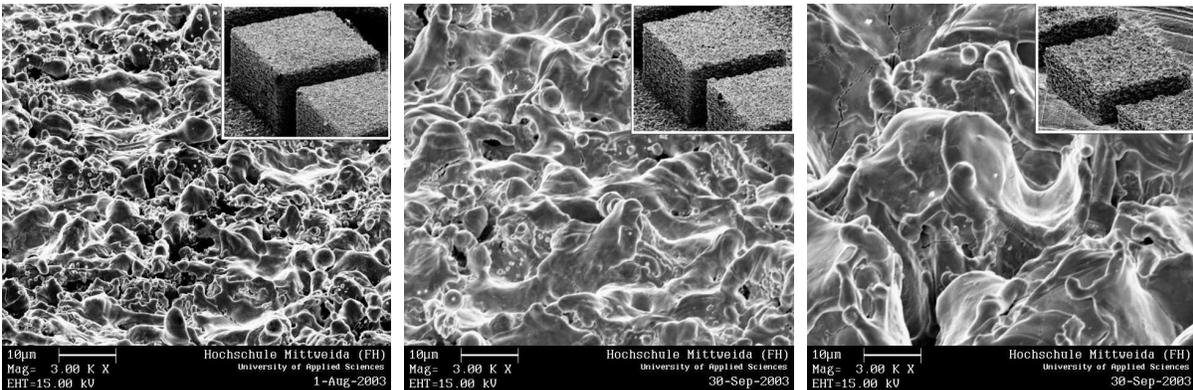


Fig. 3: Elevated side views of a coarsely sintered body displaying three characteristic features of a surface sintered by q-switched pulses: Flattened craters, deep cut-ins, frozen jets. Material: sub- μm tungsten; atmosphere: oxygen-free shield gas.



Figs. 4: Surface views - arranged according to increasing pulse energies and intensities - of highly fused bodies sintered by q-switched laser pulses. Flattened craters, cut-ins and frozen jets are detectable. The inserts are the respective overall views.

obviously had been flattened during liquid stage by a vigorous pressure jump followed by rapid solidification. It is evident that the texture had been shaped by a multitude of discrete incidents, some of them having left flat craters forming a pattern of two concentric rings, others deep and narrow cut-ins through the upper layer into the underlying substance. A third type of formation has the appearance of vertically protruding bolts consisting of two or more droplets jammed on top of each other, resembling a collapsing jet of metal. These formations can also be observed in **Figs. 4**, which are views onto the top surface of square prisms generated from tungsten powder by q-switched pulses under a defined shield gas atmosphere. By optimization of the laser parameters and the shield gas as well as the coating procedure it became possible to sinter firmly fused solids [**Figs. 4** and **5**]. The present model of mechanism of q-switched pulse sintering (laser micro sintering) is the following:

1. Irradiated material is heated by the laser pulse, and limited emanation of vapor occurs.
2. The emanating vapor or plasma - possibly along with plasma originating from the shield gas ionized by the high intensity (the consistency of the plume is still under discussion) - expands rapidly exerting a pressure on the remaining material below, allowing it to form an overheated melt pool without boiling, and at the same time forcing it downward. This is observed as the 'condensing effect' of the laser pulse upon the powder layer. In which of those hypothetical stages cut-ins occur, shall be discussed below.
3. Due to expiration of the pulse and/or exhaustive expansion of the vapor/plasma bulb a pressure break-down occurs, allowing spontaneous incidents of boiling [Fig. 6b] with rapid expulsion of solitary drops from bursting bubbles [Fig. 6c] and adjacent formations of slower jets [Fig. 6d], that either separate into droplets [Fig. 6d] or collapse before solidification in various shapes.
4. Rapid cooling due to the boiling and convection of the shield gas freezes the liquid material before it can contract into spherical droplets. Thus the phenomenon often referred to as 'balling' is prevented. Throughout the whole process also permanent cooling due to irradiation and heat flux into the contacting solid sintered structure has to be assumed.

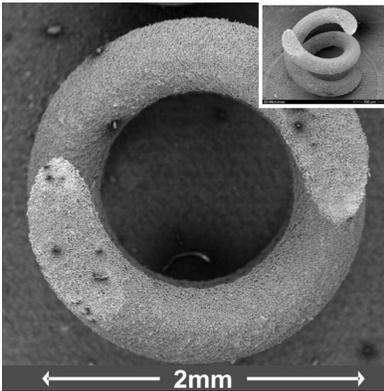


Fig. 5a: Top view of a tungsten double helix showing the typical pricked appearance of a micro sintered surface.

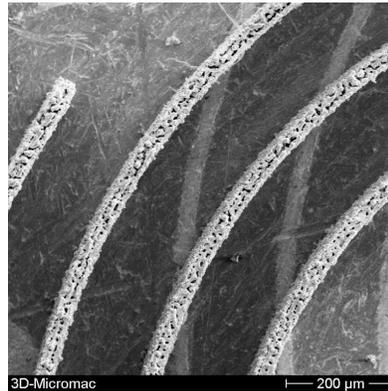


Fig. 5b: Top view of a coiled tungsten ligament (height: 300µm); the cut-ins from the pulses are clearly visible.

Fig. 6 is a photograph of a metal powder surface hit by a q-switched laser pulse. The exposure time is ca. 1ms, and considering that the laser pulse length is in the order of 200ns the picture should be an integration of all stages of the pulse effects. The metal material of the vapor/plasma plume has evidently condensed after the expansion - most probably into a mist of nanoparticles. A bright solitary drop of metal can be seen, shooting out of the plume directed towards the

right margin. It is ascribed to vigorous expulsion of liquid material by the spontaneous bursting of a vapor bubble, immediately after the breakdown of the plasma pressure. From the center of the spot a metal jet emerges vertically, obviously with a relatively low speed as the singular droplets around it do not appear as streaks on the exposure. These jets are often observed as rebound effects on liquid surfaces after the burst of a boiling bubble [Fig. 6c]. Possibly the collapse of those jets, before they have completely separated into discrete droplets, account for the typical shape of the protrusions in a laser micro sintered surface [Fig. 3]. Numerous authors have dealt with 'phase explosion' during pulsed laser ablation already and there exist already some comprehensive overviews [9].

Among other phenomena the delayed ejection of metal – after the expiration of the laser pulse – has been explicitly mentioned in their reports [10,11]. Phase explosion after the collapse of an expanding plasma bubble is also the accepted mechanism in electro discharge machining [12]. The flattened craters in a laser micro sintered surface could stem from spots with a very shallow melt pool.

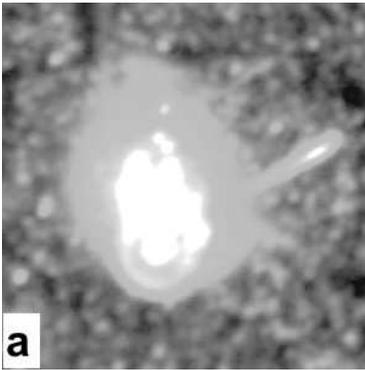


Fig. 6a: Photograph (exposure time 1ms) of a single 200ns q-switched pulse onto metal powder comprising all effects.

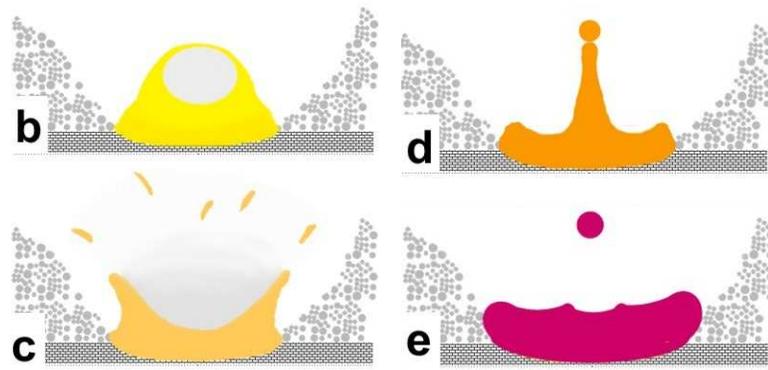


Fig. 6b-e: Assumed process phases after breakdown of the high pressure from the expanding plasma plume: Formation of a gas bubble (b), rapid bursting (c), formation of a slower jet (d), and dispersion of the jet into droplets of or collapse and solidification.

As there are several conceivable explanations for the origin of the stitch-like cut-ins in the laser micro sintered surface, an extensive discussion shall be spared. Only to mention two of the multiple possibilities: The pulse hits a location, which has a porous sinter layer underneath the powder coating or the pulse hits a location with a defect in the powder layer. There is a vast open field of imaginable further detailed explanations which, however, should be postponed until corroborating experimental results are available. Whatever the precise nature of the cut-ins may be, they have proved to be crucial for the vertical interconnection of the sintered solid and the precocious breaking of inherently generated tensions during the process. The typical texture of laser micro sintered layers from sub- μm powder that arises from the described effects are visible in **Figs. 5**. Other micro parts displaying the whole state of the art have been presented in previous publications [4-8].

Laser Micro Sintering of 1-10 μm Metal Powders

For the realization of structural features ranging down to 30 μm , laser micro sintering in its initial phase of development was performed preferentially with sub-micrometer grained powders. The demand for specific properties of the micro parts and the concomitant requirement for material diversification, however, advanced the employment of powders with grain diameters of 1 μm and above. The results showed the feasibility of laser micro sintering with coarser grained powders, thus enlarging the variety of available feedstock considerably [13]. **Figs. 7a** and **b** show two results of laser micro sintering from a stainless steel and a nickel chromium alloy powder.

Working with powders in the μm -range it turned out that the mean power of the laser as well as the pulse energy had to be increased, compared to the processing of finer grained material. A coarser resolution as well as surface roughness has to be accepted on the one hand, but a higher sintering rate can be attained on the other hand [**Tab. 1**].

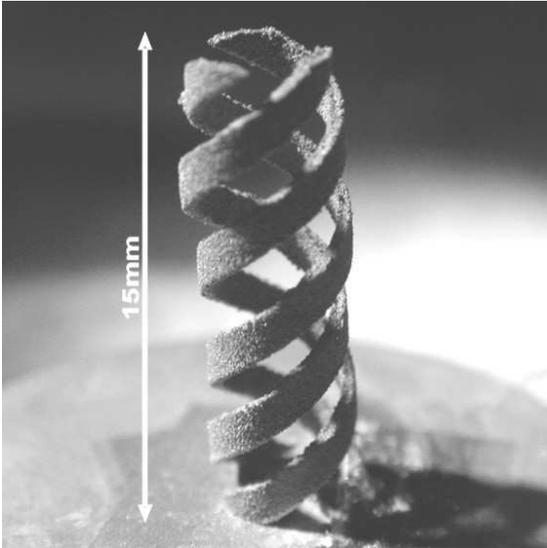


Fig. 7a: Triple helix with an overall height of 15mm generated under ambient conditions from 10 μ m sinter layers of 10 μ m grained steel 1.4404.

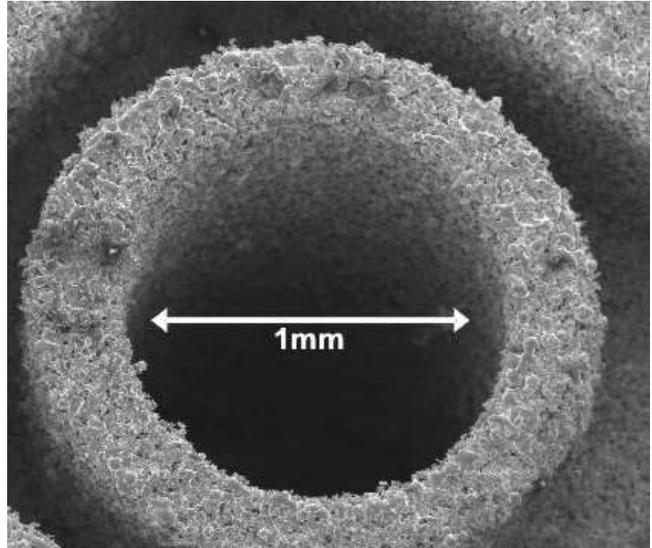


Fig. 7b: Detail of a valve generated under ambient conditions from 10 μ m sinter layers of a 10 μ m grained nickel-chromium alloy powder (80Ni20Cr).

Tab. 1: Features of laser micro sintered bodies from sub- μ m and 1-10 μ m grains

grain size [μ m]		≤ 1	10
sinter layer thickness [μ m]		1	10
min. roughness [μ m]	normal atmosphere	--	8.5-10
	special oxygen free	1.5-2.5	5.5-8.5
structural resolution [μ m]	normal atmosphere	--	125-150
	special oxygen free	20	55-60
Process time for 1000mm ³ [h:min]		35:30	02:50

Another important observation, when processing 1-20 μ m powders, was that many of the powders as well as the solidified products were not visibly oxidized, which means the process can be conducted under ambient conditions [Figs. 7a,b]. A reduced reactivity of the coarser powders compared to the sub- μ m material had been anticipated because of the lower surface to mass ratio. A multitude of factors, however, can be discussed, that could be responsible for either oxidation or inertness during a process under normal atmosphere, depending on the powder materials and process regimes. The following qualitative explanations are consistent with the up-to-date observations:

1. During a q-switched pulse (ca. 200ns), oxidation cannot be expected because of the vigorous expansion of the gas and/or plasma plume.
2. After the collapse of the plume and the adjacent boiling eruption, convection of air can take place, allowing for the transport of the gaseous reactant towards the heated material. But at this time the material has assumedly cooled down considerably and the lapse of temperature continues due to heat transport and irradiation.

3. The initiation of the oxidation requires an energy content of the reacting system above the activation energy. This is more probable at higher temperatures as described by the Arrhenius equation. If oxidation is initiated the temperature lapse can be prolonged by the released heat of the oxidation.
4. Consequently the degree of oxidation when conducting laser micro sintering under ambient conditions depends on the temperature of the sintered metal at the first access of oxygen, the specific energy of activation, the free enthalpy of oxidation, the possibility of oxygen transport and the various cooling factors.
5. As the considerations 1-5 take into account only the material immediately irradiated by the laser pulse, it should be mentioned, that the adjoining zones are also subject to the heat flux and could therefore in some cases also become sufficiently activated for oxidation.
6. During the expansion of the plume, vapor/plasma can react with ambient oxygen in the exterior zone of the torch. The above mentioned acceleration of the sintering and the lower resolution when the process is conducted under normal atmosphere can be partly attributed to the heat of this reaction.

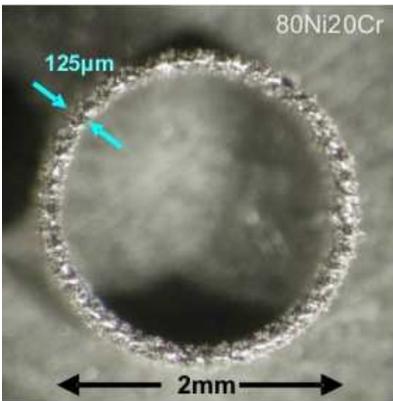


Fig. 8a: Cylinder (top view) sintered from 80Ni20Cr under ambient atmosphere.

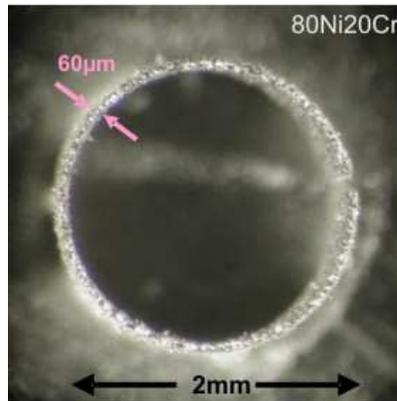


Fig. 8b: Cylinder of identical material and by the same process parameters as in Fig. 8a, under an oxygen-free atmosphere.

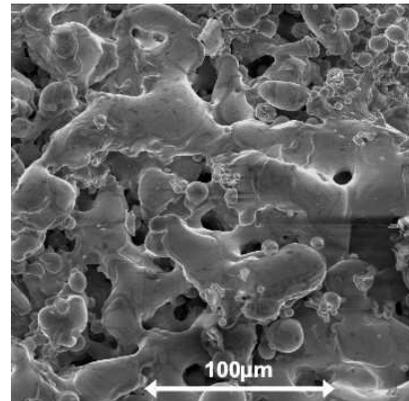


Fig. 8c: Surface of a product from 10 μm grained 80Ni20Cr powder, showing typical features of laser micro sintered layers.

[Figs. 8a,b] show two probes of a NiCr-cylinder, one processed under ambient conditions and the other one under a special oxygen-free atmosphere. No oxidation can be observed but the difference in resolution is clearly visible. A blow-up of a sintered surface Fig. 8c gives evidence that the effects of q-switched pulses hypothesized for the processing of sub-μm-grained powders have also a substantial role in the sinter mechanism with 10 μm grained materials. One can detect the typical blobs of molten material, flattened by the boiling eruption and its recoil effect, along with deep narrow stitches which often occur at the location of the beam center due to the high peak intensity. The latter ones are assumed to intensify the vertical cross linking of the sintered material.

Among other metal powders molybdenum, copper and silver have been successfully sintered under air without oxidation.

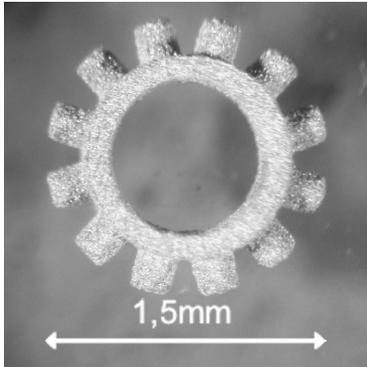


Fig. 9a: Silver cog from 2 μ m powder under air for surgical application (Courtesy of JOTEC GmbH, Stuttgart).

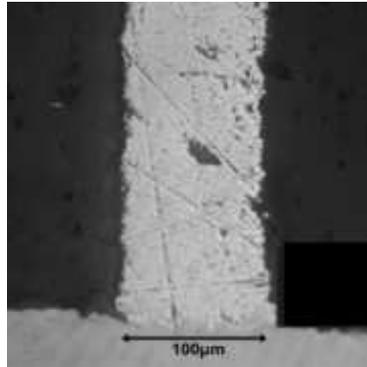


Fig. 9b: Cross section through a ligament from 1 μ m silver powder under ambient atmosphere.

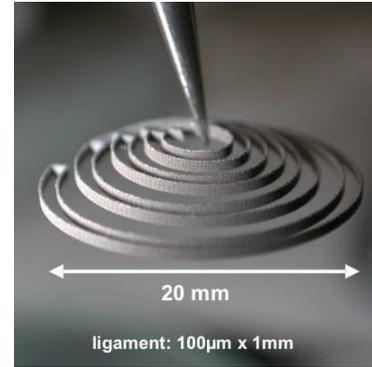


Fig. 9c: Spiral spring (lifted by a tweezers) from sintered from 7 μ m molybdenum powder under ambient atmosphere.

Figs. 9a-c show examples for silver and molybdenum parts. The silver cog wheel in **Fig. 9a** has been tested as part of a stent positioning device. Silver yielded the highest density (87%) so far achieved with mono component powders >1 μ m [**Fig. 9b**]. Also fairly high densities can be obtained with molybdenum. The spiral spring of molybdenum [**Fig. 9c**] can be reversibly deformed, obeying Hook's law. **Figs. 10a,b** present views of the surface of a molybdenum ligament.

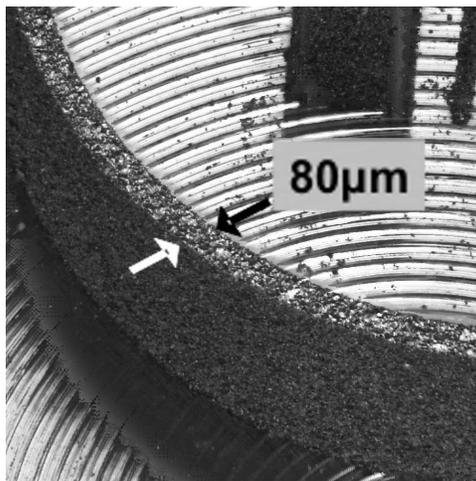


Fig. 10a: Molybdenum ligament from 7 μ m powder under ambient atmosphere.

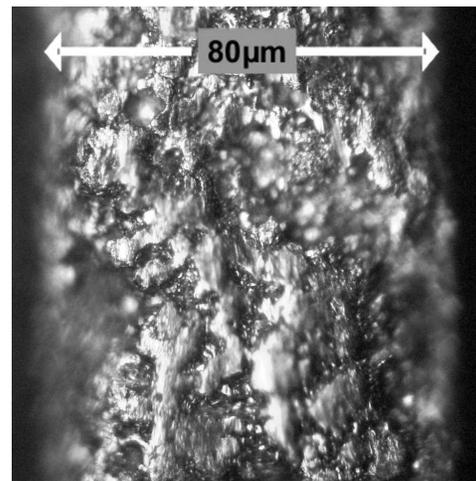


Fig. 10b: Top view onto the surface of the molybdenum ligament.

The hypothesis that the cooling rate is crucial for the prevention of oxidation is corroborated by the finding that even sub- μ m grained molybdenum powder can be processed under ambient atmosphere when the structure of the generated solid is dense enough to provide for sufficient heat flux within the sintered volume [**Fig. 11**].

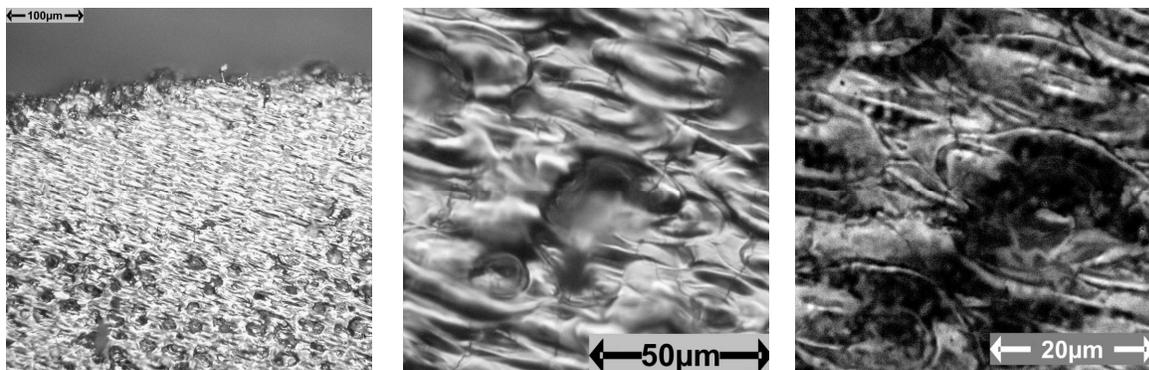


Fig. 11: Top views of a body sintered from 0.3µm molybdenum powder under normal atmosphere. The high degree of fusion yields good heat conducting properties of the sintered material. Rapid cooling after the expiration of the laser pulse can be assumed.

A cylinder consisting of copper and silver segments is shown in **Fig. 12b**. The specimen was generated without interruption of the laser micro sintering campaign, taking advantage of the availability of two coating blades in the sinter chamber **Fig. 12a**. The cross section of the fusion zone of two segments shows a tight interlocking which is most probably not only due to the pulse effects but also to the compatibility of the two adjoining metals.

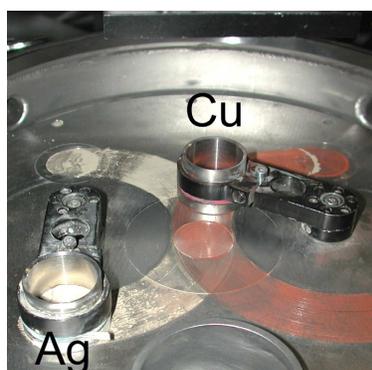


Fig. 12a: Automatic change of powders during laser micro sintering.

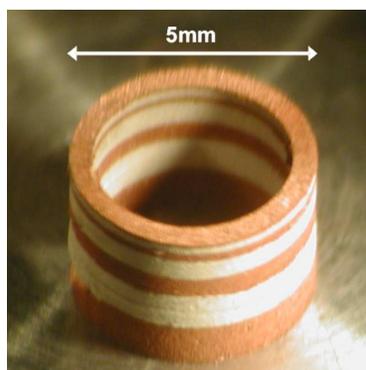


Fig. 12b: Cylinder with alternating segments of copper and silver (wall thickness: 500µm).

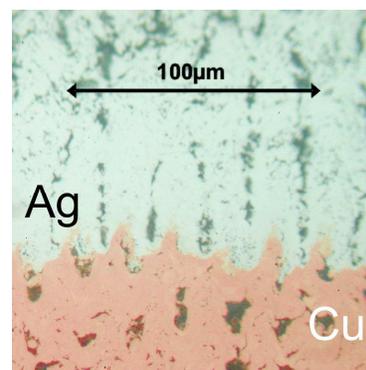


Fig. 12c: Fusion zone between a sintered copper and the succeeding silver segment.

Laser Micro sintering of Ceramics

Experiments on selective laser sintering of ceramics have been reported since about two decades ago [14,15] dealing mainly with the generation of green forms or other premature stages of the product, followed by a finishing procedure e.g. furnace sintering or infiltration. Those procedures have already reached a very high level and are nowadays performed by commercial machines [16,17].

Considerably fewer reports are available on direct selective laser sintering of this material class. Direct selective laser sintering of ceramics without the employment of a binder is reported since 1999 [18-21]. The processed materials were actually porcelains or porcelain raw materials which were coated as slurry layers and selectively laser sintered after desiccation. A recent paper reports the direct sintering of borosilicate glass to a density of 48% of the solid material [22].

Laser processing of ceramics, especially of oxide ceramics affords higher skills than the comparable processes with metals. In order to achieve resolutions of $50\mu\text{m}$ and considerably below - as it is the goal of laser micro sintering - the employment of a CO_2 -laser is not appropriate because of its diffraction limitation. Radiation from near IR and the VIS region allow for sufficiently sharp focusing but the specific problem of most dielectric materials with this range of wavelength is their generally low and temperature dependent absorption coefficient. Direct absorption of the corresponding energy quanta is usually only possible for electrons in the conduction band.

The availability of electrons above any definite energy E follows the Fermi function [Equ. 1], where $f(E)$ is the probability of an electron with at least that Energy E , and EF is the Fermi energy of the material. In our case we assume E to be the lower limit of the conduction band.

$$f(E) = 1/[1 + \exp(E - EF)/kT] \quad (1)$$

Considering the bandgaps of oxide ceramics, this probability is very low at room temperature. Working with continuous laser radiation and the concomitant moderate intensities one has to rely on the self accelerating cycle of absorption, heating, and resulting increase of absorption. At low intensities - if the absorption is compensated by heat flux and radiant emission - the process fades out before the melting temperature is attained. Upon application of a continuous laser beam at too high intensities, after an induction period an avalanche effect occurs resulting in uncontrollable heating and disintegration of the material.

Q-switched pulses turned out to be better suited for the processing of dielectrics. The high intensity achievable in q-switched pulses increases the chance of multi-photon excitation of electrons in the valence band and thus an immediate higher absorption already in the unheated material. On the other hand, due to the short pulse times (in the order of 200 ns and shorter) the evolvement of a detrimental avalanche effect can be avoided.

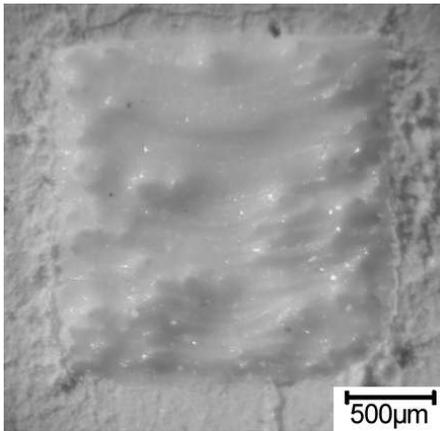


Fig. 13a: Laser sintered patch on surface of pelletized ceramic powder, processed with 1064nm cw radiation.

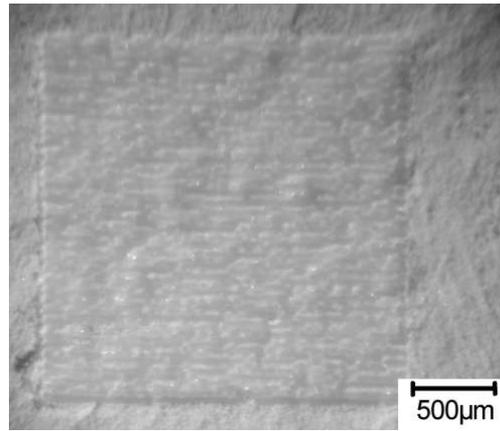
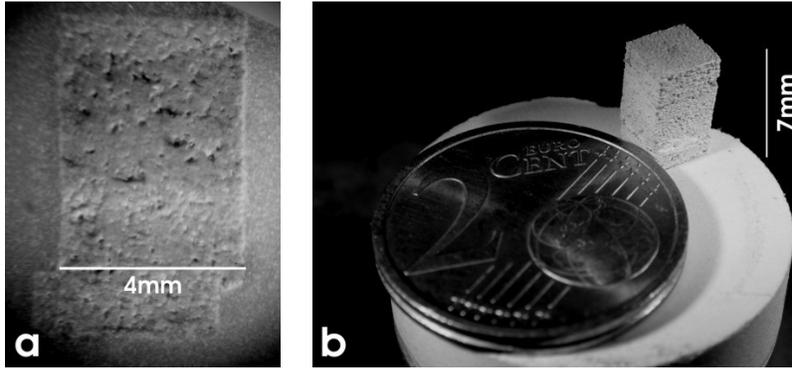


Fig. 13b: Laser micro sintered patch of a similarly pelletized powder probe, processed with 532nm q-switched pulses.

Experiments with a ceramic powder blend that consisted mainly of alumina and silica proved that by application of 532nm q-switched pulses, micro sintering could be performed without an induction period and yielded a considerably better resolution than laser sintering with 1064nm continuous wave laser radiation [23, 24]. **Figs. 13a** and **13b** allow a comparison of the two regimes.

In the initial experiments pelletizing of the dry ceramic powder was necessary because



Figs. 14: Ceramic body generated from 15µm sinter layers; overall height: 7mm. **a:** cross sectional view. **b:** size comparison with a coin.

of the low bulk density of the powder layer when coated with a doctor blade. In order to apply sufficiently dense coatings for successive layer sintering the shape of the doctor had to be adapted to the material. **Figs. 14** show a square prism composed of 15µm sinter layers with an overall height of 7mm with a relative density of ca. 80%. Meanwhile – after further

optimization of the powder composition, selection of better suited laser sources as well as sophistication of the sintering strategy – the features of laser micro sintered ceramic bodies come close to the requirements for functional parts [Table 2].

Table 2: Features of laser micro sintered oxide ceramic bodies

max. height	resolution	max. rel. density	flexural strength	crushing strength
10mm	≤ 80µm	98%	100 MPa	800 MPa

Figs. 15a,b show cross sectional views of an oxide ceramic part with a high relative density. The truncated inverted pyramid in **Fig. 15c** - generated from a blend of mainly alumina and silica - gives evidence that undercuts have already been realized.

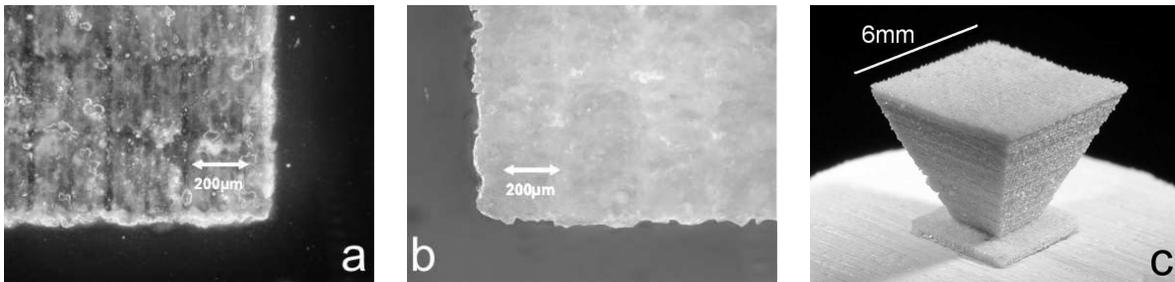
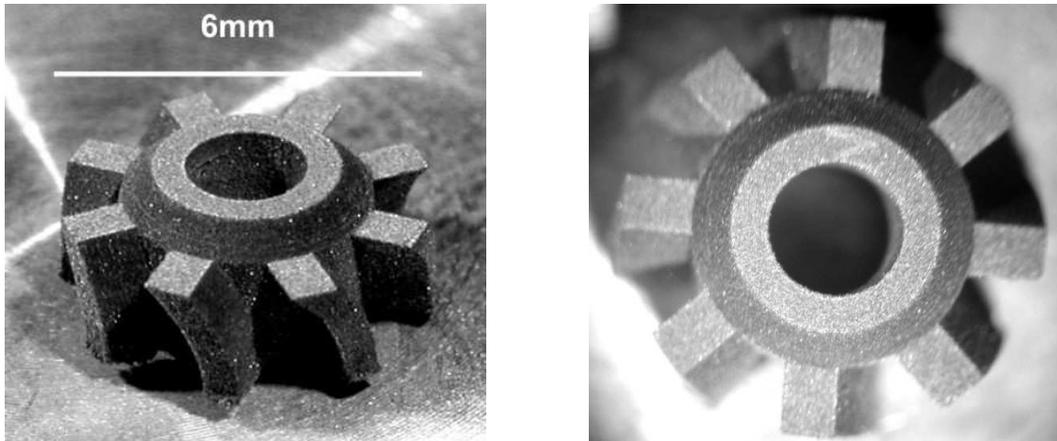


Fig. 15a,b: Cross sections through a laser micro sintered oxide ceramic body with noticeably high relative density and resolution.

Fig. 15c: Undercuts at an inverted truncated pyramid.

Non-oxide ceramic materials e.g. silicon carbide powders have different physical properties. Especially the lack of an undissociated liquid phase makes pure silicon carbide inapt for direct laser sintering. **Figs. 16** show a sample generated by direct laser sintering from a technical silicon carbide powder (SiSiC) as it is used for some furnace sintering processes. The features of the process and hypotheses of the sintering mechanism are dealt with in a separate publication [25].



Figs. 16: Gear wheel by direct laser sintering of SiSiC without subsequent infiltration.

Summary and Outlook

The application of the technique onto an enlarged spectrum of materials in the recent years have corroborated, that there is a noticeable difference between conventional selective laser sintering with continuous radiation (including pulsed continuous radiation) and laser micro sintering with a q-switched regime.

The important properties of this regime are the high intensity, the high fluence, and the short radiation period. Resulting effects in material processing are rapid heating, the generation of a plasma plume, and rapid cooling. All of these have proved advantageous for metal sintering. Additionally the tight localization of the sintering events provides for the high geometric resolution of metal and ceramic parts. The reduced risk of overflow due to the short radiation period facilitates the control of the process. Multi photon excitation due to the high intensity is possibly a factor, which eliminates the induction period of laser ceramic sintering with the denoted wavelengths.

Although since 2003 functional products have been and are produced already, the manifold other side effects of the process regime have not been investigated to its full extent. Condensing the powder and the sintered material, breaking of the tensions during sintering, precision of the resolution, are certainly only a few of the vast range of process features and new findings can be expected constantly.

Since the beginning of 2005 oxide ceramics are selectively sintered with a special variation of the procedure and a modified type of the equipment. High firmness of some of the specimens promises the first functional tests in the short range future. Non-oxide ceramics micro sintering is investigated currently. In the treatment of ceramics – both oxide and non-oxide – not only change of the aggregation state but also dissociation, recombination and further reactions have to be dealt with. Absorption also is not as trivial as in the case of metals.

In the present situation contemplations can be made on the opening of new development issues. Powders with grain sizes in the 10 nanometer region become available from a growing number of materials. Laser micro sintering will be predestined for the selective sintering of these particles. New effects are expected. Another class of powders is the polymers, the micro sintering of which also appears very promising once powder coating problems have been solved.

As far as laser sources and regimes are concerned, it can be anticipated, that with the availability of new high powered lasers with high beam qualities, the described properties of a q-switched pulse can also be generated by fast switching of cw-radiation. Additionally the shaping of such pulses should be much easier which will open new possibilities to study the process and elucidate its mechanism.

Appreciations

The research and development of laser micro sintering was supported within the scope of the cooperative project #02P1110 *Vakuum-SLS* promoted by Deutsches Bundesministerium für Bildung und Forschung which expired in 2004. Part of the presented results belong to a project supported by the European fund for regional development (EFRE) 2000-2006 in the course of technology promotion and by funds of the “Freistaat Sachsen”. Our current industrial partners are caddental GmbH (Mittweida, Germany) 3D MICROMAC AG (Chemnitz, Germany) IVS Solutions AG (Chemnitz, Germany). We also use the opportunity to thank all our former industrial partners, not mentioned so far, for the prolific cooperation.

References

- [1] Hauser, C.; Childs, T.H.C.; Dalgarno, K.W.; Eane, R.B. 1999, ‘Atmospheric Control during Direct Selective Laser Sintering of Stainless Steel 314S powder’, in D. L. Bourell et al. (eds), *The Proceedings of the 9th Annual SFF Symposium*, 1999, pp. 265–272.
- [2] Regenfuss, P.; Hartwig, L.; Klötzer, S.; Ebert, R.; Exner, H. 2003, ‘Microparts by a Novel Modification of Selective Laser Sintering’, *Rapid Prototyping and Manufacturing Conference*, May 12– 15, 2003, Chicago (IL).
- [3] Regenfuss, P.; Hartwig, L.; Klötzer, S.; Ebert, R.; Exner, H. 2004, ‘Microparts by a Novel Modification of Selective Laser Sintering’, *SME Technical paper TP04PUB185*.
- [4] Ebert, R.; Regenfuss, P.; Hartwig, L.; Klötzer, S.; Exner, H. 2003, ‘Process Assembly for μm -Scale SLS, Reaction Sintering, and CVD’, *4th International Symposium on Laser Precision Microfabrication*, June 21-24, 2003, Munich, *Proceedings of SPIE*, vol. 5063, pp. 183-188.
- [5] Exner, H.; Regenfuss, P.; Hartwig, L.; Klötzer, S.; Ebert, R. 2003, ‘Selective Laser Micro Sintering with a Novel Process’, *4th International Symposium on Laser Precision Microfabrication*, June 21-24, Munich, *Proceedings of SPIE*, vol. 5063, pp. 145-151.
- [6] Regenfuss, P.; Hartwig, L.; Klötzer, S.; Ebert, R.; Brabant, Th.; Petsch, T.; Exner, H. 2005, ‘Industrial freeform generation of micro tools by laser micro sintering’, in D. L. Bourell et al. (eds), *The Proceedings of the 15th Annual SFF Symposium*, 2004, pp. 214–219.
- [7] Regenfuß, P.; Ebert, R.; Klötzer, S.; Hartwig, L.; Exner, H.; Brabant, Th.; Petsch, T. 2004, ‘Industrial laser micro sintering’, *Proceedings of the 4th LANE 2004*, Sept. 22.-24 2004, Erlangen, pp. 413-424.
- [8] Regenfuss, P.; Hartwig, L.; Klötzer, S.; Ebert, R.; Brabant, Th.; Petsch, T.; Exner, H. 2005, ‘Industrial freeform generation of micro tools by laser micro sintering’, *Rapid Prototyping Journal*, Jan. 2005, vol. 11, no. 1, pp. 18-25.
- [9] Bogaerts, A.; Chen, Z.; Gijbels, R.; Vertes, A. 2003, ‘Laser ablation for analytical sampling: what can we learn from modeling?’, *Spectrochimica Acta*, part B, vol. 58, pp. 1867-1893.
- [10] Miotello, A.; Kelly, R. 1995, ‘Critical assessment of thermal models for laser sputtering at high fluences’, *Appl. Phys. Lett.*, vol. 67, no. 24, pp. 3535-3537.

- [11] Lu, Q. 2003, 'Thermodynamic evolution of phase explosion during high-power nanosecond laser ablation', *Physical Review*, part E, vol. 67, no. 016410, pp. 1-5.
- [12] Amorim, F.L.; Weingaertner, W.L. 2004, 'Die-Sinking Electrical Discharge Machining of a High-Strength Copper-Based Alloy for Injection Molds', *J. Braz. Soc. of Mech. Sci. & Eng.*, vol 26, no. 2, pp 138-144.
- [13] 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.
- [14] Vail, N.K.; Barlow, J.W.; 1992, 'Ceramic Structures by Selective Laser Sintering of Microencapsulated Finely Divided Ceramic Materials', *Solid Freeform Fabrication Symposium Proceedings*, vol. 3, pp. 124-130.
- [15] Beaman, J.J.; Barlow, J.W.; Bourell, D.L.; Crawford, R.H.; Marcus, H.L; McAlea, D.P. 1997, 'Solid freeform fabrication, a new direction in manufacturing', Dordrecht, Kluwer.
- [16] Castle Island Co. REV 1a. 2003, 'RP's frequently asked Questions'. Retrieved: August 20, 2004, from <http://home.att.net/~castleisland/faq/faq220.html>.
- [17] Shellabear, M.; Nyrhilä, O. 2004, 'DMLS-Development history and state of the art', in M. Geiger & A. Otto (eds), *Laser Assisted Netshape Engineering 4*, *Proceedings of the 4th LANE 2004*, September 21-24 2004, Erlangen, Germany, Bamberg-Meisenbach, ISBN 3-87525-202-0, pp. 393-404.
- [18] Petzold, J. 1999, 'Porzellanmusterherstellung mit Hilfe der Lasersinterung', *Keramische Zeitschrift* vol 51, no. 6; pp. 450 – 454.
- [19] Li, X.; Crocker, J.; Geiss, E.; Shaw, L.; Marcus, H.; Cameron, T. 2000, 'Evaluation of Microstructure and Properties for Multi-Materials Laser Densification of Dental Restorations', in D. L. Bourell et al. (eds), *The Proceedings of the 11th Annual SFF Symposium*, 2000, pp. 159–167.
- [20] Görke, R.; Krause, T.; Günster, J.; Ries, C.; Heinrich, J.G., 2000, 'Laser Assisted Sintering of Porcelain' in: J.P. Sing, N.A. Bansal, K. Niihara (eds.): *Innovative Processing and Synthesis of Ceramics, Glasses and Composites III*, *Ceramic Transactions*, vol. 108, pp.91-96.
- [21] Li, X.; Wang, J.; Augustine, A.; Shaw, L.L.; Marcus; H.L. 2004, 'Microstructure Evaluation for Laser Densification of Dental Porcelains', in D. L. Bourell et al. (eds), *The Proceedings of the 15th Annual SFF Symposium*, 2004, pp. 195–202.
- [22] Klocke; F.; McClung, A.; Ader, C. 2004, 'Direct Laser Sintering of Borosilicate Glass', in D. L. Bourell et al. (eds), *The Proceedings of the 15th Annual SFF Symposium*, 2004, pp. 214–219.
- [23] Exner, H.; Hartwig L.; Streek, A.; Horn, M.; Klötzer, S.; Ebert, R.; Regenfuss, P. 2006, 'Laser Micro Sintering of Ceramic Materials', *Ceramics Forum International*, *Berichte der deutschen keramischen Gesellschaft*, submitted.
- [24] Exner, H.; Regenfuß, P.; Ebert, R.; Hartwig L.; Streek, A.; Klötzer, S.; Horn, M. 2006, 'Lasermikrosintern von keramischen Materialien', *The Proceedings of the Rapid.Tech, users' conference for rapid technology*, Erfurt (Germany), 2006.
- [25] Streek, A; Regenfuss, P.; Ullmann, F.; Hartwig, L.; Ebert, R; Exner, H. 2006, 'Processing of Silicon Carbide by Laser Micro Sintering', in D. L. Bourell et al. (eds), *The Proceedings of the 17th Annual SFF Symposium 2006*, submitted.