# Bodies of Cermet-Like Materials by Laser Micro Sintering

M. Horn*, P. Regenfuß*, H. Exner*

* LHM, Hochschule Mittweida, 09648 Mittweida, Germany

## Abstract

Cermet-like bodies have been generated by laser micro sintering from powder blends of copper, molybdenum, silica, and alumina. Originally developed for the realization of a crack-free transition zone between LTCC-material and an adjoining body of laser sintered molybdenum the mixture of metal and ceramics powders turned out a suitable feed stock for the generation of metal bodies containing horizontal insulating layers with high electrical resistivity. As the metal-ceramic powder blends also promised to allow for a high resolution of the laser sintered bodies, micro-structures were generated with two powder blends of metal and ceramic powders: the above mentioned molybdenum-silica-alumina system and a mixture of tantalum carbide and stainless steel. In the case of tantalum carbide and stainless steel dissociation of the carbide can be assumed. The resolution of the generated bodies was higher than that of a specimen generated from a nickel-chromium powder.

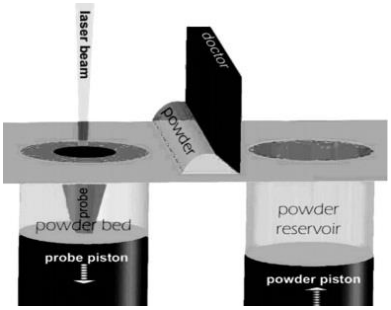
## Keywords

laser micro sintering, cermets, cemented carbides, mixed oxides

## Introduction

### *Laser Micro Sintering, an Additive High Resolution Fabrication Technology*

Laser micro sintering is a modification of selective laser sintering, which is based on repeated cycles of coating and selective densification (sintering) of powders or pasty materials with the ends of generating, layer by layer, a three-dimensional body. In accordance with the name, the sintering process is achieved by scanning a laser beam across the entire admeasurements of the intended object's cross-section (Fig. 1). Since its invention by Carl Deckard & colleagues [1] Selective Laser Sintering has been upgraded continuously to meet the requirements for the production of functional components [2]. In the beginning of the first decade after 2000 the improvement of the resolution seemed to have reached its limit at about 100µm [3]. In early 2003 Laserinstitut Mittelsachsen e.V. (Germany) presented an innovative modification, named Laser Micro Sintering, that made it possible to improve the resolution of selective laser sintering considerably below the limits commercial SLS devices had been confined to [4]. Meanwhile the smallest generated structures measure about the diameter of the applied laser focus (~12 µm).

(a) 

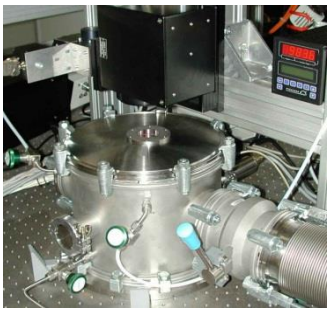
(b) 
(c) 

Figure 1: (a) Schematic of a laser sintering device; (b) doctor substituted by cylinder; (c) vacuum tight casket.

The early source of the laser pulses was a q-switched Nd:YAG – laser (λ = 1064nm) in TEM00 mode [4], lately multimode pulses and other lasers with various wavelengths are used. A beam scanner with a scan field of 25mm x 25mm steers the pulses across the powder coating. Q-switched pulses were finally chosen because of their special effects on the powder material [5,6]. Since 2001 sinter machines have been upgraded for specific requirements of laser micro sintering. The powder coating mechanism now consists of a cylindrical ring that sweeps a small amount of powder across the powder bed by the circular motion of a lever, leaving a thin powder layer that is sintered according to the respective cross section of the projected body. The process can be performed in a vacuum tight casket with a window in the lid for the incident radiation. Within this casket, the process can be conducted under a controlled and pure atmosphere, which is sometimes preferable to conducting the process under environmental conditions. Next to metal powders also ceramic powders (non-oxidic and oxidic) have been processed [7]. For laser micro sintering of oxidic ceramic powders wavelengths shorter than NIR had to be applied.

***Cermets***

Cermet is a common name for a composite material consisting of ceramic and metallic materials. Ideally, cermets are expected to feature the sum of the optima properties of its components. These are high strength, high temperature resistance, fracture toughness through the ability to undergo noticeable but limited plastic deformation, and also, beyond this limit, the properties of stiffness and hardness. In this strict sense, both components essentially should remain in their original phase, which implies the embedding of the reinforcing phase into a matrix material. In the case of the cemented carbide system WC/Co the volume partition of the matrix varies between 2 vol% and 50 vol% of the total solid volume with the mostly used ratio around 15 vol%, depending on the intended application [8].
Considering that the voids in an ideal sphere packing are about 26 vol% of the unit cell volume, the reinforcing particles cannot be embedded in most of the majority of cemented carbide composites in the sense of “enclosed”. The matrix will rather have the function of an interlocking agent, which on the other hand means limited chemical reaction on the nanometer scale at the phase interfaces.

***Motivation for the Implementation (Employment) of Cermet-like Powder Blends for Laser Micro Sintering***

The motivation for the engagement in laser micro sintering of bodies from cermet-like powder blends originated during attempts to supplement metal bodies with micro-structured ceramic parts or vice versa. It was one of the goals to supply substrates from low temperature cofired ceramics (LTCC) with microstructured metallic components. Repeated failures of the interconnection between the pure metal and the pure ceramic phases entailed a search for suitable intermediate compounds. The apparent approach was, to use a blend of metal and ceramic powders, with the ends to achieve a transition zone

with an approximately continuous gradient between the pure stages of the two adjacent materials. Besides the suitability of sintered compounds from those powder blends as bonds between metals and ceramics, two other features suggest these materials worthwhile for further investigation in laser micro sintering: The powder blends can be processed with NIR-radiation. This is contrary to most of the oxides that are used for ceramics and do not show considerable absorption of this wavelength range. Secondly, the sintering of the ceramic phase is mainly induced thermally, via the heated metal particles or agglomerates and thus is restricted to the vicinity of the metal entities. Therefore, undesired collateral melting (adjacent to the spot defined by the Gaussian radius) occurs to a lesser extent than during laser sintering of pure metal powder, or under the special regime that has to be applied for laser micro sintering of pure oxide-ceramic powders [7].
Regarding the achievable high resolution, the intention arose to investigate the possibilities of generating a high resolution part of ceramics or mixed oxides by laser sintering a metal powder blended with an oxidic ceramic and converting it into a ceramic part by subsequent furnace tempering or a metal part either by reductive sintering or by a subsequent reductive process.

## Materials and Methods

### *Powder Materials*

The ceramic component of all powder blends used for laser sintering cermets is a mixture of 80 wt % alumina and 20 wt % silica (“mullite-ceramic”) with particle diameters < 10 µm; in one case tantalum carbide was applied. Metal components were copper, molybdenum, or stainless steel with particle diameters between 3 µm and 5 µm.

### *Substrate Materials*

Substrate materials were aluminum or stainless steel for metal sintering and calcium silicate for ceramic sintering. In individual cases we used tempered LTCC (supplied by Via Electronics GmbH, Germany) or pure alumina.

### *Laser*

The probes were sintered with a 20 W Nd-YAG fiber laser from SPI Lasers Ltd., U.K.. The laser radiation has a wavelength of 1063 nm, a pulse frequency of 100 kHz and a pulse length of 200 ns was chosen. The laser optics had focal lengths of 56 mm and 100 mm.

### *Specific Laser Sinter Strategies*

In order to suppress side effects through thermal tension like warping, fissuring, and off-scaling of the sintered body the scan patterns for the laser beam were alternately chosen from the following three:
“Line-scan“ („Two-fold line-scan“):
The path of the laser beam describes a hatch of parallel lines with a spacing of 25 µm. The respective cross-section is scanned twice in succession, for the second scan the orientation of the hatch is rotated by an angle that is not an aliquot of 360° in order to avoid systematic errors.
„Square array“:
The specimen cross section that is to be sintered is divided into segments of 200 µm by 200 µm. The segments are sintered sequentially in a stochastic order. Depending on the required properties of the

product, the respective layers can be sintered comprehensively, or systematic or arbitrary voids can be spared.
„Hex array“:
The specimen cross section that is to be sintered is divided into hexagonal segments with an edge length of 200 µm. The segments are sintered in the same way as the square segments. Consecutive layers are shifted in the manner of the alternating layer positions in a cubic sphere packing.

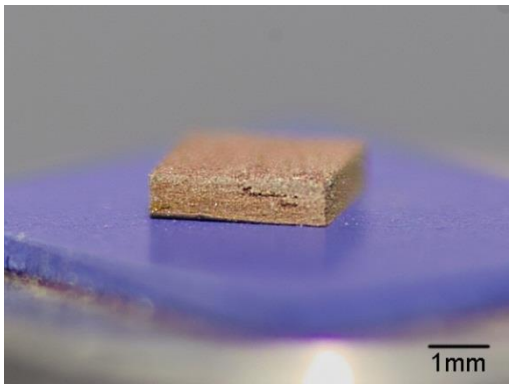
### *Tempering*

Some laser sintered specimens were subsequently tempered in a programmable high temperature tube furnace from GERO GmbH, Germany.

## Supplementation of Oxide Ceramic Bodies with Metallic Units

### *Laser Sintering of a Metal Body onto low Temperature Co-Fired Ceramics (LTCC)*

For the final goal of supplying an LTCC substrate with micro structured electric conductor, a copper block was built up by laser micro sintering onto an LTCC-slice that had been fired already to its final sinter stage (Fig. 2). The applied “line scan” strategy has proved unsuitable for the task, as only insufficient attachment of the metal block to the ceramic material could be achieved. The development of warps is especially favored by the applied sinter strategy. The cruising of the laser beam along successive parallel lines generates a heat wave with increasing temperature moving across the sinter layer at a 90° angle in respect to the lines. As the heat conductivity of the LTCC is in the range of 10 $Wcm^{-1}K^{-1}$, in the early phase of the sinter process the high thermal tension of the metal part as well as decomposition of the LTCC coincide into a detrimental effect (Fig.2a).
To prevent the sintered body from scaling off the substrate, the design of the metal supplement can be adapted to the process, in that pointed jags and narrow indentations of the contour are spared, which, of course, would mean to dispense with one of the main features of laser micro sintering, the high resolution. The application of sinter strategy that relies on segment-wise generation turned out the most expedient of all attempts to prevent the scaling. However, even with this solution deterioration of the resolution has to be taken into account. As already mentioned, the segments of the “square array” strategy have the dimensions 200 µm by 200 µm which then will be the lower resolution limit of the metal structure that is to be sintered onto the ceramic (Fig. 2b).

(a) 

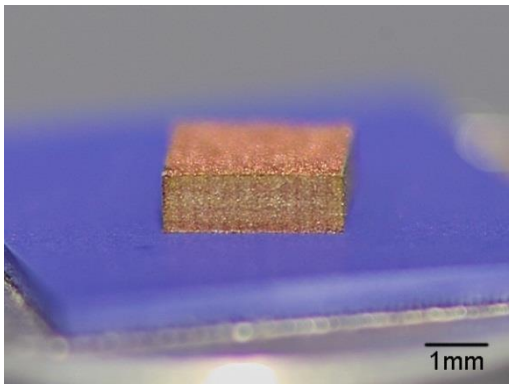
(b) 


Figure 2: (a) copper block sintered onto LTCC with a “two-fold line-scan” strategy; (b) copper bock, firmly attached to the LTCC-substrate via the “square-array” strategy.

### *Cermet Intermediate for the Attachment of the Sintered Metal Part to the Ceramic Substrate*

Both of the mentioned solutions are not really an answer to the problem of the insufficient joint between LTCC and the metal specimen because of the concomitant deterioration of the resolution. Therefore, assays with one or more mediator materials between metal and ceramics have been made.

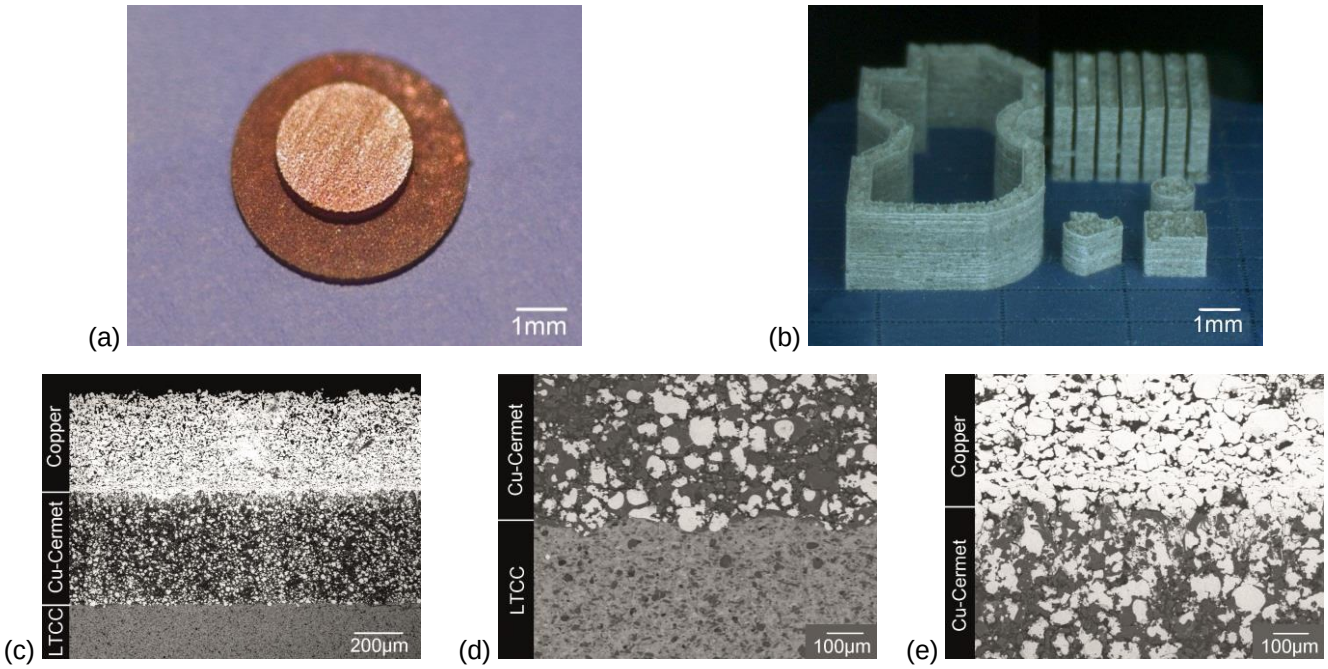



Figure 3: (a) triple sandwich of LTCC (bottom) / Cu-cermet / Cu (top). (b) laser sintered mullite-ceramics (grey) attached to LTCC (blue). (c-e) Cross section views of the interfaces in the triple sandwich LTCC/Cu-cermet/Cu.

Earlier experiments had shown that the mullite-ceramic mixture that had been used successfully for laser supported generation of micro-bodies from pure oxide ceramics [7] attaches tightly to the LTCC-sample (Fig. 3b), and copper is known to form easily composites with alumina. Consequently, the laser sintered mediator material from a powder mixture of “mullite-ceramic” and copper with a weight ratio of 1:1 proved to provide firm attachment of the metal part to LTCC (Fig. 3a). Cermets of same components with different weight ratios (down to a copper content of 2 wt %) are also applicable for this purpose, In the SEM view (Fig. 3c-e) the cross section of the triple sandwich LTTC/Cu-cermet/Cu shows tightly locked interfaces of the materials, although there are still minor horizontal fissures in the LTTC next to the interface. It should be possible to cure these fissures in an additional furnace tempering step with sinter temperatures between 800 °C and 850 °C that are commonly used for LTCC.

## Indirect Generation of Ceramic Parts from a Mullite/Molybdenum Cermet

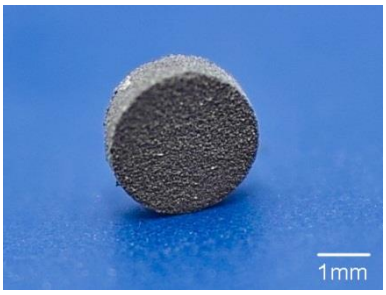
### *Attempt to Synthesize Mullite/Molybdenum Cermet by Laser Micro Sintering*

From diffusion bonding experiments the interfaces between mullite and molybdenum are known to feature strong interlocking and fracture strength [8]. The question arose if it was possible to take advantage of these cohesive properties for the generation of a firm laser sintered cermet body.
The laser sintered specimen for a mixture of mullite-ceramic and molybdenum powders with a weight ratio of 75:25 had a dark grey appearance (Fig. 4a), which is attributed to the presence of $MoO_2$. As had been expected, there were still metallic molybdenum entities in the compound even on the surface (Fig. 4b) although the laser sinter process had been conducted under environmental atmosphere. Lack of

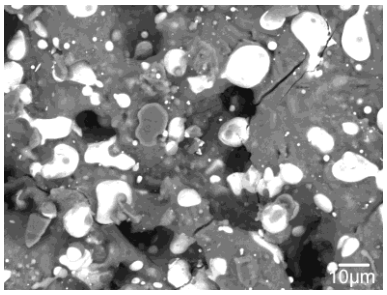
further oxidation is explained by the rapid laser sinter rate, and by the proposed reaction shield effect [7] that is typical for laser micro sintering. The cracks in the solid body occur preferentially in the ceramic material and not at the ceramic/metal interface.

As laser sintering, especially under normal atmosphere, is obviously no adequate technology to synthesize a mullite/molybdenum cermet the specimen was tempered at 1650 °C (for one hour after a heating rate of 300 °C $h^{-1}$) with the goal to obtain a crack-free body from a mixed oxide of the cations Al, Si, and Mo.

(a)




(b)

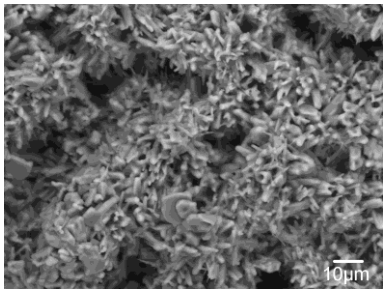



(c)

| EDX Analysis | |
|---|---|
| O | 43.32 % |
| Al | 23.61 % |
| Si | 10.21 % |
| C | 2.54 % |
| Mo | 20.31 % |

(d)


(e)




(f)

| EDX Analysis | |
|---|---|
| O | 48.79 % |
| Al | 39.08 % |
| Si | 9.67 % |
| C | 2.47 % |
| Mo | < 0.00 % |

Figure 4: (a) Laser sintered body of mullite/molybdenum cermet with a weight ratio of 75:25. (b) Surface SEM view of the body, as sintered. (c) EDX analysis of the material as sintered. (d) Specimen after additional tempering at 1650 °C. (e) Surface SEM view of the body after additional tempering. (f) EDX analysis of the specimen (results in at %) after additional tempering.

During sintering the color of the compound changed from a dark grey that is dotted with metallic entities to an almost homogeneous white. It also acquired a micro-grained porous modification. The comparison of the EDX-analyses (Fig 4c, f) shows that the content of molybdenum decreased from around 20 at% after laser sintering to a value below the detection limit after tempering. The increase of the atomic ratio of Al:Si from about 2.3 to 4.1 is evidence for loss of silicon or silica, additionally, and the loss of molybdenum at 1650 °C leads to the conclusion that no or at least no thermally stable mixed oxide between aluminum, silicon and molybdenum results, when the as laser sintered specimen (Fig. 4a) is tempered at 1650 °C.
The loss of molybdenum can be explained by evaporation of $MoO_3$ since the vapor pressure of this compound reaches the environmental pressure already at 1150 °C [9]. Conversion of $MoO_2$ and metallic molybdenum to $MoO_3$ in the as sintered body during tempering is assumed, as the equilibrium pressure of oxygen for the oxidation of $MoO_2$ to $MoO_3$ is $10^{-7}$ bar ($10^{-2}$ Pa) [8] and the tempering has been conducted under environmental atmosphere ($p_{oxygen}$ = 0.21 bar).

If the tempering at 1650 °C was continued, after six hours the entire material of the specimen had disintegrated and could not be detected any more. Presently, there is no coherent explanation for this. Comparable bodies that had been laser sintered from the pure mullite-ceramic powder could be tempered at the same temperature without noticeable loss of material.

Tempering at 800 °C, slightly above the fusion temperature of molybdenum, under environmental atmosphere also leads to the successive oxidation of the metal or $MoO_3$ to $MoO_3$, which has a vapor pressure at this temperature of 0.01 bar [9]. This is still sufficient for significant evaporation, but if the holding time is limited to 6 hours the micro-structured body, is preserved (Fig. 5).

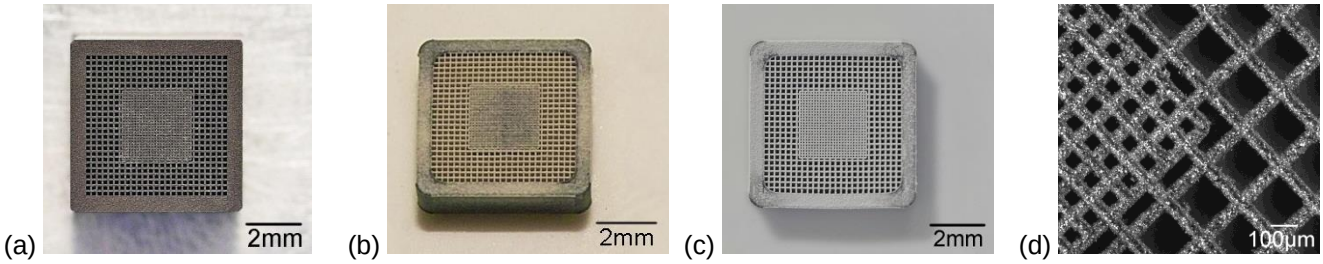



Figure 5: Micro grids of mullite/molybdenum cermet after various stages of tempering at 800 °C. (a) Un-tempered (b) After 1 h. (c) After 6 h. (d) Detail SEM micrograph of the as laser sintered specimen.

The weight gain after a holding time of 1 h is presently attributed to progressive oxidation of molybdenum. After 6 h, this gain is lost again due to assumed evaporation of $MoO_3$ (Table I).

Table I: Dependence of the mass balance on the holding time at 800 °C after ramping the temperature.

| Holding time | No tempering | 800 °C; 1 h | 800 °C; 6 h |
|---|---|---|---|
| Figure | Fig. 6a | Fig. 6b | Fig. 6c |
| Sample weight | 0.4749 g | 0.4881 g | 0.4763 g |
| Weight difference | 0.0 % | + 2.78 % | + 0.29 % |

## Reaction Sintering of Micro Structured Metal Bodies

Reductive treatment of a cermet with the ends of converting a cermet body into a metal part requires a successive reduction process. If considerable shrinkage has to be avoided, there is virtually only the option of a hydrogen treatment at elevated temperatures, which requires high instrumental effort.

### *Micro-Structured Component from a Powder Blend of Stainless Steel and Tantalum Carbide*

If laser micro sintering is conducted under normal atmosphere, the processing of a powder that contains metallic tantalum is impossible, as tantalum oxidizes rapidly. One way of avoiding the costs and effort of hydrogen reduction would be the laser generation of the micro-part from a powder that contains tantalum in form of TaC. The carbon content is capable of preventing the oxidation of tantalum and steel by consuming a certain amount of oxygen - the escaping CO respectively $CO_2$ enhancing simultaneously the reaction shield effect [7]. The expected higher resolution by cermet laser sintering compared to pure metal sintering can be regarded a beneficial side effect.

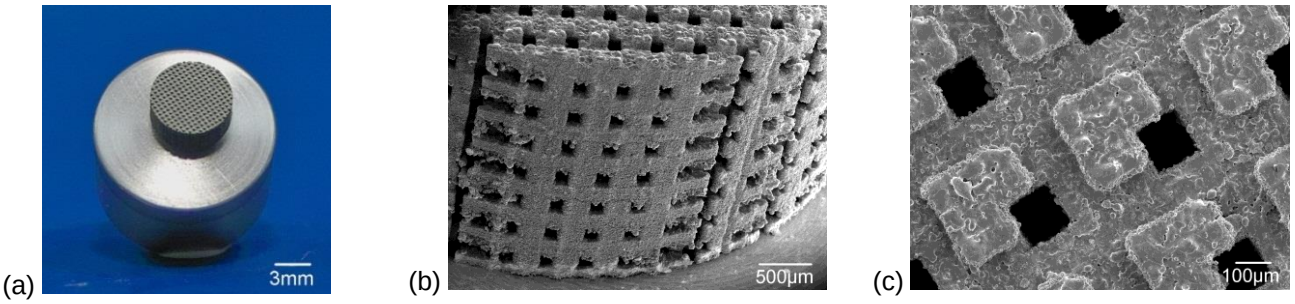



Figure 6: (a) Micropart from a stainless steel (1.4404) powder, blended with TaC. (b,c) Detail SEM views.

Fig. 6 shows a micropart (design by LUT-Metal, Lappeenranta, Finland), laser sintered from a stainless steel (1.4404) powder, blended with TaC with a steel-over-TaC mass ratio of 70:30 (volume ratio: 81:19).

Table II: EDX analysis of sintered material composite

| Element | Fe | Cr | Ni | Ta | O | **C** | Mo |
|---|---|---|---|---|---|---|---|
| Content [at %] | 59.6 | 17.7 | 7.6 | 5.7 | 4,9 | **3.4** | 1.2 |

Table II shows the EDX analysis of the material composite stainless steel 1.4404 + TaC (70:30) after laser sintering. The mere numbers do not prove that TaC has been reduced completely. However, the measured contents of oxygen and carbon correspond to the usual error values of samples that are free of these elements. On the other hand, laser sintered carbide-free stainless steel probes usually show a higher oxygen value, which gives reason to the conclusion that oxidation has been prevented by the carbide. Undoubtedly, further evidence and research is necessary for a final elucidation.

### *Classification of the Achievable Resolution*

In the introduction the hypothesis of a higher achievable resolution by cermet laser sintering is indicated in comparison to the processes performance with pure metal or pure ceramic powder. Fig. 7 shows SEM recordings of the probe described in Fig.6 and two additional probes following the design but generated from different materials: The first, a metal powder consisting of 90 wt % Ni80Cr20 alloy and 10 wt % molybdenum (Fig. 7a), and the second one the mullite/molybdenum cermet (weight ratio 75:25). All probes are in the as laser sintered stage without any additional processing. The resolution of the mullite/molybdenum cermet specimen with roughly 10 vol % metal in the original powder is the best (Fig. 7c). The poorest resolution is obtained with pure metal powder (Fig. 7a). The largest extent of collateral sintering can be observed in the cemented carbide probe 1.4404/TaC.

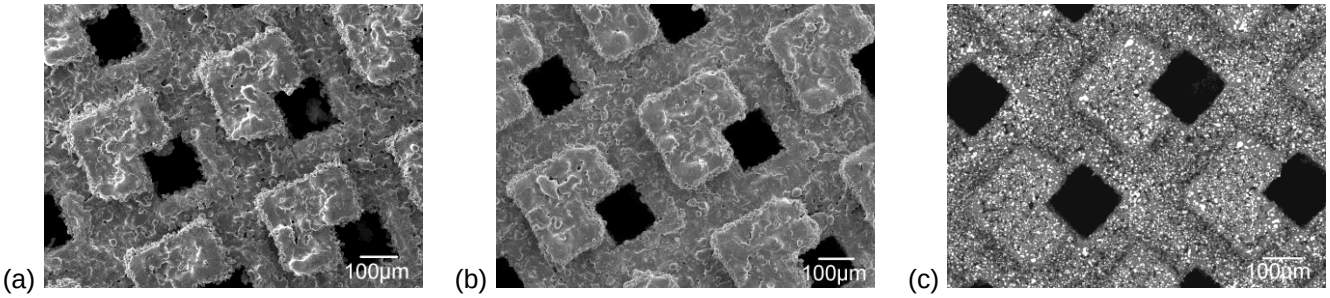
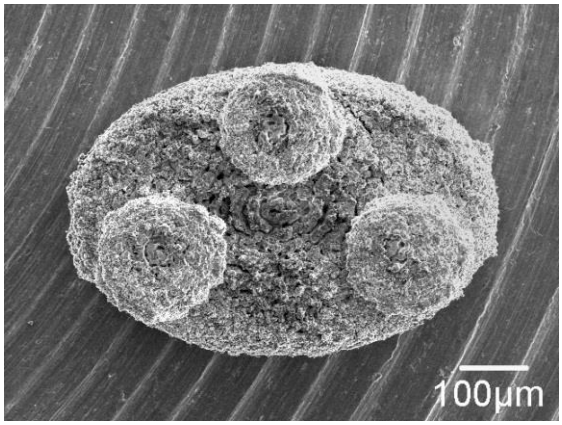



Figure 7: SEM recordings of microparts with the same design, generated from three different materials .(a) NiCr/Mo (b) Steel 1.4404/TaC(c) mullite/molybdenum cermet.

For the comparison of the resolution achievable with cermet and pure oxid ceramic, laser sintered specimens from mullite/molybdenum cermet and mullite ceramic are juxtaposed in Fig. 8.

(a) 

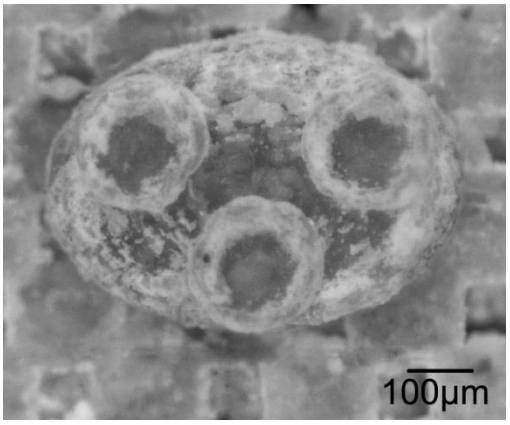
(b) 


Figure 8: Comparison of the material dependent resolutions (a) Mullite/molybdenum cermet. (b) Mullite-ceramic.

## Conclusion and Outlook

Mixtures of metal and ceramic powders have been employed for several purposes in laser micro sintering. The first objective was to produce mediator materials between a pure ceramic and a laser sintered pure metal body. In the case of mullite-ceramic on the ceramic side and copper on the metal side an intermediary body from a blend of both powders proved to fulfill the purpose.

Mullite/molybdenum powder mixtures could be laser sintered with a high resolution and dimensional exactness, and comparably low collateral melting. Attempts to homogenize the laser sintered specimen by tempering failed because of the high volatility of $MoO_3$. Experiments to volatilize specifically the molybdenum component resulted in the disintegration and evaporation of the entire material system.

Tantalum carbide, cemented with stainless steel 1.4044 was laser sintered. The low oxygen content of the specimen suggests that the carbide prevented oxidation of the steel during laser sintering under environmental atmosphere. The carbon signal of the elemental analysis did not yield inevitable evidence of carbide disintegration.

The presented study indicates applicative possibilities, and the experimental results demonstrate various material reactions of laser micro sintering with composite powders. Despite the intricacies of the material combinations, cermet laser sintering appears still a promising field of research with a vast range of possibilities.

## Acknowledgement

The research has been funded by of the German Bundesministerium für Bildung und Forschung within the program ProfUnt.

## References


1. C. Deckard, US patent 4,863,538. Filed: October 17, 1986, published September 5, 1989.
2. M. Shellabear and O. Nyrhilä, Proceedings 4th LANE 2004, Sept. 22.-24. 2004, M. Geiger and A. Otto Eds., Erlangen, Meisenbach-Verlag, Germany, ISBN 3-87525-202-0, 393-404 (2004).
3. Castle Island Co. REV 1a (2003): RP's frequently asked Questions. Retrieved: August 20, 2004, from http://home.att.net/~castleisland/faq/faq220.html.
4. P. Regenfuss, L. Hartwig, S. Klötzer, R. Ebert and H. Exner, Present. at Rapid Prototyping and Manufacturing Conference, May 12– 15, Chicago (IL), (2003).
5. P. Regenfuss, A. Streek, A.; L. Hartwig, S. Klötzer, Th. Brabant, M. Horn, R. Ebert and H. Exner, The Proceedings 17th Annual SFF Symposium, D. L. Bourell et al. Eds., Austin (TX), USA, 740-753 (2006).
6. .A Streek, P. Regenfuss, F. Ullmann, L. Hartwig, R. Ebert and H. Exner, The Proceedings 17th Annual SFF Symposium, D. L. Bourell et al. Eds., Austin (TX), USA, 349-358 (2006).
7. P. Regenfuß, A. Streek, F. Ullmann, T. Süß, L. Hartwig, M. Horn, Ch. Kühn, R. Ebert and H. Exner, cfi / Ber. DKG, 85, 65-72 (2008).
8. Retrieved: Feb 23, 2013 from http://www.allaboutcementedcarbide.com/02.html.
9. J.F. Bartolomé, M. Díaz, J.S. Moya, E. Saiz and A.P. Tomsia, *J. Eur. Cer. Soc*. **24**, 785–790 (2004).
10. D. Stull, Ind. Eng. Chem. 39, 517 (1947).