

PROCESSING OF METAL-DIAMOND-COMPOSITES USING SELECTIVE LASER MELTING

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Abstract

Powder-bed based additive manufacturing processes such as Selective Laser Melting (SLM) offer a huge degree of freedom, both in terms of part design and material options. In that respect, mixtures of different materials in powder form can offer new ways for the manufacture of materials with tailored properties for special applications. A promising field of applications is e.g. additive manufacturing of metal-based cutting or grinding tools with incorporated hard phases. For that purpose a feasibility study was performed concerning SLM of a Cu-Sn-Ti alloy powder, which is usually used for active brazing of ceramics and superhard materials, containing 10-20 vol.-% artificial, Ni-coated mono-crystalline diamonds. Even though the processing parameters were not yet optimized, stable specimens containing intact diamonds could be produced. First results on density and microstructure are presented and discussed.

Keywords: Selective Laser Melting, Hybrid materials, metal matrix composite, Diamonds, Microstructure

Introduction

Additive Manufacturing (AM) Technologies offer many advantages for the tool-less production of highly complex parts directly from CAD data. Powder-bed based processes - such as the Selective Laser Melting (SLM) process - allow the production of parts in a wide range of metallic materials. The cross-sections of the parts to be built are thereby selectively scanned into thin layers of powder material using a high power Nd-YAG laser source. There is a wide range of processable standard metal materials available. Stainless and hot-work steel [1, 17], Aluminium [2-4], Titanium [13] and Ni-based materials [12, 16] are typical metal classes. Consequently, such parts can be used in a wide field of industrial applications: From tooling industry, lightweight structures for automotive and aerospace, functionally optimized parts for diverse industrial and customized implants and instruments for medical applications.

A special field of application is the abrasive tooling industry, e.g. for grinding or cutting applications. They require materials with a special set of properties such as high wear resistance, good thermal conductivity, high material hardness and good chemical resistance. To fulfill and optimize these properties, measures can be taken on the material level and/or in structural optimizations of the tool itself, e.g. by incorporation of internal channels for local lubrication supply or tool cooling. Beside the advantage of AM for the manufacturing of complex shaped metallic parts, this powder based process offers a further potential for the

creation of new materials, e.g. Metal Matrix Composites (MMC), with improved and tailored properties. Applying these potentials of AM (SLM) in the tooling industry would therefore create a further potential to optimize tool durability both by tailored material properties (high thermal conductivity) and the incorporation of cooling channels and a local lubrication supply into the tools.

A good overview to currently used MMC-materials is given by Richardson [15], pointing out that mainly Ni- or Co-bonded WC is used in the manufacturing industry. Ding [7] created single-layers of brazed polycrystalline CBN particles on abrasive wheels using an active Cu-Sn-Ti brazing alloy. As the formation of AlN, TiN, TiB₂, TiB and TiAl₃ conforms to the chemical combination of polycrystalline CBN grains and the matrix material, good bonding of the diamond particles was achieved. Beside conventional MMC materials, diamond-containing surface coatings offer also interesting possibilities. In many cases, such coatings are produced today by electrochemical deposition methods. Buhl [5] used an active brazing alloy to bond diamond particles onto a steel substrate for grinding applications. In contrast, Kovalenko [9] created single-layers of steel- and nickel-bonded synthetic diamonds (with additional hard phases in the matrix material) on a steel substrate using a high power CO₂ laser. The very short interaction time of the laser beam with the diamond particles combined with the very high heating and cooling rates resulted in no thermal destruction of the diamonds, except for those with initial defects.

An interesting, alternative way to such new materials is the processing of mixtures of different powders, where specific hard phases are mixed with a metallic matrix material. Based on mentioned initial results, the SLM process seems to be well suited for the creation of metal-diamond composite materials. It can be expected that the high heating and cooling rates are at least similar to the ones of Kovalenko. An important difference however is the cyclic heating impact on diamond particles due to the layer-wise build process, which basically supports the tendency of diamond to graphitize. As natural diamond is known to graphitize at temperatures between about 1500°C in an inert atmosphere or vacuum and about 1000°C in normal air or in diamond-metal composites (Rabinkin [14]), a limitation of the melting temperature of the matrix material to values below about 1000°C is beneficial. Temperatures above might also be acceptable because the graphitization process is slow whereas the heating cycle is very short. To limit the melting temperature, Cu-Sn-Ti-Zr active brazing alloy with a comparably low melting point was selected. Such active brazing alloys are typical brazing filler materials to join diamonds to metals and ceramics, respectively.

In order to investigate the basic processability of metal-diamond composites by SLM, a feasibility study was performed using a mixture of Ni-coated natural diamond particles and the mentioned brazing alloy. This material combination is especially interesting for tooling applications, as the brazing alloy offers already a very high thermal conductivity, which might be even improved by the incorporation of diamond particles. In addition, a diamond-containing matrix material might also improve tool durability compared to the use of diamond-containing tool coatings.

The first results indicate that almost no graphitization of the diamond particles takes place during the successive heat input by the selective laser scanning process. Therefore, the diamond particles survive the SLM build process. The diamond particles are well bonded to the matrix material most probably due to the creation of a thin TiC interconnecting layer between the diamond particles and the matrix material. However, cracking phenomena in the matrix are resulting from either the different thermal expansion coefficients of the brazing alloy and the diamond particles and a not yet optimized alloy chemistry before the processing conditions of the SLM process. Therefore, a reduced Ti content would most probably sufficiently increase ductility of the matrix material.

Never the less, the SLM processing of metal-diamond composites seems to be an interesting and promising way to create new abrasive tools with added value in terms of internal and local lubrication supply, tooling temperature control and improved tooling durability.

Materials

Matrix material

The matrix material is a Cu-Sn-Ti-Zr active brazing alloy with the composition according to

Table 1. This alloy has been chosen for its beneficial thermal properties and high strength ($R_p \approx 550$ MPa and $R_m \approx 820$ MPa). Furthermore, Buhl [5] has successfully used this alloy to braze diamond particles on a steel substrate, achieving good bonding between the diamonds and the matrix material. This good bonding is due the 10 wt.% content of Titanium (and Zr) in the alloy, forming very stable and uniform epitaxial TiC-layers at the interface between the brazing alloy and the diamond particles, as pointed out by Rabinkin [14].

Table 1: Composition (wt.%) of the active brazing alloy “Diabrazo”

Composition	Cu	Sn	Ti	Zr
wt. %	73.9	14.4	10.2	1.5

According to the thermodynamic calculations by Wang [18], the selected ternary Cu-Sn-Ti-Zr system has a liquidus temperature of 925°C and the solidus temperature of 868°C. This is significantly lower than typical Fe-, Ni- or other alloys, thereby improving thermal stability of the embedded diamond particles during SLM-processing. In addition, the thermal conductivity of a Cu-Sn alloy is much higher than for other alloys. The Copper Alliance [11] published for a Cu-Sn12 alloy a thermal conductivity of $> 55 \text{ W(mK)}^{-1}$ at 20°C with a significant increase for higher temperatures. Even though an addition of Ti reduces the thermal conductivity somewhat, it is still much higher than e.g. for a Ni-alloy. This high conductivity supports the need for an as short thermal impact on the diamond particles as possible, thereby reducing the risk of graphitization.

The brazing alloy is available as a powder from spherical particles (Figure 1, left). The particle size distribution is $D_{10} = 7.6\mu\text{m}$, $D_{50} = 20\mu\text{m}$ and $D_{90} = 38\mu\text{m}$ (optically evaluated using the PowderShape software).

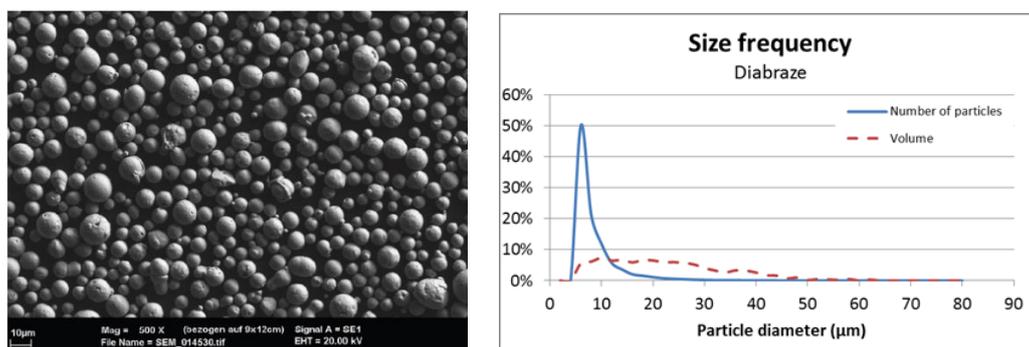


Figure 1: SEM of the Diabrazo powder material and particle size distribution

Diamond particles

The abrasive powder material that is mixed with the matrix material are Ni-coated diamond particles, where the Ni-coating accounts for 50-vol% (Figure 2) of the particles. The selection of Ni-coated diamonds should improve the thermal stability of the diamond cores during SLM-processing by forming a kind of a protective shield. The diamond particles were

measured and evaluated using the PowderShape software with regard to the particle size distribution and their shape parameters.

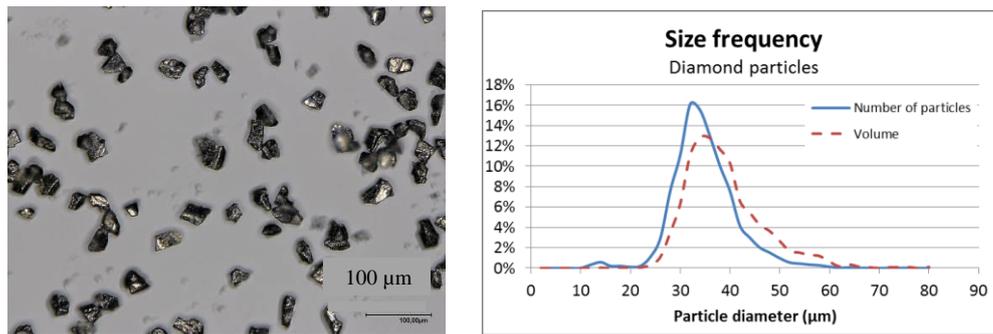


Figure 2: Diamond-Ni particles and corresponding particle size distribution.

Depending on the particle model, their sizes are $33.9 \pm 6.4 \mu\text{m}$ (cross-sectional area equal to circles) or $43.9 \pm 9.4 \mu\text{m}$ (biggest dimension of a particle), respectively. Their shape parameters are a convexity of 0.888 ± 0.03 and a Ferret ratio of 0.71 ± 0.11 . This will enable an abrasive effect for those particles that are embedded in the surface of a tool. Mixtures of 10 vol-% and 20 vol-% of Ni-coated diamond particles and the brazing alloy were created by manually mixing the corresponding powders.

Experimental Methods

SLM Machine

A SLM machine type ConceptLaser M1 was used, which is equipped with a Nd:YAG disk laser having a maximal laser power of 100W at the build platform and a laser spot diameter of about 0.2mm. The scan strategy used to produce the $10 \times 10 \times 7 \text{mm}^3$ test samples is unidirectional scanning, where the scan direction was turned by 90° for each layer. This scan strategy is close to the standard scan strategy used on ConceptLaser machines. The unidirectional scanning was applied instead of meander scanning in order to minimize heat concentration effects at the turning points of the scan vectors.

Processing of the active brazing alloy alone

In order to investigate a possible processing window for the Diabraz matrix material, several different parameter combinations were performed using the ranges given in Table 2, producing test cubes with a cross-section of $10 \times 10 \text{mm}^2$ and a height between 5mm and 7mm. For some samples the layers were scanned twice with the aim of increasing the density at a lower laser energy input.

The general aim was to reach qualitatively good samples without break-outs and with a high matrix material density. Processing was performed in protective atmosphere using Argon.

Table 2: SLM processing parameters to process Diabraz

	Laser power P_L (W)	Layer thickness t (μm)	Scan velocity v_s (mm/s)	Hatch distance d (mm)
Value / range	100	30	100 – 1'100	0.08, 0.1, 0.12

Builds were created on a steel platform, offering sufficient bonding between the brazing alloy and the steel platform.

Processing of Diabrazo with 10 to 20 vol% Ni-coated diamond particles

A DOE (Table 3) was performed with a selection of suitable processing parameters according to Table 2, producing $10 \times 10 \times 7 \text{ mm}^3$ test cubes. Processing was performed in protective atmosphere using Argon.

Table 3: SLM processing parameters to process Diabrazo with 10 vol% and 20 vol% Ni-coated diamond

	Laser power P_L (W)	Layer thickness t (μm)	Scan velocity v_s (mm/s)	Hatch distance d (mm)
Value / range	100	30	700 – 1'100	0.09, 0.1, 0.11

Sample Characterization

For SEM analysis selected specimens were prepared by cross section cutting using an Accutom automatic precision cut-off machine (Struers) at low force and 3000 rpm. For detailed analysis, cross section Ar ion milling was applied on the cutting surfaces of the free standing parts using an IM4000 (Hitachi). This preparation removes contamination and smearing effects from mechanical cutting operation and produces clear cross sections of the embedded diamonds. For SEM characterization an XL-30 ESEM-FEG (Philips) equipped with SE and BSE detectors was used at an accelerating voltage of 20kV. The phase analysis using XRD was performed on the top surface of the specimens using a Bruker D8 DISCOVER with $\text{Cu K}\alpha$ radiation.

Results and discussion

Density and microstructure of the matrix material Diabrazo alone

A high material density in the range of $>95\%$ can be achieved with the development of an appropriate laser energy input and processing strategy (Figure 3).

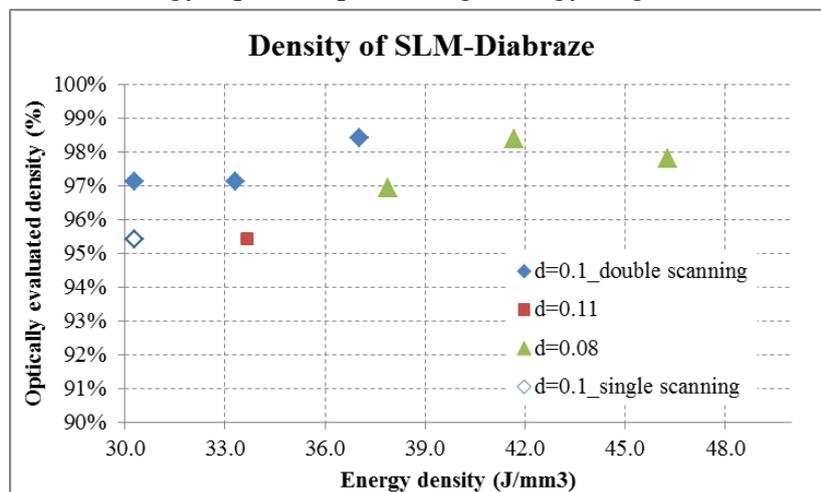


Figure 3: Optically evaluated density of SLM-processed Diabrazo matrix material

The density was measured based on the analysis of the black content (corresponding to the pores) of micrographs using the ImageJ software. The quality of the created builds depends highly on the applied laser energy density. Best density was achieved with an energy input in the range of $E_L \approx 42 \text{ J/mm}^3$, a hatch distance of 0.08mm and single-scanning. Applying double scanning with an energy input of $E_L \approx 33 \text{ J/mm}^3$ to 37 J/mm^3 and a hatch distance of 0.1mm increased the density significantly, however, resulted also in heat concentration effects in the part's corners (Figure 4).



Figure 4: Diabrazed samples. Bad sample produced with double scanning (left); good sample processed with $P_L=100\text{W}$, $d=0.11\text{mm}$ and $v_s=900\text{mm/s}$ (centre, right)

However, although quite high material density is achievable, the material tends to crack with crack orientation along the build direction (z-axis), as shown in Figure 5.

Energy input $E_L = 37\text{ J/mm}^3$, double scanning, $d = 0.1\text{mm}$



Energy input $E_L = 30.3\text{ J/mm}^3$, single scanning, $d = 0.1\text{mm}$



Energy input $E_L = 30.3\text{ J/mm}^3$, double scanning, $d = 0.1\text{mm}$



Figure 5: Cross-sections of Diabrazed samples with different specific energy input E_L , double and single scanning, but the same hatch distance d .

The results shown in Figure 3 and Figure 5 indicate a clear positive effect of the double scanning procedure on the density and the occurrence of cracks. A density increase in the range of about 1.5% to 2% was achieved (see Figure 3). On the other hand, the related increased energy input leads to unwanted heat concentration effects especially at locations with a reduced heat dissipation (corners, Figure 4 left), which might also be negative for the diamond particles (graphitization). For this reason the single-scanning procedure was applied for the processing of Diabrazed with diamonds.

Diabrazed samples with embedded diamond particles

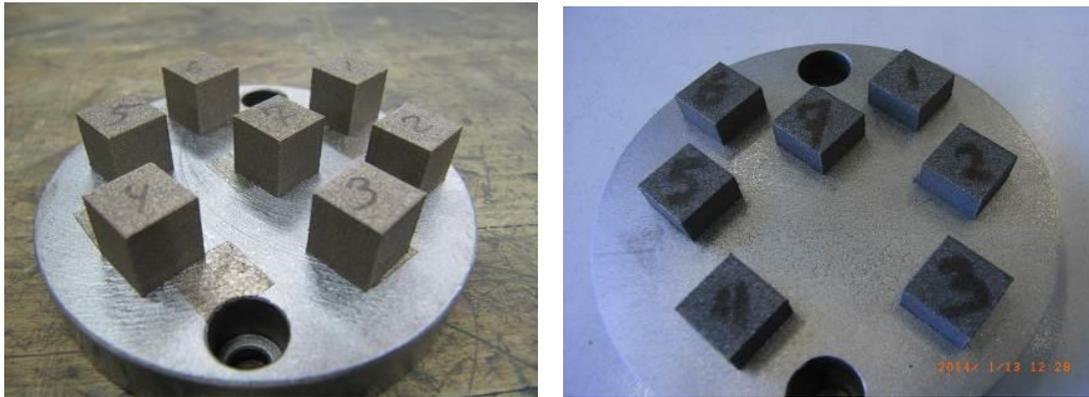


Figure 6: SLM-samples of Diabrazed with 10 vol% diamond (left) and 20 vol% Ni-coated diamond (right)

Figure 7 shows the SEM-micrographs of the Diabrazed samples with 10Vol% Ni-coated diamond particles processed with an energy input of 40.4 J/mm^3 and 50.5 J/mm^3 , respectively. Some residual porosity as well as cracks are visible in the matrix of both samples. Compared to the results of the brazing alloy without diamond particles at $E_L = 40.4 \text{ J/mm}^3$ (Figure 7, left), this porosity is somewhat higher. It is expected that this is a result of the effect of the Ni-coating, which acts as an additional heat sink, thereby reducing the energy available for the matrix. Therefore, the energy input required for a same material density as without diamond particles is increased.

The bright horizontal lines in Figure 7 are an artefact from the mechanical cutting process. Lines radiating from the top surface of the specimens are caused by the ion cross section milling. The dark dots represent the diamonds, which are homogeneously distributed in the matrix. Obviously, the majority of the diamonds survived the SLM process almost unchanged.

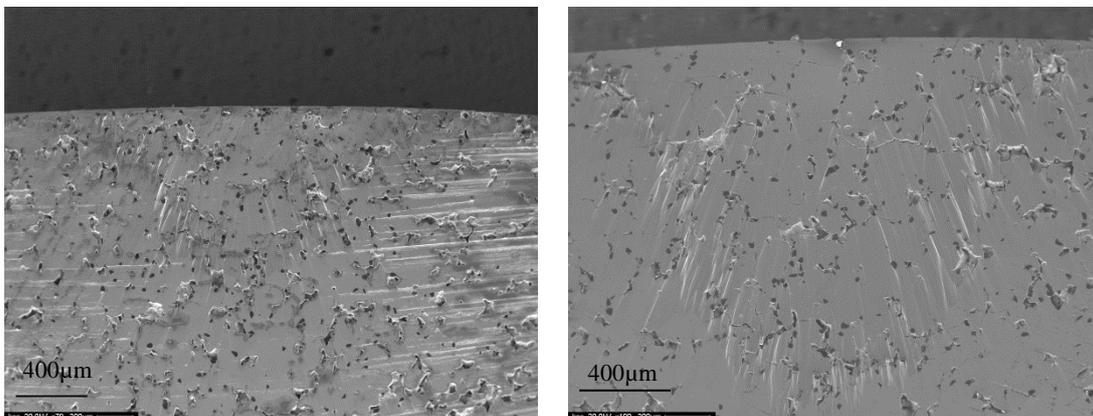


Figure 7: SEM (SE) - Micrographs of SLM-samples of Diabrazed with 10 vol% Ni-coated diamond, energy input $E_L = 40.4 \text{ J/mm}^3$ (left) and $E_L = 50.5 \text{ J/mm}^3$ (right).

The microstructures of the Diabrazed samples with 20 vol% Ni-coated diamond look similar to the ones containing 10 vol% diamond, although more and larger pores in comparison with the 10 vol% samples are visible (compare Figure 7 and Figure 8).

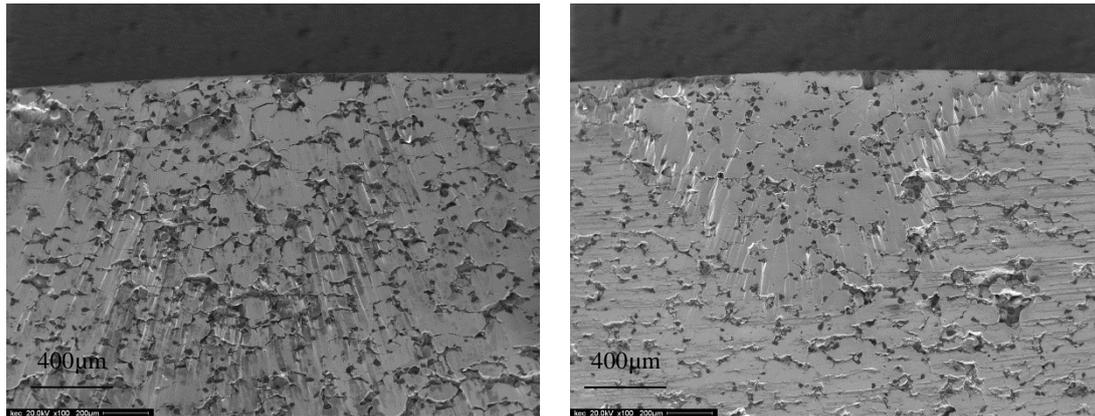


Figure 8: SEM (SE) - Micrographs of SLM-samples of Diabrazed with 20 vol% diamond, energy input $E_L = 30.3 \text{ J/mm}^3$ (left) and $E_L = 41.2 \text{ J/mm}^3$ (right).

Figure 9 shows the SEM-BSE micrographs of the 10 vol% and 20 vol% samples at a lower energy input E_L . The diamonds are fully embedded in the Cu-Sn-Ti-Zr matrix. In the left figure cracks that have formed in the vicinity of the diamonds as well as unmolten powder particles are visible. The Ni-coating of the diamonds seems to have completely dissolved in Diabrazed during the SLM-process. In both figures, a greyish phase which either appears as small dots or as elongated lines can be seen in the matrix between the diamonds (Figure 9). It is assumed that these are Ti carbides that have formed due to the reaction of the Ti from the matrix material with the carbon from the diamonds. The outer part of the diamonds obviously partly dissolves in the matrix during the SLM-process. Previous studies of Klotz [8] of the interface reactions during brazing of diamonds with Diabrazed have shown that a TiC reaction layer with a thickness between 60 and 150 nm forms at the interface between the diamond and the matrix. However, no clear reaction layer could be observed in the SLM samples so far. Due to the presence of the Ni coating on the diamonds and due to the very short interaction times of the diamond particles with the liquid alloy, it is assumed that only a very thin TiC layer might have formed which cannot be seen in the SEM.

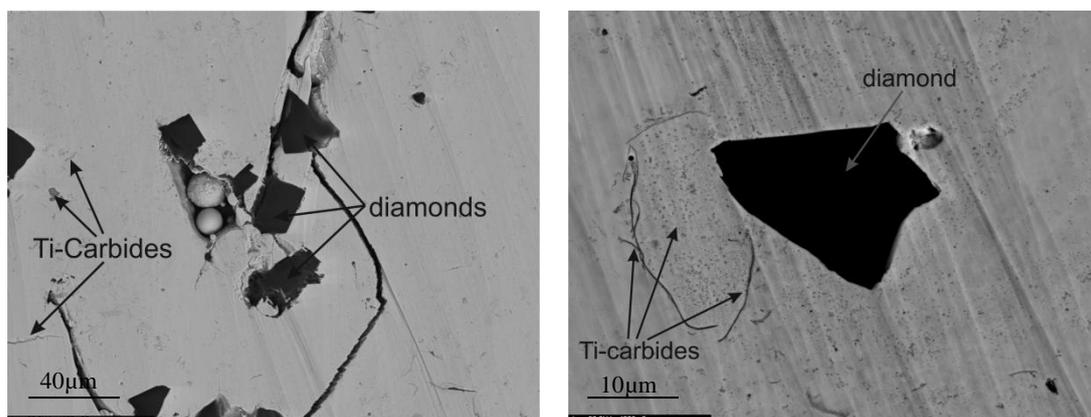


Figure 9: SEM (BSE) – micrographs; Diabrazed with 10Vol% Diamond, embedded diamonds with cracks in the matrix (left); Diabrazed with 20Vol% Diamond; intact diamond embedded in the matrix surrounded by TiC particles (right)

Figure 9 clearly shows that the diamonds remained in the matrix after SLM-processing, which is also indicated by the small peaks in the XRD spectra (Figure 10). The XRD spectra also indicates that the matrix consists of a mixture of a Cu in solid solution and $(\text{Cu},\text{Sn})_3\text{Ti}_5$ with Cu as the main phase.

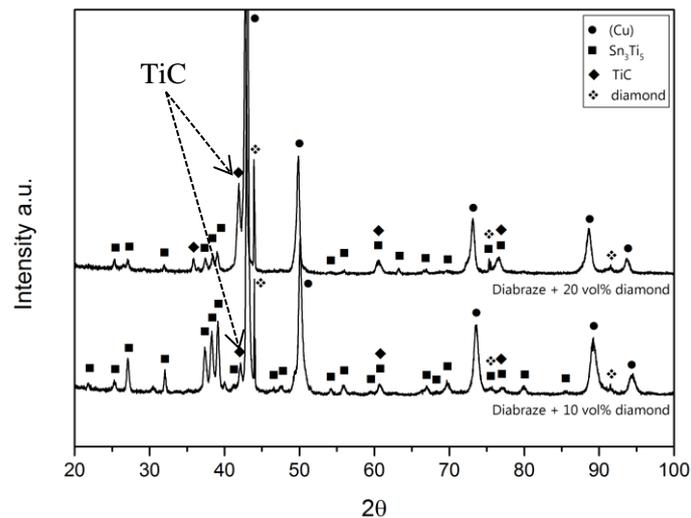


Figure 10: XRD-spectra of Diabrazed with 10 vol% Diamond (bottom) and 20 vol% Diamond (top). The identified phases are indicated.

Some smaller peaks representing TiC (◆) could be identified. These peaks were more pronounced in the samples containing 20Vol% diamond, indicating that more TiC has been formed (indicated in Figure 9). The results confirm the observations from the SEM investigations mentioned above. Ni could not be observed in the XRD spectra due to the very low Ni content, which is below the detection limit. However, Ni could be detected in the matrix by an additional EDX analysis.

Conclusions

From this feasibility study on the processing of an active brazing alloy with incorporated Ni-coated diamond particles, the following main conclusions can be taken.

- It is principally possible to process a Cu-Sn-Ti-Zr active brazing alloy with SLM, reaching a high material density. However, the used alloy chemistry is not yet optimized for a use in the SLM process, where significant internal stresses are known to arise, as pointed out by e.g. Kruth et.al. [10] and Cloots et.al [6]. Consequently, due to the brittle material behaviour cracking phenomena occur. Therefore, a lower Ti-content would be beneficial, leading to a more ductile matrix material with a correspondingly lower cracking tendency.
- The cyclic heat impact on the diamond particles, which is a result of the layer-wise SLM build process, does not lead to their graphitization. This is a result of the comparably low melting temperature of the active brazing alloy and its high thermal conductivity, which limits the heat impact significantly.
- The diamond particles are well bonded to the matrix material, most probably by the formation of a very thin TiC-layer around the diamond particles. This however is not yet approved and needs further analysis.
- The Ni-coating is fully dissolved in the matrix material, which has been confirmed by EDX measurements. We expect that the Ni-coating acts as an additional thermal prevention of the diamond particles (thermal heat shield).

Outlook

These basic observations encourage the use and further development of additively manufactured tooling materials with incorporated diamond particles. An assessment will be performed in order to qualify the abrasive properties of the SLM built tooling material against conventional grinding tools.

Furthermore, as the matrix material is not yet optimised with regard to the incorporated hard phases (diamonds) and the SLM process, specific material development is needed in order to improve the material performance.

Acknowledgements

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