Manuscript refereed by Dr Leo Prakash (WTP Materials Engineering, Germany)

Additive Manufacturing of Hardmetals

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Abstract

Additive manufacturing of polymer, metal and ceramic materials is more and more common. For hardmetals however, little work has been reported so far. Since most additive manufacturing methods are based on melting or lithography-based processes, they cannot be used for hardmetals due to the fact that hardmetals neither completely melt nor that they are transparent for the used wavelengths. Furthermore the high density of hardmetals based on tungsten carbide leads to problems with manufacturing of fine and complex structures and manageability of printed parts. Yet, the implementation of additive manufacturing in the field of hardmetals would undoubtful enhance the possibility to produce complex shaped parts which cannot be produced by conventional means and also to produce parts within hours instead of days because of the tool-free production technology.

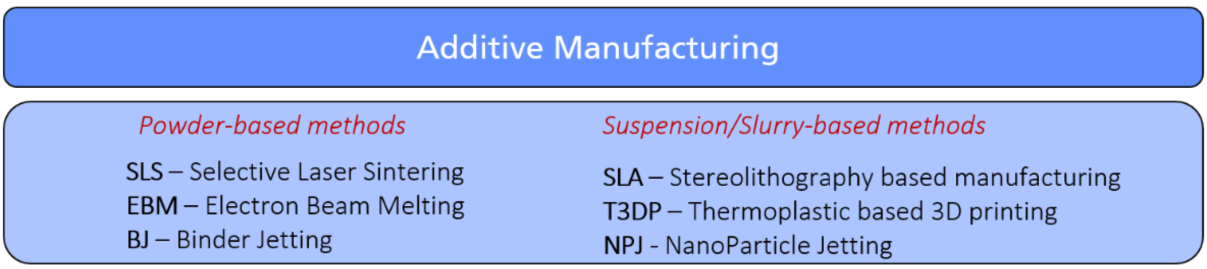
Thus, within this study limitations of additive manufacturing of hardmetals in general as well as for three dedicated manufacturing methods are investigated. These include the two powder based methods of 3D binder jetting and selective laser sintering and the suspension based method of thermoplastic 3D printing.

Overview of hardmetal and additive manufacturing

Hardmetals consists of a ceramic hard phase and a metallic ductile phase. The most commonly used component of the hard phase is tungsten carbide (WC) and the metallic ductile phase cobalt (Co). Properties of WC-Co hardmetals are primarily determined by the WC grain size and the Co content. Typical Co contents range from 2 wt.% Co to 20 wt.% Co and the WC grain sizes range from 0.1 to approx. 6 µm. Hardness increases with decreasing WC grain size and decreasing Co content and fracture toughness increases with increasing WC grain size and increasing Co content.

Even though by conventional manufacturing technologies like uniaxial dry pressing, extrusion or metal injection molding (MIM) more and more complex and detailed parts can be produced, parts with very complex inner and outer structure are impossible to produce. Additive manufacturing (AM) technology routes allow to address these limitations. Here very complex geometries can be realized. Since no tools are needed during additive manufacturing also no differences in tooling cost per part occur for producing one single special part or thousand identical parts. All additive manufacturing techniques have in common that they use as source a three dimensional (3D) file created by a computer aided design (CAD) program. The actual building or the often also as "printing" described manufacturing step of the parts is always done layer by layer. The most common methods for the additive manufacturing of metals or ceramics are divides into different groups, as shown in Figure 1.

Figure 1: Different additive manufacturing methods used for metals and ceramics



The processes within the powder bed group create green parts by selective densification of powder particles in the powder bed. Here relevant AM processes are Binder Jetting (BJ), Selective Laser Sintering (SLS)/Selective Laser Melting (SLM) and Electron Beam Melting (EBM). Advantages are that one can create complex structures with undercuts and complex shaped inner structures such as cooling channels as well as that usually none or just a basic supporting structures are necessary during printing. Disadvantages are that one always has to remove the residual powder and that, due to the reason thatone is not able to remove the remaining powder, closed inner structures are not possible.

Processes within the suspension based AM group create green parts by localized droplets or filament deposition of a powder polymer mixture. Relevant AM processes are Thermoplastic Three-Dimensional Printing (T3DP) [1,2], Drop On Demand (DOD), NanoParticle Jetting (NPJ), Fused Deposition Modeling (FDM)/Fused Filament Fabrication (FFF), Material Jetting (MJ) and Stereolithography (SLA). The advantages of all these methods with high or low viscosity of the suspension is the ability to create green parts with a high green density and in some cases also to realize 3D printed multi material composite parts. Disadvantageous is that complexes structures with an overhang and holes are only possible with supporting structures.

When looking exclusively at hardmetals the following aspects have to be considered for choosing the right AM technology:

1. Hardmetals consist of around 90 wt.% of the ceramic hard phase Tungsten Carbide (WC)
2. WC cannot be molten, but decomposes above ≈ 2800 °C [3]
3. Cobalt has a low vapor pressure
4. Since WC has a density of 15.67 g/cm³ 3D printed green parts are quite heavy
5. WC is not transparent for any wavelength.

Under consideration of these aspects, the following AM technologies can be regarded as not being suitable for the AM of hardmetals:

<u>EBM:</u> Due to the high energy input which leads to decomposition of WC and due to the needed ultra-high vacuum which leads to a high amount of Co being evaporated during the printing process.

<u>SLA:</u> Since WC is not transparent for any wavelength of light, no photo optic hardening effect can be used to produce stable green parts.

Results for the production of hardmetals using different AM techniques

The most frequently studied AM technology for the production of hardmetals is <u>Selective Laser Sintering (SLS).</u> Here the initial aim was to produce dense hardmetals parts in an in one step combined shaping and sintering process, as it is known from SLS of metals like steel [4]. However, as mentioned above hardmetals contain only a small metal content and WC doesn't melt but decomposes. First experiments done at the Fraunhofer IKTS and IWS in cooperation with the University of Mittweida [5] in 1999 showed that with optimized granulated and presintered granules samples with densities above 60 % of theoretical density can be achieved. Thus a subsequent sinterHIP step was needed to further increase density. Especially for low Co contents below 15 wt.% the energy input needed to achieve sufficient dense samples resulted in defects like abnormal grain growth and local decomposition of WC into W_2C and carbon and due to carbon loss also to the formation of eta phase. In case of higher Co contents a much more inhomogeneous grain size distribution was achieved. An example of a WC-20 wt.% Co sample produced by SLS and sinterHIP is shown in Figure 2.

Further work was done at Fraunhofer IPT from 2007 to 2009 [6,7]. Here also a large variety of Co contents were tested. Best results were achieved with high Co contents. With 25 wt.% Co a density of 98.5 % of theoretical density could be achieved. However, due to the locally present high temperatures W_2C phase was present in most samples. Also with increased laser power cracks occurred and due to the large amount of pores of the SLS samples. Without subsequent sinterHIP step the bending strength was below 350 MPa. Samples and the microstructure of WC-25 wt.% Co produced solely by SLS are shown in Figure 3 and Figure 4.

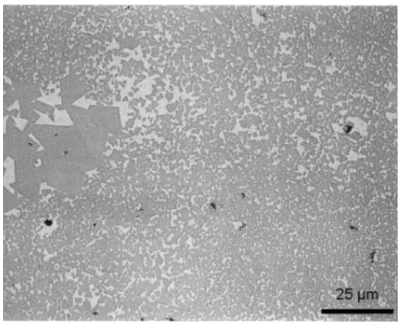


Figure 2: WC-20 wt.% Co sample

Figure 3: SLS test parts from

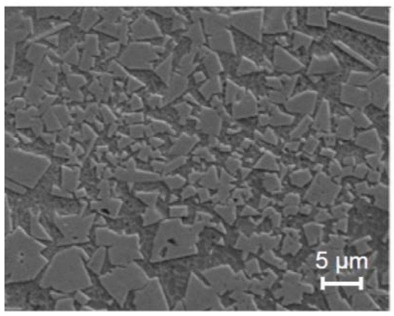


Figure 4: Microstructure of SLS parts

produced by SLS and sinterHIP from Fraunhofer IKTS/IWS [5]

Fraunhofer IPT [6]

with a content of 25 wt.% Co from Fraunhofer IPT [7]

Work with lower Co contents was also done by Kumar of the University of Utah in 2009 [8,9]. With 9 wt.% and 12 wt.% Co theoretical densities of 92 % and 96 %, respectively, were achieved. To further enhance the density, samples were infiltrated with bronze. However, even after infiltration the samples were not totally dense.

Uhlmann et al. of Fraunhofer IPK [10] showed in 2015 that hardmetal with a content of 17 wt.% Co with a density of 96 % theoretical density and different geometries can be produced by SLS as shown in Figure 5. Besides density also the loss of Co due to evaporation was measured as a function of different process parameters. In SLS a certain loss of Co during the SLS process has always to be considered due to locally occurring high temperatures as can be seen in Figure 5. Furthermore the work concludes that via SLS either a high density or a good microstructure with a limited loss of Co is possible.

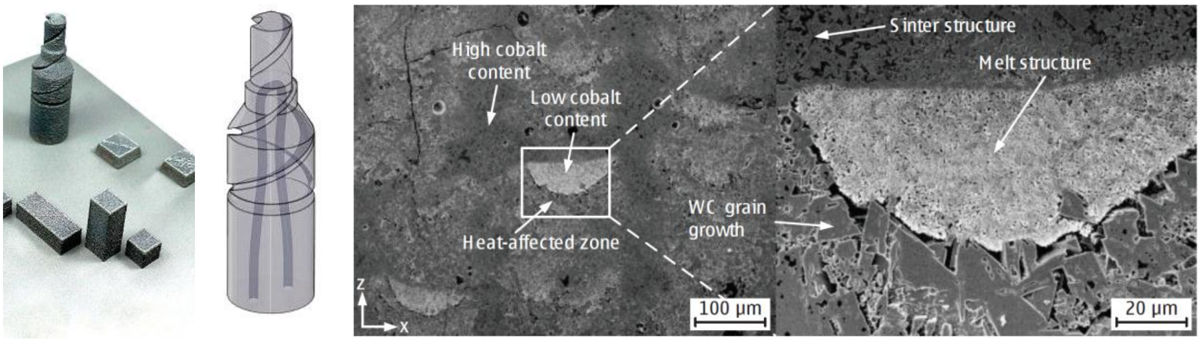


Figure 5: Overview, details and the microstructure of parts produced by SLS from Fraunhofer IPK [10]

Similar results were also presented by Baumann et al. during the Hagener Symposium in 2016 [11].

SLS of WC-Co is a promising techniques which has the advantage of direct forming and densification in one step. Unfortunately, 100 % dense samples are not possible and due to the locally high energy input chemical imbalances like W_2C, carbon or eta phase formation and locally different Co contents occur which lead to cracks and inner residual stresses. So far the microstructure and mechanical properties obtained by SLS are inferior to conventionally produced hardmetal parts.

<u>Binder Jetting</u> of hardmetals green parts was first published by E. Sachs and A. Kelley from MIT in 1998 [12–14]. Like SLS it is a powder bed based AM technique. In contrast to SLS the particles are not selectively “sintered” but “glued” together by organic binder, which is applied layer by layer using a special print head. Thus, the printed parts are green parts and their green density is mainly based on the powder density of the used starting material. After printing, the organic materials used during printing have to be removed during a debindering step and the samples must be sintered.

Further work was done by the printer producer VoxelJet in cooperation with other partners [15] and also by the printer producer ExOne in co-operation with the University of Louisville [16]. Here too, most work was focused on the production of suitable green parts.

At Fraunhofer IKTS different compositions were developed and used successfully for printing and sintering of complex parts. Besides variation in composition and printing parameters also debindering and sintering parameters had to be optimized. Samples with Co contents between 12 wt.% and 20 wt.% were produced by using sintering temperatures between 1400 °C and 1470 °C. The main aim was to produce hardmetal samples which have the same microstructural and mechanical properties as conventional produced ones. Densities achieved are above 99.8 % of theoretical density and hardness as well as fracture toughness are comparable to standard hardmetal grades with the same composition. Details on properties of medium grained hardmetals with 12 wt.% and 17 wt.% Co are given in

Table 1.

Table 1: Physical and mechanical properties of binder jetted and sintered hardmetals

Chemical composition	wt.%	WC-12 Co	WC-17 Co
Density	g/cm³	14.28	13.81
	%	99.8	99.9
Closed porosity	vol%	< 0.06	0.00
Hardness	HV10	1170	1020
	HV50	1160	1000
Fracture toughness	$MPa \cdot m^{1/2}$	22.1	-
Magnetic saturation (mS)	$\mu T m^3 kg^{-1}$	22.3	33.5
	% theoretical mS	92	96
Coercive force	kA/m	8	6
Average WC grain size	(classification)	medium	medium

Complex geometries with inner cooling channels were developed based on simple wire draw parts. Photos of such geometries are given in Figure 6.

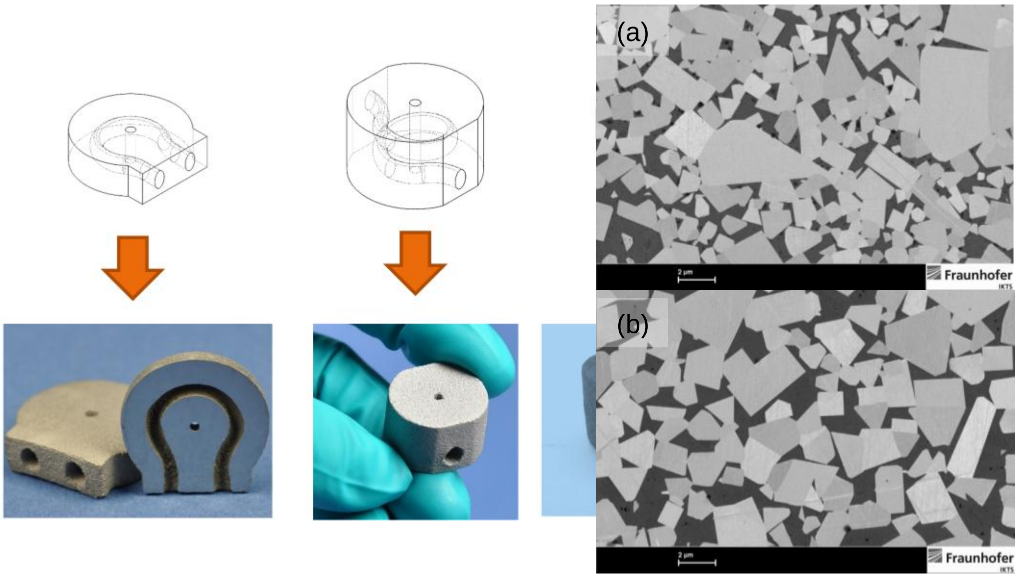


Figure 6: CAD- drawing of wire drawing dies with inner cooling channels and photos of sintered dies and microstructure of binder jet printed and sintered parts with 12 wt.% Co (a) and 17 wt.% Co (b)

Microstructural analysis show for the 17 wt.% Co samples a very homogeneous microstructure. Samples with 12 wt.% Co showed some larger WC grains, which can be avoided by using a composition with grain growth inhibitors such as Cr_3C_2 or VC. The microstructure of 12 wt.% and 17 wt.% Co containing hardmetal samples is given in Figure 6.

<u>Thermoplastic 3D printing (T3DP)</u> has been developed as an AM technology within the last 10 years. It can be used for the production of dense ceramic, metallic or hardmetals parts independently of the physical properties of the used powders (e.g. light absorption) as well as for production of multi-material-components to combine multi-functional properties with freedom in design. The main advantages of T3DP is the combination of precise deposition of small droplets with the fast deposition of filaments. Small droplets enable a high resolution in critical volumes and the deposition of filaments guarantees a high production speed for volumes where no change in material is needed. So far it was successfully used for the production of dense alumina [17] and also multi-material composites of stainless steel and zirconia [1,18].

Experiments done at Fraunhofer IKTS using T3DP show promising results for hardmetals too. WC-10 wt.% Co samples were successfully produced with nanoscaled WC powders (*WC DN3.5* from H. C. Starck Tungsten), very fine Co powder (*Half Micron* from Umicore) and grain growth inhibitors [19]. The hardmetal content in the organic suspension is 67 vol% which results in a quite high green density compared to conventional hardmetal fabrication. Samples were debindered under standard conditions with H_2 and sinterHIPed at 1350 °C with 60 bar Ar HIP pressure. The results given in Table 2 show that by T3DP totally dense and homogeneous hardmetal parts can be produced and that the properties are comparable to conventional (via uniaxial pressing) produced samples.

Table 2: Properties of samples made by T3DP or conventional pressing and sintering made from the same starting mixture of WC DN4 and 10 wt.% Co

Sample	Density		Hc	mS		DIN Porosity
[process]	[g/cm³]	[% theor.]	[kA/m]	[µTm³/kg]	[% theor.]	[A-B-C]
T3DP	14.23±0.01	100.0	47±1	15.1±0.3	80.7	02-00-00
Uniaxial pressing	14.22±0.01	99.9	47±1	15.3±0.3	81.8	02-00-00

Images of a T3DP printed green part as well as the microstructure after sintering is shown in Figure 7

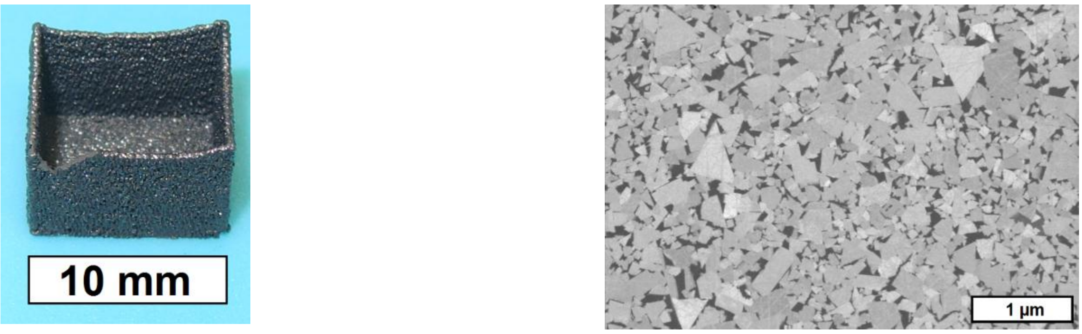


Figure 7: T3DP printed WC-10 Co test piece (left) and microstructure of sintered part (right) [19]

Even more work has to be done to investigate the limitations and possibilities of T3DP. It shows a high potential as additive manufacturing technique which can produce hardmetals in different compositions.

Further development is also done in the area of 3D printing of hardmetal suspensions with a low viscosity like in inkjet printing [20]. Here, due to the small droplet size a very detailed surface can be printed. However, due to low viscosity, geometrical freedom is limited. Because of the deliquescence of the used suspensions the printing of overhangs is nearly impossible. Thus, here mostly only in 3D expanded 2D geometries with walls of max. 95 ° are possible and larger overhangs, undercuts or even inner cooling channels are very difficult and mostly impossible.

Summary, outlook and conclusion

Additive manufacturing of hardmetals is a challenging task. Due the low amount of metallic phase direct powder to part processes like SLS or EBM are (not) possible without sacrificing the quality standards known from conventional produced hardmetal parts. To avoid pores, cracks and local inhomogeneity of the chemical compositions found in both SLS and EBM two step (printing + sintering) AM techniques are preferable. Here either powder bed based techniques like binder jetting or suspension based techniques like the thermoplastic 3D printing can be used. The latter allows to produce parts independent on the metallic binder content, while binder jetting has most likely some limitations when producing hardmetals with lower binder content. In regard of freedom in geometry powder based techniques offer the advantage that nearly all geometry features are printable and that only little and often even no supporting structures are needed. In suspension based AM technologies this can partially be solved by using a multi-material approach, in which supporting structures of a second, later easily removable, material is printed. For a high resolution, suspension based techniques using a low viscosity suspension and a very small print head are maybe a solution. Here, however, the freedom in geometry is again limited due the low viscosity of the suspension. Thus holes, overhangs and similar feature are difficult or not at all possible.

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