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# Development of Detonation Flame Sprayed Cu-Base Coatings Containing Large Ceramic Particles

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**Metal-matrix composites (MMCs) containing large ceramic particles as superabrasives are typically used for grinding stone, minerals, and concrete. Sintering and brazing are the key manufacturing technologies for grinding tool production. However, restricted geometry flexibility and the absence of repair possibilities for damaged tool surfaces, as well as difficulties of controlling material interfaces, are the main weaknesses of these production processes. Thermal spraying offers the possibility to avoid these restrictions. The research for this paper investigated a fabrication method based on the use of detonation flame spraying technology to bond large superabrasive particles (150-600 μm, needed for grinding minerals and stones) in a metallic matrix. Layer morphology and bonding quality are evaluated with respect to superabrasive material, geometry, spraying, and powder-injection parameters. The influence of process temperature and the possibilities of thermal treatment of MMC layers are analyzed.**

**Keywords** composite coating, grinding tool, MMC, process detonation sprayed, process parameters, reproducibility, substrate temperature, superabrasive composite, treatment—preheating

## 1. Introduction

Thermal spraying technologies are well known for producing wear-resistant coatings. Arc spraying, plasma spraying, high-velocity oxyfuel (HVOF), and detonation flame spraying are some of the common technologies commercially available to produce metal-matrix composites (MMCs) (Ref 1-3). Coatings based on WC-Co, $Cr_3C_2$-NiCr, WC-NiCrBSi, and many more are state of the art (Ref 1-7). Though the technology is used for making wear-resistant MMCs, it is not yet exploited for producing superabrasive composites for grinding applications.

Superabrasive composite coatings are quite similar to wear-resistant MMCs, but differ significantly in size and shape of the hard particles embedded in the matrix. Small hard spherical particles with sizes less than 50 μm uniformly dispersed in a metal matrix provide high hardness and high ductility for wear resistance (Ref 4-8). Angular hard particles with sharp edges and a size of 150 to 600 μm (according to the grinding task) are needed for machining stones and concrete. Tungsten carbide (WC), c-BN, and diamond are typically used for these applications (Ref 9, 10). Usually, the hard material concentration of diamond for stone machining tools must be 10 to 15 vol.% (Ref 11-13) in the layer.

A metallic matrix (typically, cobalt-, nickel-, iron-, or copper-base) guarantees good embedment of the dispersed hard particles and compensates for their low fracture toughness. Cobalt (Co) alloys are mostly used as a matrix material because of their adapted abrasion resistance and good bonding properties with diamond and carbides by establishing small surface reaction zones (Ref 14, 15). The high price and carcinogenic effect of Co alloys compel a search for alternative materials. Copper (bronze) alloys with similar strength and hardness showed high potential in several applications based on sintering technologies (Ref 9, 14, 16).

Reference 17 reports that diamond copper (Cu) coatings for grinding applications could be produced by thermal spraying. Diamonds of 50 up to 100 μm were embedded well into copper layers by detonation flame spraying and HVOF processes. Thermal spraying offers new possibilities as it is more flexible and has an easier assembly process than sintering or brazing methods.

Using thermal spraying for the manufacture of diamond composite layers for the qualification profile of machining stone does present a lot of procedural challenges. For example, diamonds are quite temperature sensitive. In an oxygen atmosphere they react at a temperature of 500 °C and form carbon monoxide and carbon dioxide (Ref 18-20).

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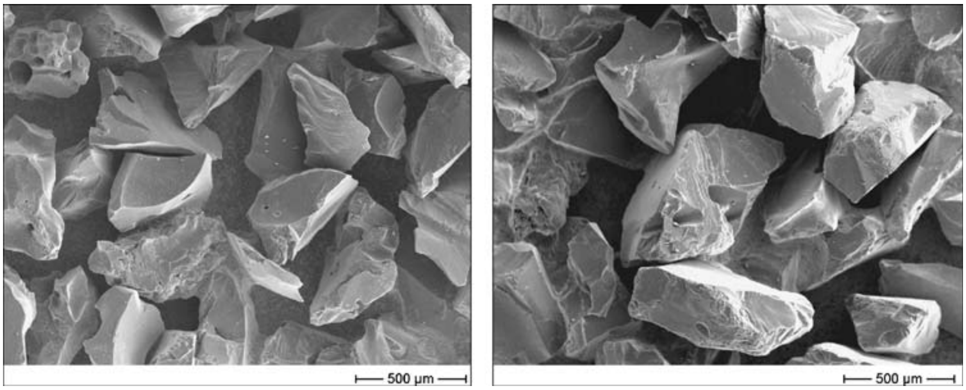

**Fig. 1** Sprayed hard materials (left: $Al_2O_3$ 250-354 µm; right: SiC 200-500 µm)

**Table 1 Sprayed materials**

| Material | Manufacturer | Grain size, µm | Hardness, HV | Density, g/cm$^3$ |
|---|---|---|---|---|
| $Al_2O_3$ | SWARCO GmbH | 250-354 | 2200 | 3.92 |
| SiC | ESK-SiC GmbH | 200-500 | 2800 | 3.21 |
| Cu | GTV GmbH | 45-90 | 70 | 8.94 |
| CuSn 85/15 | GTV GmbH | 45-90 | 240 | 8.60 |

Therefore, the coating process has to ensure a low thermal influence. Detonation flame spraying has shown the potential to produce these composite coatings in the past (Ref 17). Compared to other spraying technologies, detonation flame spraying allows independent control of the kinetic energy of superabrasive and matrix particles and the coating temperature. High velocities of particles in the process (up to 1200 m/s, Ref 21-23) offer the best possibilities to implant large superabrasives during the impact into the matrix material. Excellent embedment of the voluminous superabrasive particles into the matrix coating material can be achieved without damaging the superabrasives through a thermal influence (SiC or diamond) to produce high-quality composite layers for grinding applications of stone and concrete.

In line with the results of Ref 17, implantation of diamonds with a particle size of 50 to 100 µm by detonation flame spraying large $Al_2O_3$ and SiC (>150 µm) in a matrix of copper and bronze is the center of the research work published in this paper.

## 2. Experimental

### 2.1 Base Materials

$Al_2O_3$, SiC, Cu, and CuSn 85/15 were used as base materials to produce composite coatings by detonation flame spraying. $Al_2O_3$ (Swarco Vestglas, Recklinghausen, Germany) and SiC (ESK-SiC GmbH, Gräfrath, Germany) have to be a certain size to fulfill the cutting acquirements for grinding tools to be applied in concrete or stone machining (Table 1). With an angular shape and sharp edges they also lead to form fit joints in the matrix. Scanning electron micrographs of the hard material are given in Fig. 1.

Typical thermal spraying copper and bronze powders were used as matrix material. Spherical shape and grain sizes of 45 to 90 µm (GTV GmbH, Betzdorf, Germany) led to a dense structure and a good cohesion of the matrix. High adhesive strengths with the copper substrate can also be achieved. Details of the powders used are shown in Table 1. Rectangular Cu sheets (Cu-DHP) with dimensions of 150 by 20 by 5 mm were used as substrate.

### 2.2 Spraying of Composite Coatings

The investigations were carried out using detonation flame spraying equipment (Surface Advanced Technology Inc., Warsaw, Poland). Two different powder hoists (Feeder 1, Electro-Plasma Inc., Irvine, California; Feeder 2, Single-10C, Plasma-Technik AG, Switzerland, modified with bigger feeder plate for voluminous hard particles) were used to insert superabrasives and matrix material independently.

Cu substrates were neither cleaned nor grit blasted before coating. Good bonding quality between the substrate and the MMC coating was achieved only by impacting $Al_2O_3$ or SiC during the spraying process in combination with substrate preheating and optimized spraying parameters.

### 2.3 Testing

Tensile tests at high temperatures were carried out on Cu-DHP specimen according to DIN 50125 (Jan 2004) Form B, which is shown in Fig. 2. Tests from room temperature up to 600 °C were carried out on a RMC-100 tensile tester (Schanck-Trebel, Darmstadt, Germany) with a three-zone kiln (MTS, Berlin, Germany, max. temperature 1000 °C) under atmosphere conditions. Corresponding to DIN EN 10002-5 (Feb 1992) the samples were drawn with a velocity of 0.2 mm/min with a temperature deviation of less than 3 °C.

Hardness Vickers tests were examined on a universal hardness tester (Wolpert, Hahnkolb GmbH, Stuttgart,

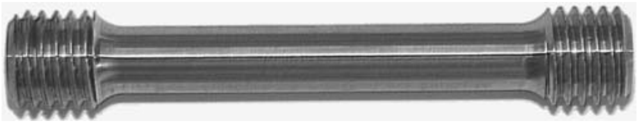

**Fig. 2** DIN 50125 Form B Cu-DHP sample

Germany) concerning DIN EN ISO 6507-1. Optical microscopy (Axiophot, Zeiss, Germany) with analytic module (KS 300, Zeiss, Germany) was used to characterize the coating morphology and hard-particle content and distribution.

## 3. Results and Discussion

### 3.1 High-Temperature Tensile Tests of Massive Copper

To produce thermally sprayed composite layers for grinding applications, the necessary voluminous superabrasives need to be bonded well into the matrix. This can be achieved by producing superabrasive metal composite coatings employing high-energy coating processes. The amount of particles implanted in the matrix depends on the kinetic energy, shape, and size distribution of the impacting superabrasives as well as on the hardness and toughness of the matrix surface.

Temperature influences the hardness and toughness of metallic material. At higher temperatures, the substrate and matrix become softer. For impacting hard particles it is assumed that the amount of particles implanted could be increased by heating the substrate and the deposited coating. To verify this assumption, corresponding bulk samples were tested. Before spraying compound materials, tensile tests at high temperatures were carried out to estimate the behavior of Cu-substrate material. The results of the tensile tests are given in Fig. 3.

It was confirmed that the strength of Cu-DHP decreases significantly at 400 °C. The yield stress of massive copper loses 89% of the original strength at 400 °C, compared to room temperature. Based on these results, it becomes obvious that for a decent implantation of superabrasives during thermal spraying it is crucial to heat the substrate at elevated temperatures.

### 3.2 Implanting $Al_2O_3$ in Massive Cu

The injection of $Al_2O_3$ particles in copper samples was investigated to correlate the results of the tensile tests mentioned previously to the implantation of hard particles. The hard particles were accelerated by the detonation flame spraying equipment. Several heating methods were approved to ensure exact substrate temperatures.

Torch preheating of the substrate was investigated first. The possibility of implanting superabrasives under high temperatures was shown. However, torch preheating does not guarantee a fixed temperature in spraying process. When the substrate temperature is above 200 °C, the gradient to the environment is high enough to cool down the copper samples quickly. Furthermore, irregular oxidation of the material was detected.

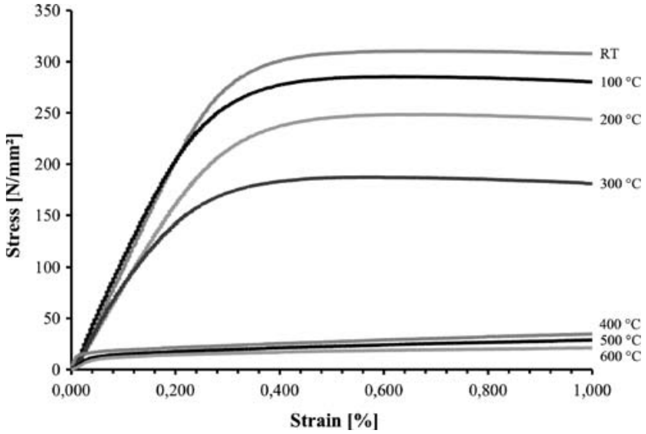

**Fig. 3** Result of the Cu-DHP tensile test under various temperatures

Electric heating systems with automatic temperature adjustment should allow controlled substrate heating especially during spraying. Hence, sample holders of copper infiltrated with NiCr heating conductors of 300 and 400 W have been designed. This was sufficient to heat the copper substrates up to 400 °C. However, the air flow during the spraying process causes the temperature of the substrate to fall below 300 °C. To maintain accurate substrate temperatures, 550 and 650 W heating systems have been designed. These heating systems guarantee precise sample heating up to 500 °C with a deviation less than 20 °C in spraying process.

With this equipment, detonation flame spraying experiments have been conducted to implant $Al_2O_3$ particles with grain sizes of 250 to 354 μm in Cu (Fig. 4). The results of the implantation experiment are in accordance with the results of tensile test. The depth of hard-particle penetration and the implantation rate increases significantly at higher temperatures.

### 3.3 Spraying Parameter Optimization for Composite Coatings

The spraying and heating parameters were optimized for every composite coating examined. In addition to parameters such as propane and oxygen flow rate, ignition frequency, powder feed rate of matrix material and hard particles, spray distance, sample movement, preheating of substrate, and temperature of the composite during the spraying process, the effect of hard-particle addition in different positions was examined.

Usually, spraying powders are fed into the system directly in front of the detonation. In the barrel, the particles are accelerated a long way to the substrate. To prevent deterioration of the superabrasive particles caused by their brittleness and thermoshock sensitivity, it is crucial to feed them at the right position within the spraying equipment.

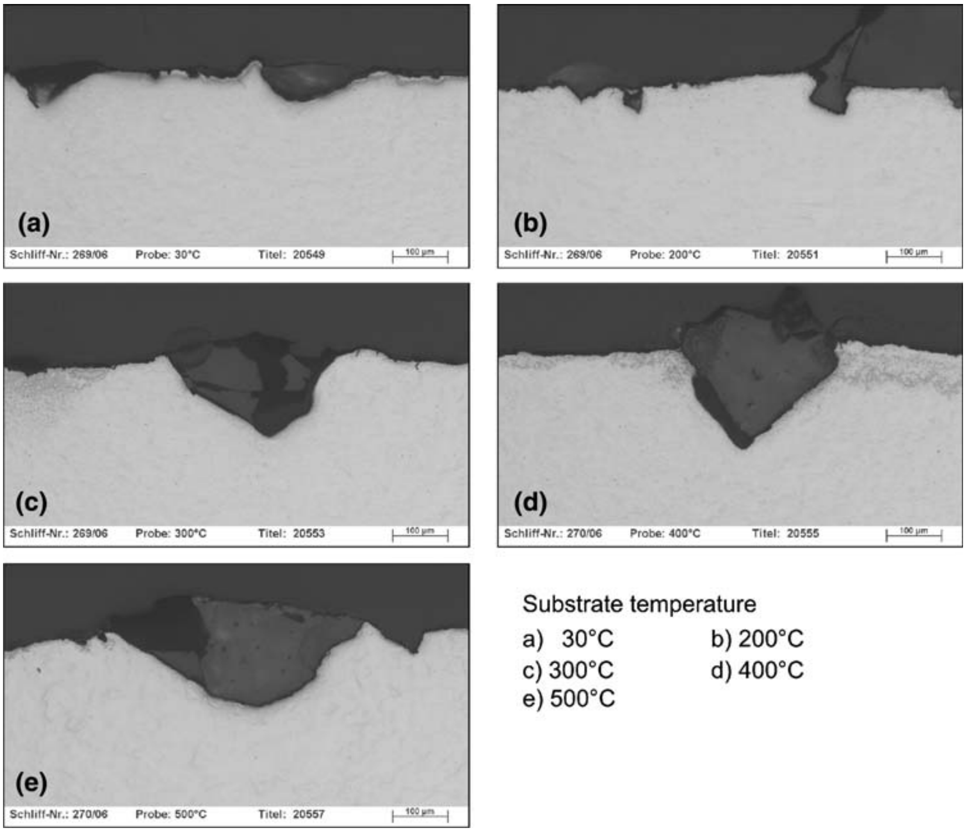

**Fig. 4** Implantation of $Al_2O_3$ through detonation flame spraying under various temperatures in Cu-DHP

Whereas matrix powder was induced into the shock wave near the detonation chamber, location and velocity (powder feeding position 1 and 2) as well as the angle of hard-particle ($Al_2O_3$) injection (powder feeding position 2) were investigated Fig. 5).

The experiments with hard-particle injection in injection position 2 in front of the detonation barrel (Fig. 5 and 6) have shown that, independent of injection parameters chosen, the kinetic energy of the superabrasives was not high enough to implant the superabrasive particles into substrate or matrix coating. Impacting on substrate and Cu coating, particles rebounded instead of being integrated into the coating. Only a few $Al_2O_3$ particles smaller than 50 µm (deviant in used material) stuck in coatings during spraying onto heated (400 °C) samples.

Though the implantation of the hard particles could not be achieved, a densification effect of the copper-matrix coating was recognized. By inducing the $Al_2O_3$ in an angle of 90° with a distance of 2 cm in front of the barrel (feeding position 2, Fig. 5 and 6), the highest density of thermally sprayed copper was attained (Fig. 7).

Figure 7 shows that the quality of sprayed copper layer improved significantly compared to that shown in Ref 17 and 24. Almost no porosity, less copper oxidation, and perfect bonding to substrate are evident.

With respect to the objective of producing a homogeneous superabrasive composite coating, best results were achieved by injecting the voluminous hard particles directly into the barrel in front of the detonation chamber (injection position 1, Fig. 5). In the detonation front they mixed with the Cu powder and were accelerated to high velocities. Based on the substrate material, temperature, and hardness as well as hard particle size and shape, calculations from the implantation results gave the superabrasive particles a velocity of ~815 m/s before impact. The increased kinetic energy caused $Al_2O_3$ particle implantation into the Cu substrate and the Cu coating. Depending on spraying parameters and external sample heating, particles up to 300 µm could be well embedded. Larger hard particles were mostly removed during the following detonation because of their proportionally reduced implantation depth.

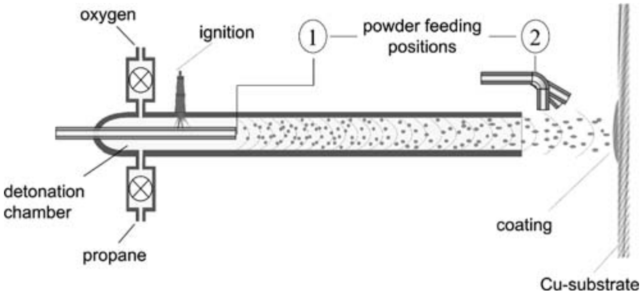

**Fig. 5** Detonation flame spraying equipment with illustration of used hard-particle injection positions

Again, sample heating was analyzed to achieve a better embedment of bigger superabrasives. However, thermal treatment is limited owing to intensive copper oxidation at temperatures above 400 °C. The best results to produce desired composite coatings were achieved at a substrate temperature of 350 °C (Fig. 8).

Low porosity (<3%), acceptable copper oxidation, few hard-particle cracks, and good bonding quality between superabrasives and matrix are characteristics of these composite coatings. An $Al_2O_3$ content of ~18% was measured in the composite coating using the optical analysis module. Though there was no external substrate roughening or cleaning process prior to the coating operation, excellent adhesion between substrate and composite coating was registered because of the blasting effect of impacting $Al_2O_3$.

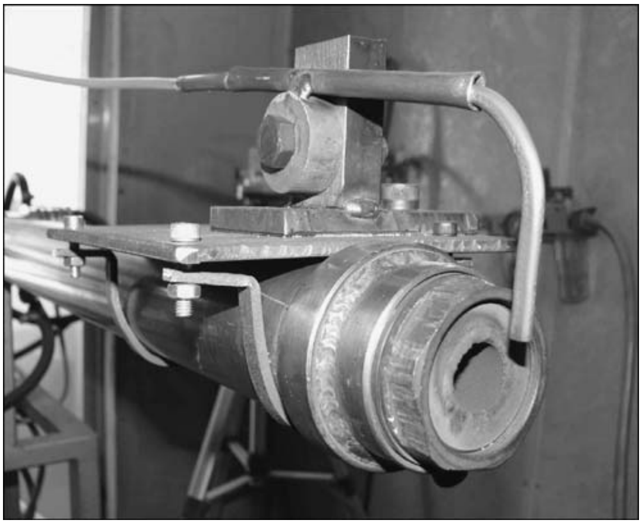

**Fig. 6** Hard-particle insertion in front of the detonation tube

### 3.4 SiC-Cu Compounds

$Al_2O_3$ superabrasives are not suitable for grinding applications of concrete and stones; their hardness of 2200 HV and their brittleness reduce the applicability of this material. SiC offers more opportunities with higher hardness and strength (Table 1). However, spraying SiC composites has some restrictions. Because of thermodynamic reasons $Cu_3Si$ and graphite are formed by the reaction of Cu and SiC at elevated temperatures (Ref 25-27).

Using detonation flame spraying can prevent the decomposition of SiC. High particle velocity and less thermal energy promise good bonding quality and less SiC deterioration. Figure 9 shows the resulting composite with a SiC content of ~13% in the coating. Spraying parameters are given in Table 2.

### 3.5 CuSn Matrix

Bronze has higher hardness and greater strength than pure copper. For grinding applications of stones and concrete it offers longer service life. However, matrix wear is necessary for the self-sharpening effect of the grinding tool, and it has to be adjusted to the individual task. In most cases, copper is too soft. Typically, CuSn 90/10, 85/15, 80/20, and 60/40 are used for stone machining

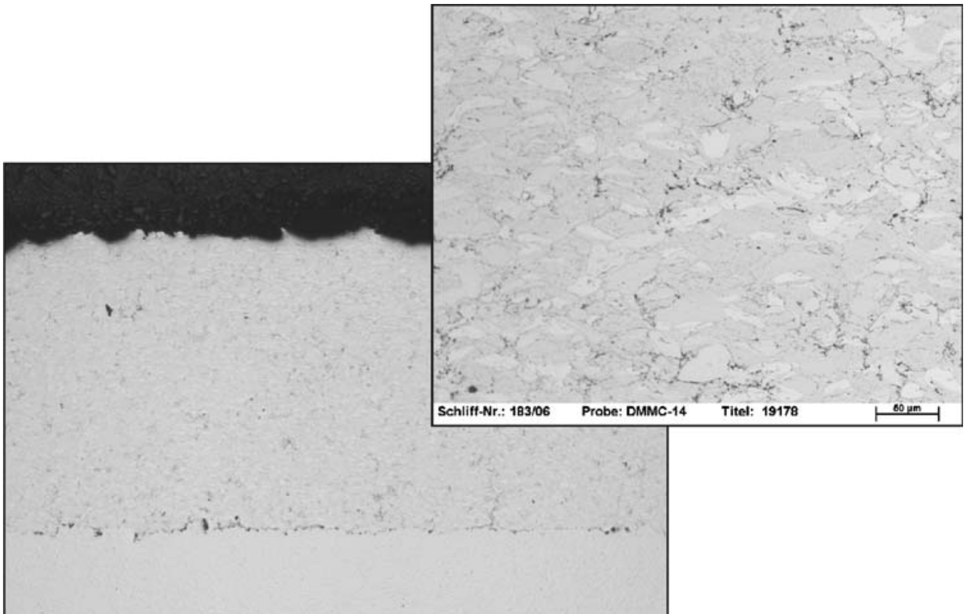

**Fig. 7** In situ densed detonation flame sprayed Cu coating on Cu substrate

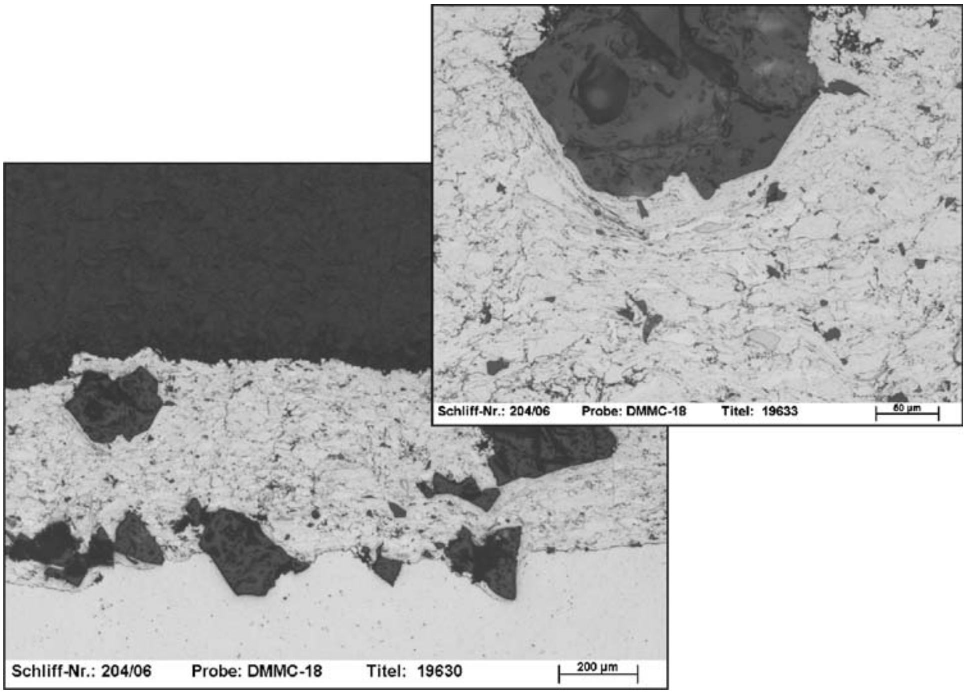

**Fig. 8** $Al_2O_3$ impregnated Cu composite on Cu substrate

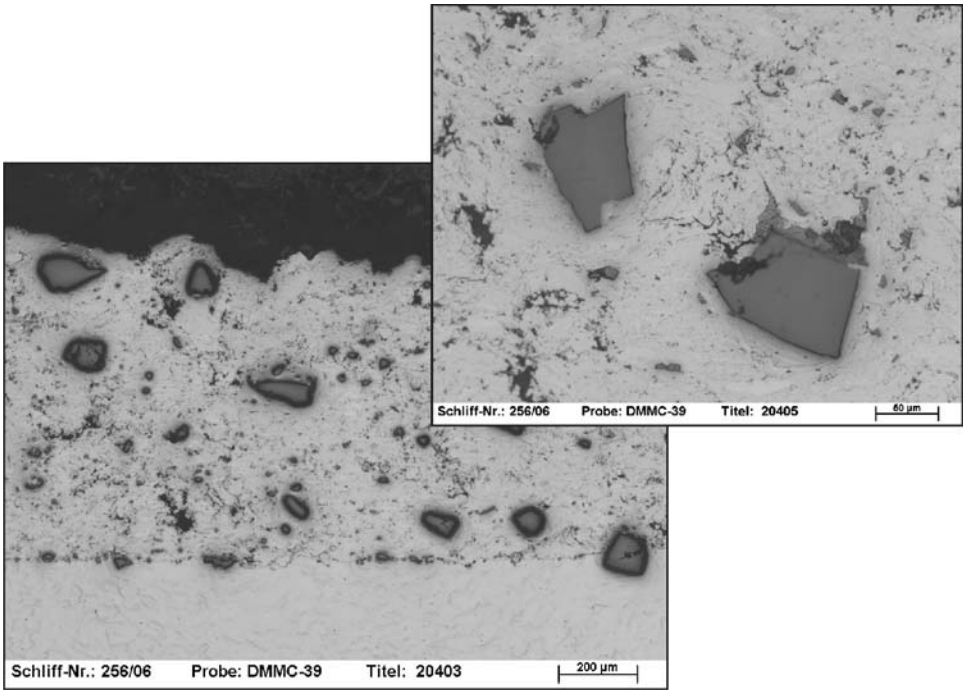

**Fig. 9** SiC impregnated Cu composite on Cu substrate

grinding tools (Ref 9, 14, 16). Therefore, first experiments with CuSn 85/15 have been conducted. $Al_2O_3$ as well as SiC have been employed as hard material for this matrix-material.

Based on previous work with copper as matrix material, first positive spraying results with bronze have been achieved quickly. Figure 10 gives an example of hard-particle infiltrated bronze.

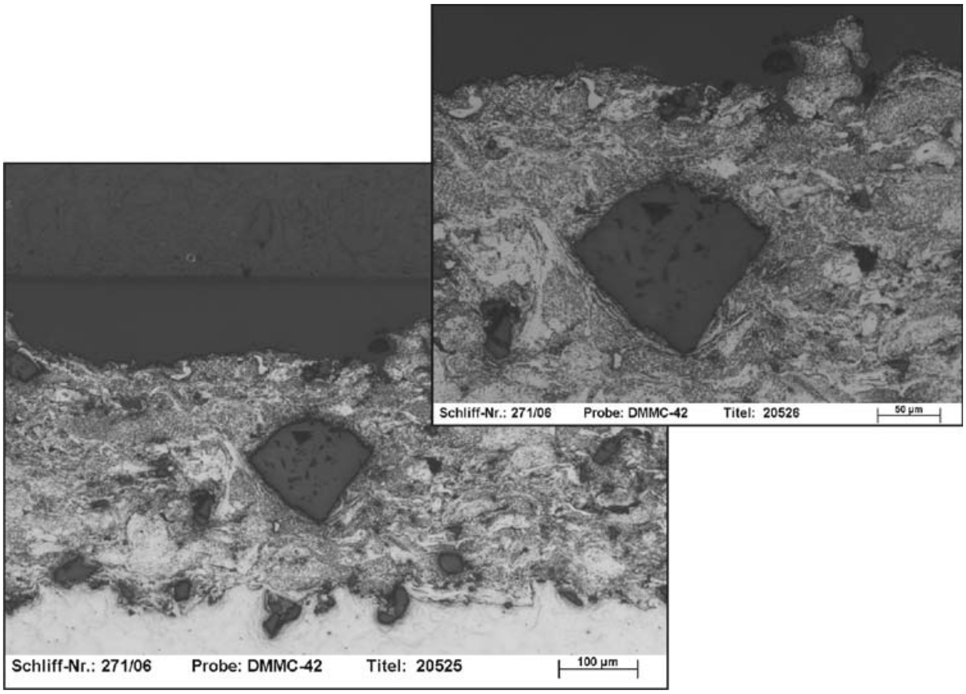

**Fig. 10** $Al_2O_3$ impregnated CuSn 85/15 composite on Cu substrate

**Table 2 Optimized spraying parameters for $Al_2O_3$ and SiC impregnated copper**

| | | | |
|---|---|---|---|
| Substrate | Material | Cu-DHP | Cu-DHP |
| | Dimensions, mm | 120 × 20 × 5 | 120 × 20 × 5 |
| Sprayed material (1) | Analysis | Cu | Cu |
| | Size, µm | 45-90 | 45-90 |
| | Feed rate, g/min | 24 | 20 |
| Sprayed material (2) | Analysis | $Al_2O_3$ | SiC |
| | Size, µm | 250-354 | 200-500 |
| | Feed rate, g/min | 6.8 | 6.8 |
| Spray parameters | $O_2$, L/min | 29 | 44 |
| | $C_3H_8$, L/min | 17 | 26 |
| | Detonation frequency, Hz | 2 | 3 |
| | Distance, mm | 200 | 200 |
| Substrate temperature, °C | Preheating | 365 | 350 |
| | While spraying | 350 | 350 |
| Others | Number of overruns | 10 | 10 |
| | Layer thickness, µm | ~510 | ~380 |

Evaluating the layer quality bronze composites shows a reduced superabrasive penetration compared to the Cu-matrix material. Because of the higher hardness of the base material (155 HV30 for sprayed CuSn 85/15 after cooling to room temperature compared to 129 HV30 for pure Cu) only smaller particle sizes of less than 250 µm were well embedded. For better comparability, Fig. 11 shows the typical microstructure of a sintered abrasive compound of diamond/CuSn 85/15 for concrete grinding applications. It can be seen that the detonation flame sprayed coatings are viable to produce superabrasive composites with an adequate morphology and even lower porosity, which is useful for the grinding process.

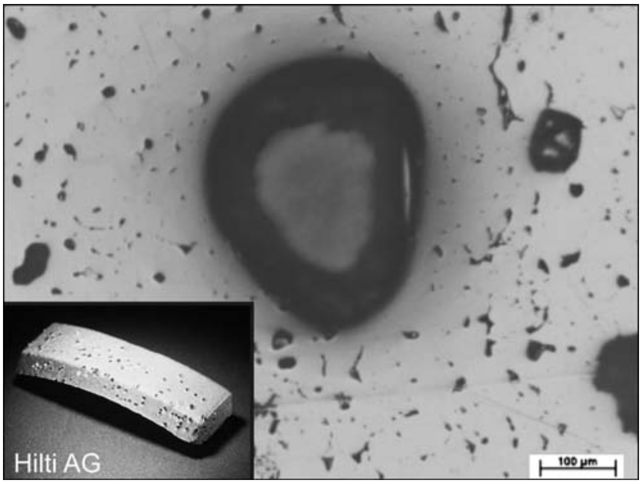

**Fig. 11** Microstructure of a sintered stone grinding tool of diamond CuSn 85/15. *Source*: Ref 28

## 4. Conclusion and Outlook

Grinding tools fabricated by thermal spraying are not established yet. However, the possibility of producing complex geometry tools and of repairing damaged surfaces shows a high future potential.

Hard particles with a size larger than 150 µm uniformly dispersed in a metal matrix give high abrasiveness for grinding stones and concrete. Therefore, the challenge for thermal spraying is to produce a homogeneous composite coating employing superabrasives with particle sizes exceeding 150 µm.

In line with the results of diamond impregnation (Ref 17) the possibility of $Al_2O_3$ as well as SiC implantation has been investigated in this publication. Detonation flame spraying has proved to provide the relevant kinetic energies necessary to achieve sufficient penetration and bonding of large superabrasive particles.

The study revealed that the implantation rate of the high kinetic energy particles could be affected positively by thermal treatment. An optimum was confirmed for copper matrix at a sample temperature of 350 °C during the spraying process. With a low matrix oxidation it was possible to implant hard particles up to a size of 300 μm effectively. The desired hard-particle content of 10 to 15% was achieved.

Further investigations with bronze 85/15 material have shown the possibility of using harder matrix materials for the proposed application of the composite coating. However, additional studies are needed to improve implantation of larger superabrasives into CuSn 85/15 as well as CuSn 90/10, 80/20, and 60/40, which are typically used for the desired grinding applications. Furthermore, evaluation of corresponding diamond containing composite coatings is planned. Comparisons of concrete grinding tests with detonation flame sprayed, sintered, and hot isostatic pressed tools will be conducted soon.

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