Interface Design in Copper-Diamond composite by using PVD and CVD coated diamonds

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Abstract. One of the key problems in copper-diamond composites is the interface between the metal matrix and the diamond reinforcement. In order to take advantage of the high thermal conductive diamond filler in a composite the design of the interface is crucial. One approach to minimize the thermal contact resistance between metal and diamond reinforcement is to coat the diamonds with functional layers, e.g. Mo or W. For coating of diamonds PVD and CVD have been used followed by characterization of coating thickness by different methods. The coated diamonds were used for composite manufacturing and the thermal diffusivity of the compacted materials was measured.

Introduction

One of the key problems in copper-diamond composites is the interface between the metal matrix and the diamond reinforcement. The interface has a significant influence on the thermal properties and the thermal cycling performance. A low thermal contact resistance (TCR) is necessary in order to take advantage of the high thermal conductivity of the filler material. At the same time a good mechanical bonding is needed to exploit the low thermal expansion of the diamond filler and to ensure the long term stability of thermal properties during thermal cycling.

Basically there exist two possibilities to tailor the interface in a composite material which is produced by a powder metallurgical process: either a modification of the matrix material is made or the inclusions are pre-treated/modified.

Modification of the Matrix: this can be obtained via a modification of the matrix, e.g. by introduction of alloying elements which promote a carbide formation. Basically here two different routes are possible: either pre-alloyed copper powder are used (e.g. Cu-Cr, Cu-Ti) or elemental powder mixtures of copper and active elements are applied.

Modification of the reinforcement: here a surface modification/treatment can be made (e.g. oxidation, heat treatment) or a coating (consisting of an active element (carbide forming element) or its carbide) can be applied by different coating processes.

Within this work the focus will be on the last concept. For coating of the diamonds two different processing techniques will be investigated. A few publications have already demonstrated that PVD and CVD methods can be used for coating of particles or powders. CVD is suitable for the

deposition of various metals or their oxides, nitrides and carbides [1-3]. The PVD process has a number of advantages such as the possibility to modify the inclusion/metal interface by a plasma pre-treatment, the easy realization of interlayers or even multilayers and the broad variety of elements or alloys which can be deposited [4,5]. Nevertheless one of the main challenges for the PVD methods, concerning the coating of 3D shaped parts, is to provide a uniform coating thickness. For single parts this can be realised either by multi-target sputtering (arranged in cylindrical or, ideally, spherical shape) or by rotating the part during deposition. If however a batch of particles or fibers has to be coated, several additional measures are necessary to avoid clustering or mutual shadowing. Methods based on vibrating or shaking [6-8] the particles have been investigated. As well as using a rotating cage [9,10] or rotating wing drums [11].

Experimental Procedure

Chemical and Physical Vapor Deposition (CVD and PVD) have been used to coat diamond particles with a size of approx. 120 µm (MBD4, 120/140 mesh) with either W or Mo thin films. The thickness of the coatings was ranging from some nanometers (for Mo) to several hundreds of nanometers for W coatings. The coated diamonds were subsequently mixed with copper powder (ratio 1:1 in volume) followed by hot pressing. The obtained composite materials were characterized with respect to thermal properties (thermal diffusivity).

CVD coating of Diamonds

For the coating of diamonds with a tungsten coating, a CVD process was used. In order to provide a uniform coating of the diamond, particles were coated in a rotating barrel reactor. The schematic arrangement of the coating process is shown in Fig. 1. Two gases are used for chemical coating of the diamond. The rotation of the barrel reactor is responsible for a permanent movement of diamond particles while the reaction gas is consisting of a mixture of tungsten hexafluoride and hydrogen which react in the heated zone (at temperatures of approx. 500°C) resulting in a tungsten film on the diamonds. By selecting the deposition conditions (temperature, reactant gas flow,..) in an appropriate way a homogenous W coating on the diamonds particles can be obtained. The coating thickness of the W coating was in the range of 100 nm to 2 µm.
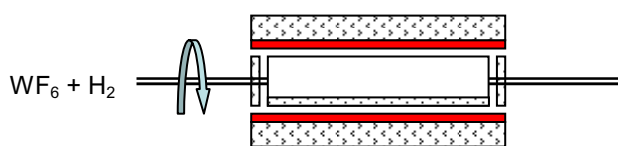

Figure 1: Schematic overview on CVD process

Figure 2: Device for PVD coating of diamonds (insert: set-up of the rotating dishes)

PVD coating of Diamonds

For the deposition of Mo thin films a sputter deposition equipment was used. Since sputter deposition is a line of sight method, it is necessary to keep the diamond particles in movement in order to obtain a uniform coating and avoiding shadowing effects. Therefore rotating dishes were used. These dishes are aligned to the horizontal axis in a specific angle (which depends on particle size, loading of the dish, rotation speed) allowing a permanent movement of the diamond particles

during the deposition process. The molybdenum target in this deposition chamber is mounted on the top flange. By using this device diamonds have been coated with homogenous thin films with a thickness in the nanometer range (1-10 nm).

Characterization of coated diamonds

The characterization of the thickness of the deposited films on the diamond particles requires a special attention. Since the conventional preparation of cross sections is in principle possible by grinding and polishing and suitable for thick coatings (several micrometers) within this work different methods have been applied for the measurement of the coating thickness, especially for coatings below 1 μm. These methods are:

- Cross sections using Focused Ion Beam technique (FIB) in combination with HR-SEM

This method is suitable especially for thin coatings (below 100 nm) in order to allow a detailed analysis of the interface as well as the coating uniformity as well as to study the bonding and interface to the diamond particle. For this method a special SEM device is used which allows to prepare in-situ a cross section of a coating-substrate system by using an ion beam. Immediately after the preparation of the cross section it is possible to analyze the cross section in the SEM. Fig. 3 shows the results of the SEM image of a PVD Mo coating on a diamond particle. This method is suitable if a continuous coating on the substrate/particle is available. Of course the results from this analysis only represent a strictly local information and this method consequently is not the best choice for the characterization of a big batch of coated diamonds. The coating thickness of this Mo film can be derived from a high resolution image. The top view of the coating consists of fine Mo islands which are on top of a dense Mo film. The thickness of the coating was approx. 15 nm (see Fig. 3 insert).

- Qualitative Analyses of coated diamonds by SEM (BSE mode) and quantitative analysis by Electron Microprobe Analyses (EMPA)

The BE (backscattered electrons) image mode of SEM allows getting element sensitive maps of coated diamonds. Information about the homogeneity of the coating can be derived by this method. It is further possible to determine whether a continuous or irregular coating is available. Fig. 4 shows the BSE images of CVD coated diamonds (Thickness approx. 1-2 μm). The diamond particles are in general homogenously coated with some defects but the variation of coating thickness cannot be assessed.
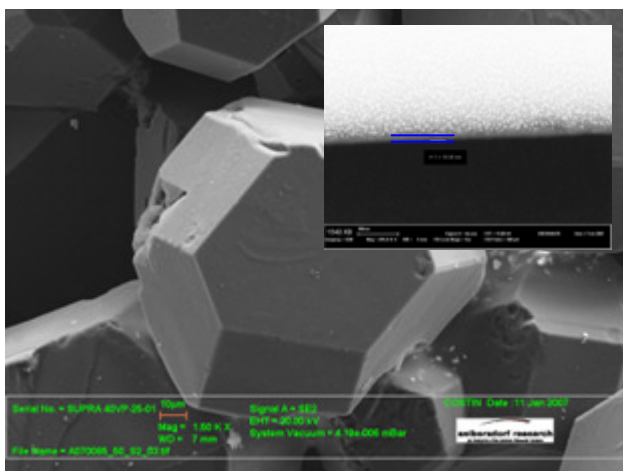

Figure 3: Homogenous PVD coatings (Mo) on diamond. The insert shows the cross section which was prepared by FIB (sample S50-1).
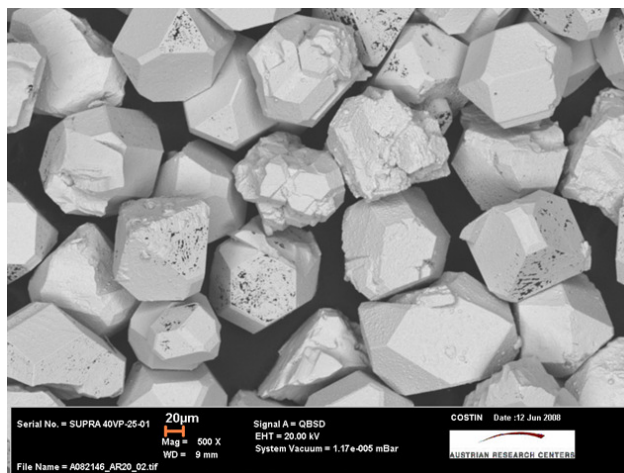
Figure 4: Overview on CVD coated diamonds (coated with W)

The second method for the analysis of single-constituent thin coatings is a special method of X-ray microanalysis which is dedicated for thin coatings, lower than 1 μm [12, 13]. By measuring the x-ray intensities of all components of the samples at various accelerating voltages one can get information about the in-depth distributions of the element concentrations in the analyzed sample. Commercial correction program has been used to obtain the thicknesses and concentrations of all elements in the analysed coatings. For all investigated diamonds the quantitative X-ray microanalysis of the element concentrations was made using Wavelength Dispersive Spectrometer.

The results obtained from this measurement are shown in Table 1. For the Mo PVD coatings the determined average coating thickness is below 10 nm, while the CVD coatings are around 500 nm and 1μm which is in a good agreement with the coating thickness which derived by mass change in the case of the W coatings before and after the coating process.

- Transparency measurement – determination of the diameter

As a third method an optical method was employed which is a method based on size and/or transparency variations which are caused by the additional coatings. For analysis of the optical properties (transparency) a Diascanner is used. A representative number of diamonds is put on a dia frame and an image is scanned. By using particle recognition software it is possible to deduce a value for the mean diameter of the diamonds. Since the diamonds are used in a narrow size range between 120 and 140 mesh it is possible to determine a mean diameter for the uncoated diamonds. At the same time the software allows to evaluate the transparency of the individual recognized diamonds or the coated diamonds. Synthetic diamonds are transparent which allows to determine a reference value. By applying a coating, especially thin coatings in the range of nanometers to some hundred nanometers, a certain reduction of the transparency is observed. The reduction can be used and correlated to the coating thickness obtained by other methods. Since the transparency of a metallic coating is a function of the layer thickness a correlation can be derived. Nevertheless it must be mentioned that it is self-evident that the detectable transparency values strongly depend on the used metal element or carbide. Due to the possibility to investigate a large number of diamonds this method has its strength for the determination of coating uniformity/homogeneity (indicated by the scattering of the transparency values). The method is simple and quick and especially suitable for process control of a coating process from one batch to another. To derive absolute thickness values a calibration with other methods is necessary (see Fig. 5).
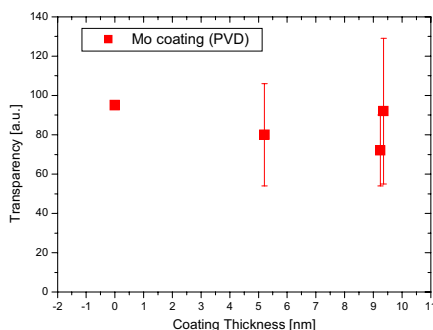

Specimen denotation	Coating/ Process	Mean thickness [nm]
M58-S1	Mo-PVD	9,3
M58-S2	Mo-PVD	5,2
M58-S3	Mo-PVD	9,4
AR-W01	W-CVD	484,6
AR-W02	W-CVD	963,4

Figure 5: Results of transparency measurements and thickness determination using EMPA method

Table 1: Results of thickness measurements obtained by EMPA measurements for PVD and CVD coatings

Composite materials

The diamonds coated by PVD and CVD process were used to manufacture a composite material. The powders were mixed followed by hot pressing at different temperatures. The results of these compaction experiments are shown in Fig. 6 and 7. The first diagram shows the results of the Mo coated diamonds which shows a strong influence of the coating thickness, coating uniformity and the hot pressing temperature on the measured thermal diffusivity. For the thin coating (~5nm) the consolidation temperature plays a big role. At a medium hot pressing temperature (T2) thermal diffusivities (>200mm²/s) have been achieved but with no further increase if the hot pressing temperature was increased. A coating with a thickness of approx. 10 nm and a narrow variation of the coating thickness indicated a strong influence on the hot pressing temperature. Here at a medium hot pressing temperature (T2) the highest thermal diffusivity was measured. With increasing of the thickness the diffusivity decreases again. The PVD coated diamonds with 10 nm Mo coating and a strong variation of the coating thickness show a continuous increase of the thermal diffusivity with increasing temperature.
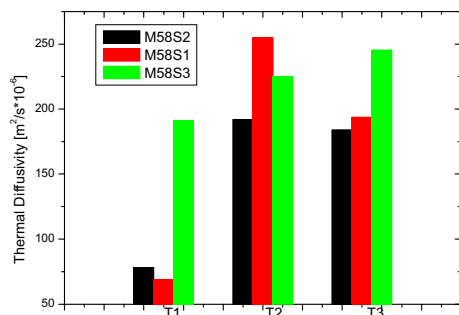

Figure 6: Thermal Diffusivity of composites made from PVD (Mo) coated diamonds (T1=950°C, T2=1000°C, T3=1050°C)
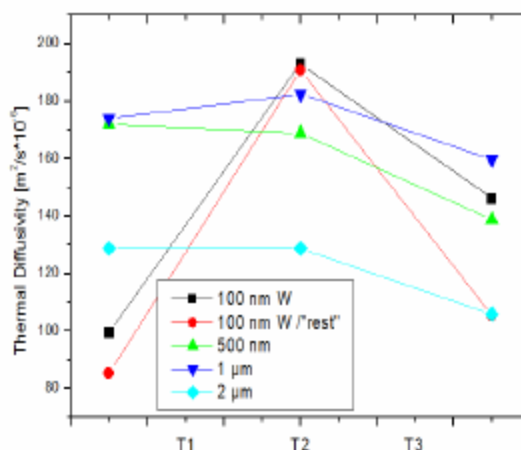
Figure 7: Thermal Diffusivity of composites made from CVD (W) coated diamonds (T1=950°C, T2=1000°C, T3=1050°C)

In the case of the CVD coated diamonds the variation of coating thickness was made between 100 nm and 2 μm. As a general trend it was found, that with increasing of the coating thickness (2μm) a degradation of the thermal diffusivity values is correlated. Thin coatings (100, 200nm) resulted in the best thermal performance but here the processing window (consolidation temperature) is very narrow. From this result it could be concluded that a preferable coating thickness for the CVD W layer is in the range of 100nm to 1μm, more preferable between 500nm and 1μm due to a larger processing window.

Summary and Conclusion

The paper describes an approach to design the interface in copper-diamond composites by using coated diamonds. Two different coating techniques (CVD and PVD) were used for coating of diamonds in the thickness range of some nanometers (Mo) to some micrometers (W). The coated diamonds were investigated by different characterization techniques in order to identify the coating thickness, coating morphology, coating uniformity/homogeneity. For the characterization several different methods such as FIB in combination with SEM, EMPA analyses and transparency measurements were used. The investigated techniques have certain advantages and disadvantages

but in generally useful for the specific analysis of the interface between coating and diamond, the determination of precise coating thickness (FIB+SEM), for the determination of average coating thickness values (EMPA or transparency measurements can be used as a routine control for the characterization of coating quality for comparing different coating batches).

The influence of thin coatings (either PVD or CVD) on the thermal properties in a copper-diamond composite was shown. Even coatings with a small thickness <100 nm show a significant effect on the thermal performance of the material. In addition it was found that also the corresponding consolidation process parameters (temperature/time) must be chosen carefully in accordance for a full exploitation of the thermal conductivity/diffusivity of the diamond filler.

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