Surface Modification of Diamonds in Diamond/Al-matrix composite

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Abstract. Fe- or Mn-powders were mixed with the diamonds and the mixtures were heat treated under different gas atmospheres like hydrogen or argon gas and at varying temperatures in order to roughen the surface of the diamond particles. Subsequently the reaction layers are removed by the addition of aqueous solutions of HCl. The modified surface structure after the etching process is investigated by electron microscopy showing increased roughening of the formerly flat faces of the diamond particles with increasing heat treatment temperature. After drying the diamonds, composites were prepared by gas pressure infiltration with pure Al. For treatments in the temperature range from 750 to 850°C the thermal conductivity can be improved by up to 20 percent compared to composites based on un-treated powders.

Introduction

The aiming for improved heat sink materials exhibiting highest thermal conductivities at tailored coefficients of thermal expansion motivates the search for improved composite materials and for improved interfaces between any matrix and highly conductive inclusion phases. Diamond MMCs are amongst the most promising candidates to fulfill all the challenging requirements. In order to make use of the full potential of the inclusions, the interface must be carefully addressed. Research so far has mainly focused on using carefully adjusted matrix alloys or on the use of suitable coatings of the inclusions [1, 2, 3]. For this, the diamonds can be either coated with carbide forming elements like B, Si or Ti, or formation of a strong interface can be conferred by using alloys containing reactive elements like Fe, Ni, Mo, B, Si, Cr etc., the kind of element mainly depends on the used matrix metal.

A rather rarely employed approach is to increase the specific surface area between the matrix and the inclusions to improve mechanical adhesion and heat flow. Since the diamond surfaces exhibit quite smooth and plane faces the specific surface for a given inclusion size is rather low. In order to increase the specific surface the faces of the diamond must be structured or roughened.

To obtain a rough surface on the synthetic cubed-octahedral diamond grains, a thermal etching method at 700-1100°C in air at atmospheric pressure has been applied [4]. Such oxidizing conditions resulted in a preferable attack of the {111} face of the diamonds, as the etch rate is here higher than that of the {100} face, resulting in an increased surface area of a diamond grain. It has been shown that on etching at 900°C for 15 min, surfaces become fully covered with clear etch pits and the surface area shows maximum value. Etching with mixtures of gases at temperatures of 800-1400°C has shown that O and water vapor are the relevant constituents of air in the formation of well-defined etch pits. Surface graphite formation below 1400°C is also considered [5]. The mechanism of formation is essentially a chemical reaction and not connected with a purely physical phase change.

Others report the use of NaNO₃ or KNO₃ for etching diamonds [6], whereas also a controlled reaction between carbide forming elements like Mn, Co or Fe can be used [7, 8]. To increase the surface of the diamond grains to at least double the natural area, the grains are embedded in metal particles at >700°C with passage of a stream of H₂ or H₂-containing gas. The carbon (diamond)

diffuses into the metal and reacts with the metal-activated hydrogen progressively and creates pinpoint pores. After this roughening the diamond grain may be cleaned with acid.

In this contribution we have used fine Fe and Mn powder as reactive environment to expose the diamond. After cleaning of the diamond from the carbides formed at high temperature, the diamond powder is packed in composites made by gas pressure assisted infiltration of liquid aluminium into the powder beds. The changes in diamond surface structure and of the metal diamond interface are quantified by electron microscopy and by the thermal conductivity of the resulting composites, respectively.

Experimental

The method used for the roughening of the original smooth surface of the diamonds comprises the mixture of the respective diamond powders (Qiming Superabrasive Materials, Henan, China) with fine Fe-, or Mn-powders (BASF carbonyl iron powder CN, Mn-powder: Merck) at a weight ratio of diamond:metal = 1:1 followed by a heat treatment under inert (Ar gas or N₂) or reducing gasatmospheres (H₂ gas) in a muffle furnace. Subsequently, the reacted mixtures are etched by the addition of boiling aqueous solutions of HCl in order to completely remove the reaction layers and therefore end up with overall attacked - "etched" - diamond surfaces.

The heat treatment procedure for the diamonds was varied regarding time, temperature and atmosphere. Various isotherm heat treatments in the range between 700°C and 900°C were selected, either applying Ar- or H₂-atmosphere during processing. The isothermal holding time was selected as 1h for temperatures of 700°C, 750°C and 800°C, and 1.5 hours for 850° and 900°C. The diamonds selected were of MBD4 and JR1 quality and had a grit size of 70/80 (i.e. average particle diameter 200 µm) or 500/600 (only MBD4; i.e. average particle diameter 30-35 µm). The crystals of JR1 are irregularly flaky and needle-like with rough surfaces, whereas the MBD4 quality contains more perfect crystals with smooth surfaces. The diamonds were subsequently gas pressure infiltrated with pure Al. To this end the diamond powder was filled and packed to roughly 60 vol.pct into a cavity machined in a graphite mould that had the slightly conical shape of a sample for thermal conductivity, i.e. a height of 36 mm and a diameter of 13.3-13.7 mm. The graphite mould was inserted in a graphite coated alumina crucible and an ingot of 4N aluminium was placed on top. The crucible was inserted in a cold wall reactor equipped with an induction coil and a graphite susceptor. After having slowly pulled a vacuum down to below 0.1 mbar, the insert was heated to 750°C at a rate of 100-200 K/hour. After stabilization at the infiltration temperature for 30 min argon gas pressure was applied to 0.75 MPa. The infiltrated powder was solidified under pressure. Thermal conductivity measurements at room temperature were performed by a steady-state; equal heat flow method in which the temperature gradients of a reference and the sample connected in series is compared.

"Etched" diamonds were characterized by scanning electron microscopy SEM (Quanta 200 Mk2). Reactions between the Fe and Mn-powders and the diamonds were studied in detail by using a combined Differential Thermal/Thermogravimetry Analysis (DTA/TGA) equipment by heating up the mixtures under Ar gas atmosphere (H₂ gas atmosphere was not applicable) and simultaneous detection of evolving gases from reactions by mass spectroscopy MS (Netzsch STA 449C + QMS 403C: heating rate 20 K·min⁻¹).

Results and Discussion

Fig. 1A reflects the results for a reaction of the diamonds mixed with Fe-powders and heated under Ar gas atmosphere up to 900°C. The dashed curve represents the TG signal (mass loss); the bold line corresponds to the DTA signal [μ V/mg]. The DTA signal indicates a reaction at approx. 750°C, and the TGA measurement gives a mass loss at 690°C (mass change -0.15%). The simultaneous recording of the isotope m44 (CO₂), m28 (CO or N₂), m32 (S or O₂), m18 (H₂O), m15 (organic compounds or CH₃) and m12 (C) by mass spectroscopic measurements indicate evolving gases by

reactions during heating. The results show a distinct reaction starting at approximately 470°C, as well as a very pronounced one at about 680°C, with its maximum at about 730°C, both characterized by evolving CO/CO₂ gases (m44 and m28). m12 (C) and m32 (O₂) give a simultaneous signal, but give no further relevant information. Therefore both - together with m18 and m15, which also show no relevant signals - are not displayed in Fig. 1.



Fig. 1. STA/TG-MS analysis of MBD4 70/80 diamonds + Fe-powders (Ar-atmosphere) (A) and MBD4 70/80 diamonds + Mn-powders (Ar-atmosphere) (B) at temperatures up to 1000°C, simultaneous gas analysis by mass spectrometry for isotopes m44 (CO₂) and m28 (CO or N₂). m32 (S or O₂), m18 (H₂O), m15 (CH₃) and m12 (C) measured but not displayed.

No marked reactions can be deduced from DTA and TG analysis of diamonds and Mn-powders under Ar gas atmosphere, and no significant production of gases (Fig. 1B). Only the significant DTA-signal at approximately 750°C was detected again, but there is no correspondence in the TG-signal. This might be attributed to a graphitization of the diamonds in presence of metallic catalyst. Additionally characterization of the Mn-treated surface by RAMAN spectroscopy (not displayed) shows the signal of pure diamonds, no graphite can be detected.

Mass loss of MBD4 and JR1 diamonds 70/80 by reaction with Fe-powders under H_2 -atmosphere indicate a generally higher loss for JR1 diamonds, than for MBD4 (Fig. 2). Therefore the attack must be higher for the JR1, than for MBD4 diamonds.



Fig. 2. Mass loss of MBD4 and JR1 70/80 diamonds during reaction with Fe-powders (H₂atmosphere) at 750 - 900°C

SEM analysis of diamonds - heat treated and etched by HCl (Fig. 3) – confirm the increasing attack of the JR1 diamonds compared to MBD4. All crystallographic faces are attacked, no preference is visible. Increasing time and temperature additionally increases the degree of the attack; diamonds are increasingly being "etched". Fig. 4 shows a different surface morphology of MBD4 diamonds reacted with Mn-powders under N₂-atmosphere. All faces are uniformly corroded, leaving behind small dimples on the original smooth surfaces.



reacted with Fe-powders at different temperatures and times with H₂-atmosphere; reaction layers removed by HCl

powders at 750°C for 30 min and N₂-atmosphere; reaction layers removed by HCl

In view of the much more pronounced attack by the iron powders, only diamonds reacted with Fe have been used. The evolution of the thermal conductivity as a function of the heat treatment temperature is given in Fig. 3 for the JR1 70/80 and the MBD4 70/80. For comparison the level of conductivity reached by the untreated powder is also indicated in Fig. 3.



Fig. 3. Thermal conductivity of composites as a function of etch-treatment temperature for composites based on MBD4 70/80 and JR1 70/80 together with the respective level of conductivity of the untreated powders.

For the treatment at 700°C only a small improvement in thermal conductivity of the resulting composite compared to those based on the untreated powder can be seen in case of JR1 diamonds. This is in line with the first pronounced reaction indicated by the TGA and mass spectrometry analysis occurring at 730°C (which is, incidentally, also the temperature of the eutectoid in the iron carbon binary system). For the heat treatment at 750°C the resulting composites exhibited the highest thermal conductivity for both JR1 and MBD4 diamond. Although the incremental increase is higher for JR1, than for MBD4 diamond composites, the later ones are the ones with the highest overall TC of all tested composites. For higher heat treatment temperatures the conductivity decreases slightly and for the MBD4 at least falls below the thermal conductivity of the un-treated powder. It is to be noted that the three points at 900°C are from two different powder batches, the lowest points stemming from the same batch. For the JR1 powder the improvement with regard to the untreated powder is more than 20 percent at 750°C, and, with regard to the MBD4, the difference becomes very small, giving an economical advantage to the use of the much cheaper JR1 powder instead of the MBD4.

The improvement in thermal conductivity of the JR1 based composites however is difficult to be rationalized by an increase in specific surface area: According to unpublished results of the authors, the interface thermal conductance of the Al/diamond couple is on the order of $5 \cdot 10^7$ W/(m²K), in line with results from dedicated measurements of e.g. Stoner and Maris [9]. Therefore, an increased specific surface area, tantamount with an improved interface thermal conductance, is not expected to give a large improvement at a diamond particle size of 200 µm, since the effective inclusion conductivity [1] is not strongly affected by varying *h* (which is the interface thermal conductance, defined as the ratio of heat flux and temperature drop across the interface) by, say, a factor of 2. The situation is different for a powder with a particle size of 30 µm only, i.e. a grit size of 500/600. For this reason, we have performed a thermal treatment at 800°C on a diamond powder of a grit size of 500/600 in order to verify that the increased surface area has indeed the expected effect. For the untreated powder the composite containing 57 vol.-pct diamond reached a thermal conductivity of 200 W/mK. A similar composite based on etch-treated powder yielded a thermal conductivity of 321 W/mK, an improvement of 60%.

Conclusion

Diamond particles can effectively be etched by thermo-chemical etching in Fe- and, to a lesser extent, Mn-powders. The optimum etching temperature seems to be in the range between 750 and 800° C, eventually 850° C. Lower temperatures do not produce sufficient attack and higher temperatures seem to lead to too strongly attacked diamonds. The thermal conductivity of composites based on the etch-treated diamonds improves slightly for the large MBD4 diamond and by over 20% for the large JR1 diamond. Small diamonds, i.e. MBD4 diamonds with about 20 μ m average size profit the most from the treatment yielding a thermal conductivity increased by 60 percent compared to the composites based on untreated small diamonds.

References

- [1] R. Tavangar, J.M. Molina, L. Weber: Scripta Mater. 56 (2007) 357-360
- [2] L. Weber, R. Tavangar. Scripta Materialia 57 (2007), 988-991
- [3] T. Schubert, B. Trindade, T. Weissgärber, B. Kieback. Mat. Sci Eng. A 475 (2008), 39-44
- [4] H. Tokura, M. Yoshikawa. Journal of Materials Science (1989), 24(6), pp 2231-8
- [5] T. Evans, D.H. Sauter. Philosophical Magazine (1798-1977), (1961), 6, 429-440

- [6] A.R. Patel, S.M. Patel. Journal of Applied Crystallography (1969), 2 (Pt. 4), 183-1888
- [7] D. Borse. German patent DE3625753 A1 (1988)

[8] J. Wang, J. Margrave, H. Robert. Proceedings – Electrochemical Society, 97-39 (High Temperature Materials Chemistry, 755-761), Publisher: Electrochemical Society. (1997)

[9] R.J. Stoner, H.J. Maris: Phys. Rev. B. 48 (22) (1993) 16373-16387

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