

UNDERSTANDING AND TAILORING INTERFACIAL BONDING STATES OF A DIAMOND/AL COMPOSITE FOR THERMAL MANAGEMENT APPLICATIONS

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ABSTRACT

A diamond/Al composite for thermal management applications has been developed by powder metallurgy using vacuum hot pressing (VHP) and spark plasma sintering (SPS) techniques. Multiscale microstructure characterization in terms of X-ray diffraction, scanning and (high-resolution) transmission electron microscopy has been used to evaluate the effects of interfacial configurations on interfacial bonding states and overall thermal conductivity (TC). We found that the three different kinds of interfacial bonding states, i.e. non-bonded, diffusion-bonded and reaction-bonded interfaces can be acquired by VHP, where the presence of the 'clean' diffusion-bonded interface at the micrometer scale is the most favorable for overall TC enhancement. Comparatively, due to a large temperature gradient spontaneously generated, SPS only allows to acquire a mixed interface including all the above-mentioned states. In this case, the amount of diffusion-bonded interface, being tailorable by SPS parameters, determines the efficiency of overall TC enhancement.

1 INTRODUCTION

In the microelectronic industry, improving energy efficiency of devices has been an active area of materials research over the last few decades, stemming mainly from the drive of computing industry to maintain Moore's law. Power density of a today's CPU is easily exceeding that of a nuclear reactor and is comparable to that on the Sun's surface [1].

Electronic packaging involves interconnecting, powering, protecting and cooling of semiconductor circuits for use in a variety of microelectronic applications. For example, a CPU is typically pressed against a copper heat spreader that is cooled by a heat sink. For microelectronic circuits, the main type of failure is thermal fatigue, due to the different coefficients of thermal expansion (CTE) of semiconductor chips ($< 6 \times 10^{-6} \text{ K}^{-1}$) and packaging materials (e.g. $17 \times 10^{-6} \text{ K}^{-1}$ for Cu). In addition, because the power density increases rapidly, the ability to dissipate heat becomes a very important factor for the reliability of electronic systems from individual microprocessors to data centers. An effective packaging material with a high thermal conductivity (TC) can eventually lead to good heat dissipation and, thereby effective thermal management. In return, this renders high performance and possible further miniaturization of the components [2]. Among all the developed composite materials for thermal management applications, an Al matrix composite reinforced with synthetic diamond particles (namely diamond/Al composite) has attracted considerable attention since its first discovery in 1993 [3]. The reasons are that despite undesirable machinability and price, synthetic diamond has a high TC in the range 1000-2000 W/m K and a low CTE of 1-3 ppm/K. Pure Al as the matrix candidate material has a relatively high TC of around 240 W/m K among pure metals, and low density and price.

Vacuum hot pressing (VHP) and spark plasma sintering (SPS) are two popularly used powder metallurgy techniques. Compared with conventional VHP, the main advantages of SPS include a faster heating rate (up to 1000 °C/min), a lower sintering temperature and a shorter holding time. As a result, the SPS process can result in ultrafine and/or nanoscale grain structures in final materials by effectively limiting recrystallization and grain coarsening [4,5]. Use of a pulsed dc current during SPS can further have a significant impact on solid-state reactivity and mass transport as well as current and temperature distributions [4,5]. In our previous work, the highest TCs of the VHPed diamond (50 vol.%) / Al composite has reached around 500 W/m K [6] and 600 W/m K by using W-coated diamond particles [7]. The SPS technique has been used but failed to compete with VHP to produce samples with comparable TCs. For example, the SPSed diamond (45 vol.%) / Al composite has the highest TC of around 400 W/m K [8], while the TC of the SPSed diamond (50 vol.%) / Al composite can only extend from 310 to around 490 W/m K by using Ti-coated diamond particles [9].

It is well-known that the interface between reinforcement particles and matrix plays a crucial role in determining the overall TC of a composite; an ideal interface should provide good adhesion as well as minimum interfacial thermal resistance (ITR) [10,11]. In the diamond/Al composite, interfacial reaction via the follow equation: $\text{Al} + \text{C} \rightarrow \text{Al}_4\text{C}_3$ provides an opportunity for tailoring ITR and interfacial bonding state by varying Al_4C_3 morphology, quantity and distribution. Surface modification of diamond particles by coating a carbide-forming layer (e.g., W, Mo) is also an effective way allowing to tailor interface during the following sintering process [12]. However, the underlying relationship between diamond/Al interfacial configurations and interfacial bonding states, i.e. non-bonded, diffusion-bonded and reaction-bonded interfaces, has not been thoroughly revealed so far.

In this work, we have developed an diamond/Al composite by means of VHP [6] and SPS techniques [13] and surface modification [7]. Microstructure of the composite samples has been characterized at length scales from the macro to the nanoscale in order to investigate presence of Al_4C_3 in particular, and more generally the detailed diamond/Al interface assembly configurations by X-ray diffraction, scanning (SEM) and (high-resolution) transmission electron microscopy ((HR)TEM). We aim at developing understanding of the effects of tailor-made diamond/Al interfaces on interfacial bonding states, ITR and overall TC. Results of a few typical interfacial configurations revealed at the micrometer and nanoscales will be shown and discussed in this paper.

2 EXPERIMENTAL

A synthetic diamond powder (Type HWD40 and average particle size of 200 μm) was purchased from Henan Huanghe Whirlwind International Co. Ltd., China. A pure Al powder (around 99.8 % in purity) having the particle size in the range 75-105 μm was used as matrix material. The as-received diamond particles were first ultrasonicated in distilled water to eliminate impurities on the surface, and then they were dried and directly mixed with pure Al powders. Diamond volume fraction was varied in the range 20-55 %. The powder mixtures were first cold pressed into powder compacts, and then sintered by VHP in a graphite mould. Uniaxial pressure in the range 34-135 MPa was applied and sintering temperature was set to in the range 550-655 °C. Vacuum level was maintained lower than 0.005 Pa during the whole VHP process. A model 2040 SPS apparatus (Sumitomo Coal and Mining Co., Ltd.) was used as an alternative sintering process in quick heating and cooling mode. Vacuum level of sample chamber was pumped down to 5×10^{-2} Torr before heating. Constant uniaxial pressure of 50 MPa was kept during heating and cooling stages and holding time of 5 min was used for all the SPS processes. The SPS temperature in the range 540-560 °C was tested. More information concerning preparation details can be found in [6, 13]. A cost-effective sol-gel approach followed by heat treatment was used to introduce W nanoparticles onto the surface of initial diamond particles [7].

Nearly-perfect surface of the as-fabricated composite samples was prepared by triple ion beam (TIB) cutting technique and characterized using a HITACHI S-4700 scanning electron microscope (SEM) equipped with a field emission gun (FEG) and a Noran energy dispersive X-ray (EDX) spectrometry system. A STRATA DB 235 dual beam FIB instrument was employed to prepare specimens having diamond/Al interface of interest for TEM study. A Philips CM30 (operated at 200 kV), a FEI Tecnai G2 (operated at 200 kV) and a FEI TITAN Themis 300 microscopes (operated at

120 kV and equipped with a probe aberration corrector) were used for (HR)TEM characterization in TEM and scanning TEM modes.

Relative density (ρ) of the sintered samples was measured by the Archimedes' method. Thermal diffusivity (α) was measured by a laser flash technique using a Netzsch LFA447 thermal constant analyzer in the applied laboratory of Netzsch company, Shanghai China. TC (λ) of the composites was calculated using the following equation $\lambda = \alpha \rho C_p$, where ρ and C_p represent density and specific heat capacity, respectively. C_p of the diamond/Al composite was calculated by the rule of mixtures using C_p values of the constituents: 512 J/kg K for diamond particle and 890 J/kg K for Al matrix.

3 RESULTS AND DISCUSSION

By optimization of VHP and SPS parameters, a series of diamond/Al samples have been produced and then, analyzed in terms of relative density and TC measurements and microstructure characterization at the multiscales. Figs. 1 and 2 compare the interfacial structure at the micrometer scale of the two diamond(40 vol.)/Al samples obtained by VHP and SPS in optimized conditions. The interest for such a comparison is that despite different techniques and conditions, both samples have high relative density of around 97 %, while different TC of 475 and 330 W/m K in the VHP and SPS cases, respectively. The similar and high relative densities indicate, at least, achievement of good physical bonding at the diamond/Al interface in both samples. As a result, the observed TC difference mainly depends on interfacial chemical nature and bonds, and related formation of the diffusion or reaction bonded interfacial states. Note that the matrix grain structure has marginal effects on TC compared with the interface issue in metal matrix composites (MMCs). XRD examination shows that the SPSed (but not VHPed) sample contains a few detectable peaks corresponding to the Al_4C_3 phase (referred to [13] for XRD patterns). This means that the Al_4C_3 quantity in the SPSed sample is higher than in the VHPed one due to the interfacial reaction.

In the VHPed sample (Fig. 1a), the diamond particles closely stick to the Al matrix in the polished surface to show a good bonding state. The zoom-in images in Figs. 1b-1d further reveal that the diamond/Al interfaces are tightly adhered without any defects and interfacial products like Al_4C_3 . Comparatively, in the case of the SPSed sample, the SEM image of the polished surface in Fig. 2a shows first two imprints where diamond particles have been attacked away during the TIB preparation process due to locally poor interfacial bonding. Second, different from the overall 'clean' diamond/Al interfaces in the VHPed sample, the three different types of interfacial configurations including interfacial fractures (Fig. 2b), interfacial products (Fig. 2c) and 'clean' interface (Fig. 2d) are distinguished at this micrometer scale. As also shown in Fig. 2c, the platelet-like interfacial products having the length of about several micrometers and their nature has been identified by SEM/EDX analysis corresponding to Al_4C_3 , being in agreement with the XRD result. Besides, there are finer interfacial particles having the size in the sub-micrometer range which cannot be surely identified by SEM.

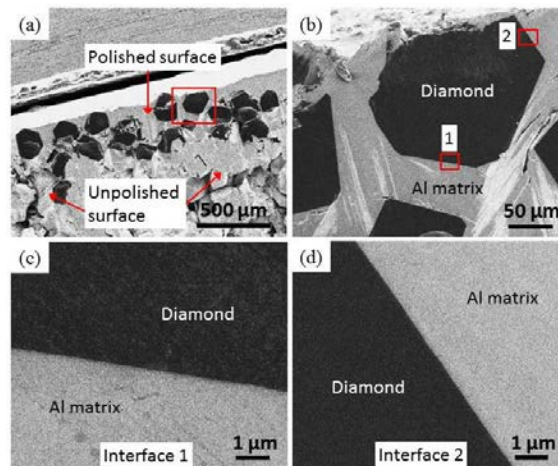


Figure 1: SEM images showing (a) an overview of polished and unpolished surfaces of the VHPed diamond(40 vol.%)/Al composite sample, (b) diamond/Al interfaces in the polished flat surface selected by a rectangle box given in (a) and (c) and (d) zoom-in of ‘clean’ diamond/Al interfaces in boxes numbered by Nos. 1 and 2 shown in (b).

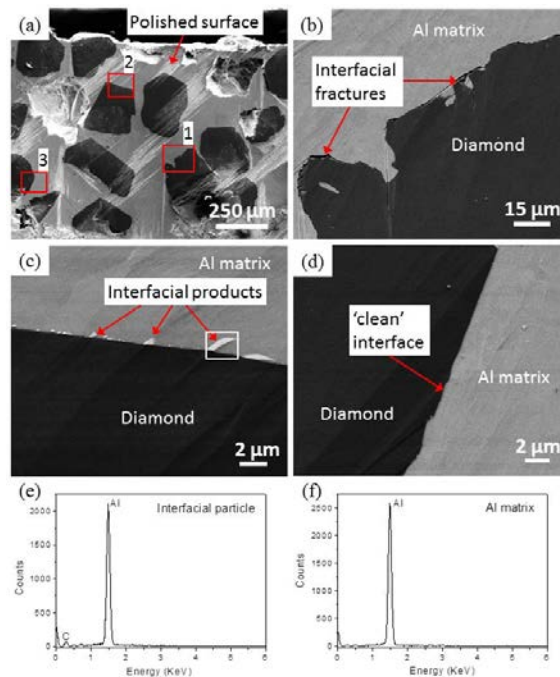


Figure 2: SEM images showing (a) an overview of polished surface of the SPSed diamond (40 vol.%)/Al composite sample containing mixed interfacial features, (b) fracture interface in the box No. 1 shown in (a), (c) interface with visible reaction products in the box No. 2 shown in (a) and (d) ‘clean’ interface in the box No. 3 shown in (a); (e) and (f) are EDX spectra of the platelet-like interfacial particle in the box shown in (c) and the Al matrix next to this particle, respectively.

A closer look at a typical area of the ‘clean’ interface in the VHPed sample (Fig. 3) reveals an $\text{Al}/\text{Al}_2\text{O}_3/\text{Al}_4\text{C}_3/\text{diamond}_{\{100\}}$ multi-interface and the crystallographic relationship $\{003\}_{\text{Al}_4\text{C}_3}/\{111\}_{\text{diamond}}$. This result indicates that Al_4C_3 nucleates at the $\{111\}$ facet of the $\{100\}$ diamond surface. Contrast to this, Fig. 4 shows a sharp $\text{diamond}_{\{111\}}/\text{Al}$ interface homogeneously covering an Al_4C_3 interfacial layer where individual Al_4C_3 can be further extended into the Al matrix. The thin layer has the thickness of around 10 nm and the relationship $\{003\}_{\text{Al}_4\text{C}_3}/\{111\}_{\text{diamond}}$ is also confirmed since the measured spacing of $\{006\}_{\text{Al}_4\text{C}_3}$ planes ($d=0.416$ nm), being parallel to $\{111\}_{\text{diamond}}$, is exactly twice smaller than that of $\{003\}_{\text{Al}_4\text{C}_3}$ planes ($d=0.832$ nm) (Fig. 4b). It is well-known in diamond/Al composite processed by liquid infiltration that dissolution of carbon atoms at the $\{100\}$ surface of diamond crystal is much easier than those at the $\{111\}$ surface due to its weak two-fold bonding state. As a result, platelet-like Al_4C_3 has often been observed to nucleate and growth at the $\text{diamond}_{\{100\}}/\text{Al}$ interface, while the $\text{diamond}_{\{111\}}/\text{Al}$ one can still remain unattached by liquid Al [14,15]. Our TEM results confirm the beginning of the reaction bonded interface state by forming the nanoscale Al_4C_3 at both $\{100\}$ and $\{111\}$ surfaces of diamond. Similar to being reported in the literature, the heterogeneous interfacial features mainly originate from the different properties of the $\{100\}$ and $\{111\}$ surfaces of diamond. In general, the results of XRD, SEM and TEM indicate that the VHP technique performed in thermodynamically equilibrium conditions provides a large processing window and homogenous temperature field enabling to tailor the ‘clean’ diffusion-bonded interface at the micrometer scale but not at the nanoscale. The SPS technique is featured by a large temperature gradient which is beneficial for locally conserving nano and/or ultrafine grain structure [4,5]. However, regarding the key issue of interface engineering, the conventional VHP technique is

definitively more feasible than the SPS technique to allow the unique -if any- diffusion-bonded interfacial state to be tailored, in the diamond/Al composite (at the micrometer scale) and in the SiC/Al composite (at the nanoscale) [16], in order to maximize the effectiveness of TC enhancement. The SPS only allows to acquire a mixed interface including locally non-bonded, diffusion-bonded and reaction-bonded states whatever adjusted parameters (see Fig. 2). In this case, the amount of diffusion-bonded interface, being tailorable by SPS parameters, determines the efficiency of overall TC enhancement. Hence, the TC enhancement is possible but less effective by only increasing the amount of diffusion-bonded interface in the SPSed sample.

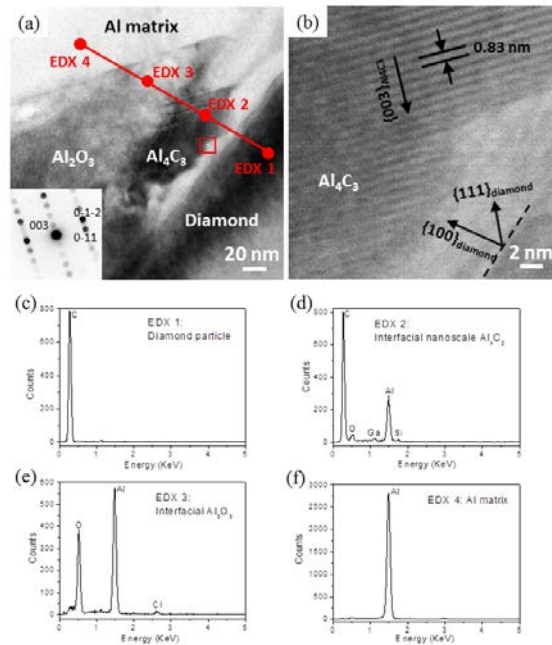


Figure 3: (a) TEM bright-field image highlighting an interfacial area containing Al_2O_3 and Al_4C_3 , (b) zoom-in lattice image of the area in box shown in (a), (c)-(f) typical EDX spectra recorded from the diamond, interfacial Al_4C_3 and Al_2O_3 and Al matrix. Inset in (a) is the [100] ZAP of Al_4C_3 with adjusted orientation relationship with respect to image.

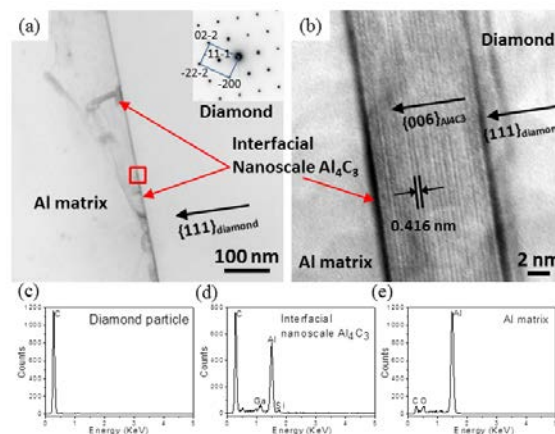


Figure 4: (a) TEM BF image showing a straight diamond_{111}/Al interface of the VHPed diamond (40 vol.%) / Al composite in the as-prepared FIB sample, (b) zoom-in lattice image of interfacial area in the box in (a) showing an Al_4C_3 interfacial layer having the thickness of around 10 nm, (c), (d) and (e) typical EDX spectra recorded from the diamond, interfacial Al_4C_3 and Al matrix, respectively. Inset in (a) is the [011] ZAP of diamond side with adjusted orientation relationship with respect to image.

4 CONCLUSIONS

The diamond/Al composite has been produced by VHP and SPS techniques and characterized at the multiscale by XRD, SEM and (HR)TEM. Both techniques allow densification to have high density in a comparable way, while demonstrate very different capability for tailoring interfacial bonding states, i.e. non-bonded, diffusion-bonded and reaction-bonded states being important for overall TC enhancement. The conventional VHP technique provides a large processing window by adjusting sintering temperature and time showing definitive advantages for tailoring ‘clean’ diffusion-bonded interface at the micrometer scale, being ideal for TC enhancement. Comparatively, the SPS technique performing in a quick heating-cooling mode and featured by a large temperature gradient unavoidably generated inside the sample is unable to acquire a unique diffusion-bonded interface. Instead, the mount of such an interface can be tailored by optimization of SPS parameters. In terms of this mechanism, the overall TC can be enhanced but in a less effective way than in the VHP case. From the technical point of view, the unusual characteristics involved in the SPS process should be reevaluated for producing specific MMCs for functional applications.

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