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Effect of sintering on the relative density of Cr-coated diamond/Cu composites prepared by spark plasma sintering

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Abstract: Cr-coated diamond/Cu composites were prepared by spark plasma sintering. The effects of sintering pressure, sintering temperature, sintering duration, and Cu powder particle size on the relative density and thermal conductivity of the composites were investigated in this paper. The influence of these parameters on the properties and microstructures of the composites was also discussed. The results show that the relative density of Cr-coated diamond/Cu reaches ~100% when the composite is gradually compressed to 30 MPa during the heating process. The densification temperature increases from 880 to 915°C when the diamond content is increased from 45vol% to 60vol%. The densification temperature does not increase further when the content reaches 65vol%. Cu powder particles in larger size are beneficial for increasing the relative density of the composite.

Keywords: metal matrix composites; copper; diamond; relative density; spark plasma sintering

1. Introduction

Diamond/Cu composites have drawn intensive attention in recent years because of their potential excellent thermophysical properties, such as high thermal conductivity and tailored coefficient of thermal expansion (CTE) [1–4]. Diamond/Cu composites can be prepared by powder metallurgy or metal infiltration. However, regardless of the preparation method, the thermal conductivity of such composites is much lower than that of Cu itself if diamond particles are compounded directly with Cu, resulting from the chemical incompatibility and weak mechanical bonding between Cu and diamond [4]. As a result, their interface thermal resistance is so high that the composites exhibit low thermal conductivity. To improve interfacial bonding between Cu and diamond, strong-carbide-forming elements [5–14], such as Cr [1], Ti [2], B [1], and Zr [13], are usually introduced into the interface by directly coating them on the surface of diamond particles or by adding them as alloying elements into the Cu matrix. These elements can effectively improve the bonding strength and thermophysical characteristics by forming a thin nano-sized carbide layer at the interface between Cu and diamond. Schubert *et al.* [4] produced 50vol% diamond/Cu composites by powder metallurgy and increased the thermal conductivity from 200 to 640 $W\cdot m^{-1}\cdot K^{-1}$ by using the atomized Cu alloy with the addition of 0.8wt%Cr. They also observed that adding 0.3wt%B to the Cu matrix greatly increased the thermal conductivity of the diamond/Cu composite. Using similar Cu–B and Cu–Cr alloys, Weber and Tavangar [1] fabricated diamond/Cu composites with a thermal conductivity greater than 700 $W\cdot m^{-1}\cdot K^{-1}$ by gas pressure infiltration.

In addition to the diamond/Cu interface, the composite properties can be greatly affected by the characteristics of diamond. Diamond is easy to graphitize at temperatures greater than 1000°C. The graphitization of diamond substantially reduces its thermal conductivity. Thus, the temperature used to prepare diamond/Cu composites should be as low as possible. Compared with pressure infiltration, which requires temperatures greater than 1080°C, spark plasma sintering (SPS), as a powder metallurgy route, offers numerous advantages with respect to producing particle-reinforced metal composites, including the short sinter-

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ing period and low sintering temperatures [15–17]. Diamond/Cu composites were also previously prepared by SPS [7]; in most cases, these previous studies focused on improving the Cu–diamond interface and usually involved the fixed process parameters. The effects of specific parameters in SPS process (e.g., the sintering temperature, the method of pressure application, and the characteristics of raw powder) on the properties of diamond/Cu composites have not been fully elucidated. Thus, the effect of sintering temperature, pressure, size, and volume fraction of matrix powders on the relative density and thermal conductivity of diamond/Cu composites was investigated in this paper and the optimal SPS processing parameters were determined.

2. Experimental

2.1. Preparation of composite

Synthetic MBD4-grade diamond particles in a diameter of 100 μm were coated with an approximately 1-μm-thick Cr layer by vacuum microdeposition technology in this work. Electrolytic Cu powders with different particle sizes were first mixed with the diamond powders in a designed volume fraction. The mixture was then sintered by SPS at a certain sintering pressure and sintering temperature. Finally, the diamond/Cu composites were fabricated. Fig. 1 shows the morphologies of Cr-coated diamond particles and Cu powders, respectively.

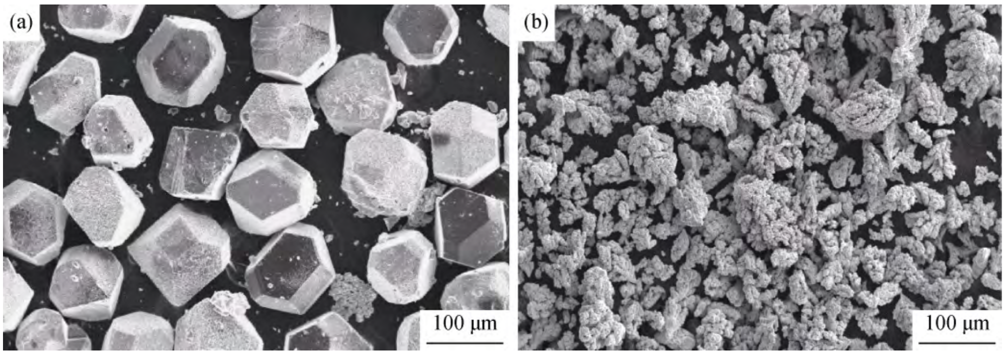

Fig. 1. Morphologies of the Cr-coated diamond particles (a) and electrolytic Cu powders (b).

2.2. Property testing

Cylindrical disc specimens with a diameter of 10 mm and a thickness of 3 mm were produced for testing thermal diffusivity. Thermal conductivity is specifically associated with the product of density, thermal diffusivity, and specific heat. In this work, thermal diffusivity and specific heat were measured using laser flash and calorimetric techniques, respectively. The density of the composites was measured by the Archimedes method. The microstructures of the composites were observed by scanning electron microscopy (SEM, Carl Zeiss LEO1450).

3. Results and discussion

3.1. Sintering pressure

The mixture of Cr-coated diamond particles and Cu powders was densified at a certain temperature and pressure. In previous research, Ti-coated diamond/Al composites were prepared by SPS [18], which affected the densification of the mixture by a certain pressure during the heating operation. It was found that, the density of the composite was greater when the final sintering pressure was directly applied to the mixture before the heating operation than that when the pressure was gradually applied up to the final value as the sample was heated to the final sintering temperature. The effect of sintering-pressure loading methods on the relative density of diamond/Al by SPS was attributed to the presence of an Al_2O_3 film on the surface of Al powders [18]. However, compared with Ti-coated diamond/Al composites, the effect of sintering-pressure loading methods on the densification of the mixture of Cr-coated diamond particles and Cu powders in the present work was the opposite. Fig. 2 shows the changes in relative density of 60vol% diamond/Cu composites as a function of sintering pressure loading by two different methods. The final designed sintering temperature was 915°C.

As shown in Fig. 2, under the same sintering pressure, the relative density is greater for the composite prepared by applying pressure gradually to the final value during the heating process than that prepared by applying the final sintering pressure directly before the heating. This result differs from Ref. [18] for diamond/Al composites, which is attributed to differences in the characteristics of matrix powders. In the case of Al powders, the pressure applied before heating can break up the oxide Al_2O_3 film and may avoid the local discharging of the loose powders, which could induce an increase in local temperature and result in the uneven melting of powders. The surface of Cu powders is not coated with an oxide film, and the temperature distribution among the mixture of Cu powders and diamond particles is also uniform. The pressure applied to the mixture before heating is not beneficial for flowing and filling the melting Cu among the diamond particles.

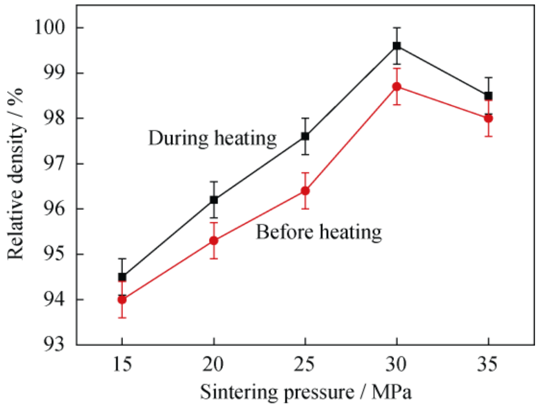

Fig. 2. Relative density change of diamond/Cu composites with increasing sintering pressure by different loading methods.

Additionally, as evident in Fig. 2, the relative density of the 60vol% diamond/Cu composite sintered at 915°C increases with the increase in pressure from 15 MPa to 30 MPa and then decreases as the pressure is further increased to 35 MPa. This behavior is attributed to molten Cu being squeezed out of the die at higher pressures; thus, the Cu content of the matrix in the composite will be lower than the designed composition. Thus, the real density of the composite is lower than the designed value. Therefore, the relative density is also lower if the same theoretical value is used in relative density calculations for all samples.

3.2. Sintering temperature and time

Fig. 3 shows the change in relative density of the 45vol%–65vol% diamond/Cu composites with increasing sintering temperature. The sintering pressure was 30 MPa, and the holding time was 15 min.

As evident in Fig. 3, the densification temperature differs for diamond/Cu composites with different volume fractions of diamond particles. It increases from 880 to 915°C as the volume fraction increases from 45% to 60%. However, the densification temperature does not further increase after the content reaches 65vol% and the maximum relative density also decreases. The sintering temperature of pure metal or alloys is known to be approximately 0.7–0.8 melting temperature (T_m), e.g. approximately 758–866°C for pure Cu powders [18]. When the diamond particles are added to Cu powders, they absorb some of heat around the Cu powder particles; as a result, a higher sintering temperature is needed to densify the Cu powders. In addition, interfacial densification between the Cu powder particles and the diamond particles also requires higher temperatures to ensure that they could wet each other and that the Cu phase could fully spread over the surface of the diamond particles. Therefore, the sintering densification temperature reasonably increases with increasing volume fraction of diamond particles. In the case of lower densification temperatures for the 65vol% diamond/Cu composite, the closest packing fraction of the diamond with a single size of 100 μm is approximately 63vol%, which is less than 65vol%, meaning that the content of Cu powders is not sufficient to fill the space among the diamond particles; thus, both the temperature and the relative density are lower.

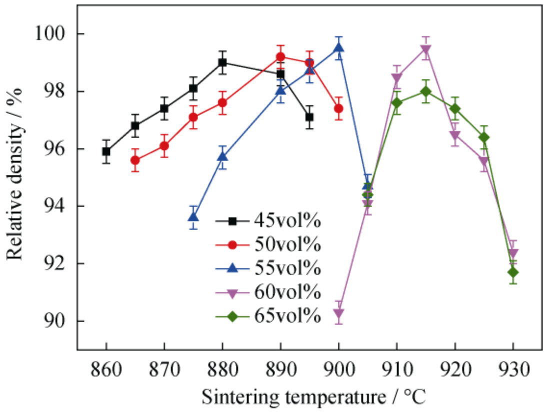

Fig. 3. Relative density change of 45vol%–65vol% diamond/Cu composites with increasing sintering temperature.

Fig. 4 shows the thermal conductivity of the dense composites with 45vol% to 60vol% diamond particles. The thermal conductivity increases with increasing diamond content. Additionally, considering the combined effects of particle size, volume fraction, and interfacial thermal resistance, the *H–J* model was adopted to calculate the theoretical value of the composite as the following equation [19].

$$\lambda_c = \lambda_m \left[\frac{2\left(\lambda_p/\lambda_m - \lambda_p R_c/a - 1\right)V_p + \lambda_p/\lambda_m + 2\lambda_p R_c/a + 2}{\left(1 - \lambda_p/\lambda_m + \lambda_p R_c/a\right)V_p + \lambda_p/\lambda_m + 2\lambda_p R_c/a + 2} \right] \tag{1}$$

where λ_c refers to the thermal conductivities of the composite, $W{\cdot}m^{-1}{\cdot}K^{-1}$; λ_m the thermal conductivity of the matrix, $W{\cdot}m^{-1}{\cdot}K^{-1}$; λ_p the thermal conductivity of the reinforcement, $W{\cdot}m^{-1}{\cdot}K^{-1}$; V_p the volume fraction of the reinforcement, vol%; a the particle size of the reinforcement, m; and R_c the interfacial thermal resistance, $m^2{\cdot}K{\cdot}W^{-1}$. All of these parameter values can be obtained from Ref. [7]. As evident in Fig. 4, the experimental value of thermal conductivity of the composite with 55vol% or 60vol% diamond is similar to the theoretical value; by contrast, the value is substantially lower than the theoretical value when the diamond content is 50vol% or 45vol%. This discrepancy is attributed to the different interfacial thermal resistance of the composite resulting from the different interfacial structure.

Fig. 5 presents interfacial scanning electron microscopy (SEM) images and Cr element distribution in the composites with 50vol% and 60vol% diamond. The interfacial layer of the 50vol% diamond/Cu composite is much thicker than that of the 60vol% diamond/Cu composite, which is attributed to the lower densification temperature of the 50vol% diamond/Cu composite, reducing the thermal diffusivity of the Cr layer into the Cu matrix and resulting in a thicker interfacial layer and a greater thermal resistance. Therefore, the 50vol% diamond/Cu composite exhibits a lower thermal conductivity than the theoretical value based on a smaller interfacial thickness in the 60vol% diamond/Cu composite, although both of them have the similar maximum relative density.

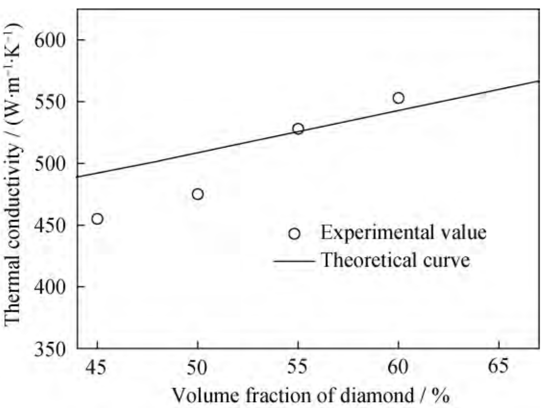

Fig. 4. Thermal conductivity of composites with different diamond contents.

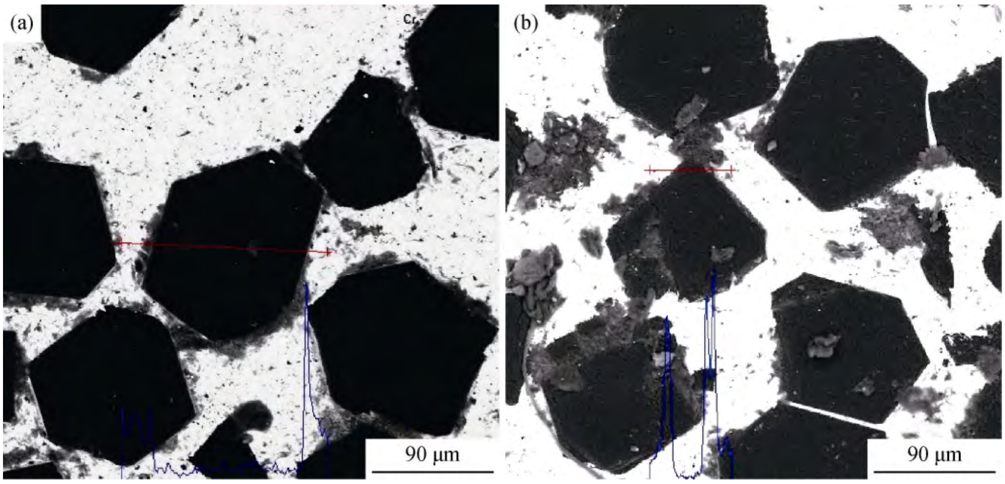

Fig. 5. SEM images and Cr element distribution on the interface in composites with 50vol% diamond (a) and 60vol% diamond (b).

Fig. 6 shows the relative density and thermal conductivity of the 60vol% diamond/Cu composite as a function of sintering time. The sintering pressure was 30 MPa, and the temperature was 915°C. Both the relative density and the thermal conductivity of the composite are observed to increase as the sintering time is increased from 5 min to 15 min. With a further increase to 30 min, the relative density exhibits no obvious change, although the thermal conductivity decreases. The composite with a lower relative density exhibits a lower thermal conductivity because pores within the composite can severely degrade its properties. The composite sintered at 915°C for 30 min exhibit a lower thermal conductivity than that sintered for 15 min although their relative densities are similar, which is attributed to their different interfacial structures.

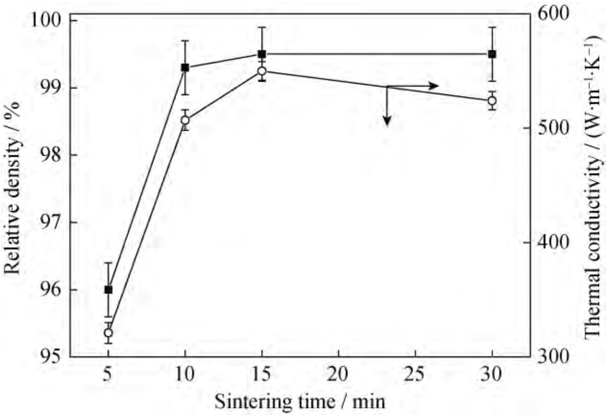

Fig. 6. Changes in relative density and thermal conductivity of 60vol% diamond/Cu composites with increasing sintering time.

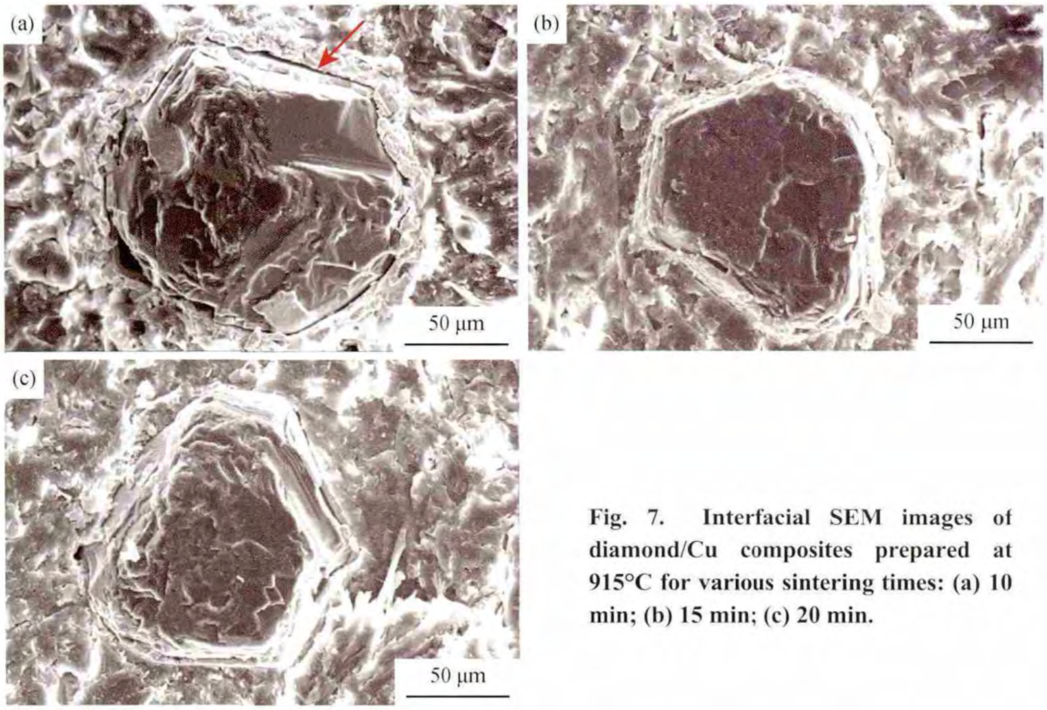

Fig. 7. Interfacial SEM images of diamond/Cu composites prepared at 915°C for various sintering times: (a) 10 min; (b) 15 min; (c) 20 min.

Fig. 7 shows the interfacial SEM images of the composites sintered for 10, 15, and 30 min. Interfacial bonding sintered for 10 min between Cr-coated diamond and the Cu matrix is bad. As indicated by the red arrow, obvious gaps are observed; these gaps can degrade some properties, such as relative density and thermal conductivity. When the sintering time is increased to 15 min, the interface becomes dense and the interfacial bonding is good. With a further increase to 30 min, the local interface layer becomes thinner and even disappeared; thus, the thermal conductivity decreases.

3.3. Cu powder size

Cu powders with the particle sizes of 30, 60, and 120 μm were used to study the effect of particle size on the properties of diamond/Cu composites. As shown in Fig. 8, the Cu powders with larger particle sizes result in a higher relative density of the composites.

The effect of Cu particle size on the relative density of diamond/Cu composites is attributed to the density difference between diamond and Cu powders. Cu powder separation from the mixture is also greatly influenced by the size difference between Cu powders and diamond particles. Cu powders in smaller sizes fall through the diamond particles more easily. Fig. 9 shows the SEM images of fractures (parallel to the pressure direction) in the top and bottom of the composite prepared by 30-μm Cu powders. Fig. 10 shows the SEM micrographs of the top and bottom of the composite prepared by 120-μm Cu powders. Fig. 9 clearly shows that the content of Cu powders in the top position is too low to fill the space among diamond particles, whereas the bottom position is dense. This difference is due to the leakage of Cu powders among diamond particles from the top to the bottom of the specimen. However, a density difference is not observed in Fig. 10. Both the top and the bottom of the composite exhibit a dense and even microstructure, resulting from the similar size between Cu powders and diamond particles; in this case, the Cu powders cannot easily leak through diamond particles.

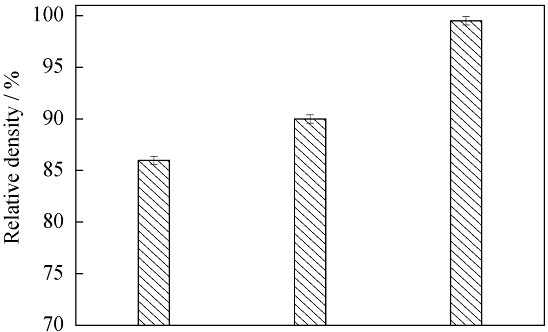

Fig. 8. Relative density of the composites with different particle sizes of Cu powders.

4. Conclusions

(1) With an increase of sintering pressure from 15 to 30 MPa, the relative density of the 60vol% diamond/Cu composite increases. When the pressure is further increased to 35 MPa, the relative density decreases because molten Cu is

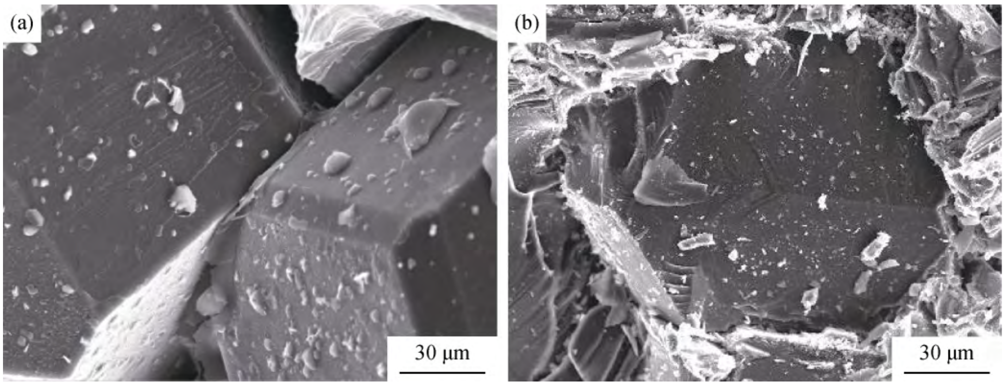

Fig. 9. SEM images of fractures (parallel to the pressure direction) in the top (a) and bottom (b) of the composite prepared by 30-μm Cu powders.

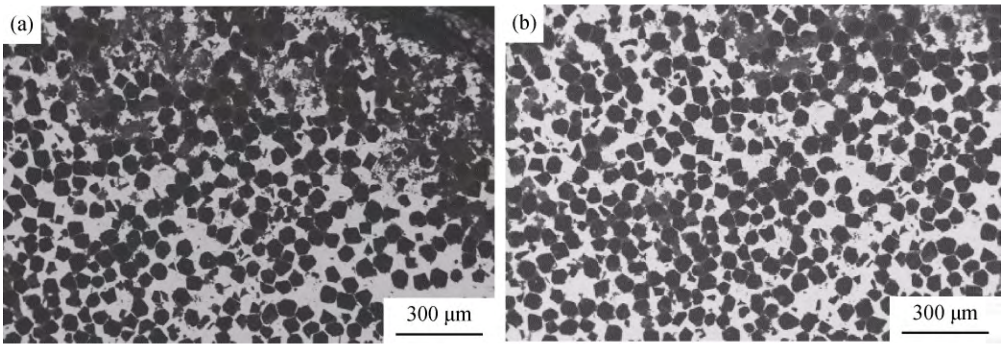

Fig. 10. SEM micrographs of the polished fracture surfaces in the top (a) and bottom (b) of the composite prepared by 120-μm Cu powders.

squeezed out of the die at higher pressures and the content of Cu in the composite matrix is less than that designed initially.

(2) The densification temperature increases from 880 to 915°C as the diamond volume fraction is increased 45% to 60%. When the content reaches 65vol%, the temperature does not increase further and the maximum relative density decreases, because more diamond/Cu interfaces require a higher temperature to ensure that diamond and Cu could wet each other.

(3) Both the relative density and thermal conductivity of the composite increase as the sintering time increases from 5 to 15 min. When the sintering time is further increased to 30 min, the relative density does not obviously change; however, the thermal conductivity decreases because of the change in interfacial structure with increasing sintering time.

(4) Cu powders with larger particle sizes are beneficial to increase the relative density of the composite. The effect of Cu particle size on the relative density of diamond/Cu composites is attributed to the density difference between diamond and Cu powders.

Acknowledgement

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