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Brass-matrix silicon carbide whisker composites prepared by powder metallurgy

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Brass (Cu-18Zn)-matrix and copper-matrix composites containing 0–50 vol% silicon carbide whiskers were fabricated by powder metallurgy using both the admixture method and the coated filler method, such that the fabrication of the copper-matrix composites did not involve a liquid phase whereas that of the brass-matrix composites did during the sintering process. The coated filler method gave composites with lower porosity, greater hardness, higher compressive yield strength, lower coefficient of thermal expansion (CTE), higher thermal conductivity and lower electrical resistivity than the admixture method, though the differences were much larger for copper-matrix composites than brass-matrix composites due to the liquid phase present during the fabrication of the brass-matrix composites. The mechanical properties of the brass-matrix composites were similar to those of the copper-matrix composites (also made by the coated filler method) at >35 vol% SiC, but were superior to those of the copper-matrix composites at <35 vol% SiC. The CTE was lower for brass-matrix composites than copper-matrix composites at >35 vol% SiC. The thermal conductivity was lower and the electrical resistivity was higher in brass-matrix composites than copper-matrix composites at <50 vol% SiC. *© 1999 Kluwer Academic Publishers*

1. Introduction

Copper-matrix composites have attracted considerable attention due to their combination of high strength, high thermal conductivity and low electrical resistivity, which are properties of importance to electronic applications. The copper-zinc, or brass, alloys with less than 35 wt% Zn are substitutional solid solutions (α-phase in the Cu-Zn phase diagram) of zinc in copper. Both strength and ductility of brass are higher than those of copper, though the thermal conductivity is lower and the electrical resistivity is higher. Due to the high strength and ductility of brass, the use of brass instead of copper as the matrix of a metal-matrix composite is of interest. However, there has been no previous report of any brass-matrix composite. Thus, brass-matrix composites constitute the subject of this paper.

Powder metallurgical fabrication of copper-matrix composites with discontinuous reinforcements is conventionally performed by sintering a mixture of matrix powder and the discontinuous reinforcement–a method referred to as the admixture method. An alternate method involves coating the discontinuous reinforcement with the matrix and then sintering the coated reinforcement – a method referred to as the coated filler method. The latter method gives copper-matrix composites of lower porosity, higher hardness, higher compressive yield strength, lower CTE, higher thermal conductivity and lower electrical resistivity than the former method when the filler is SiC whiskers at >30 vol% [1]. At whisker contents less than 30 vol%, the difference between composites made by the two methods is negligible. The superior properties of the composites made by the coated filler method is due to the more effective sintering of copper coated filler units compared to the sintering of intermixed filler and matrix, when the sintering temperature is fixed (950 °C [1], at which no liquid phase is involved during sintering). When sintering involves a liquid phase, the flow of the liquid will enhance the sintering of intermixed filler and matrix, so that the coated filler method may result in a composite that is not too different from the admixture method. It is an objective of this paper to investigate the usefulness of the coated filler method compared to the admixture method in fabricating composites by sintering that involves a liquid phase.

2. Experimental methods

The SiC whiskers (SiCw) used in this work were supplied by Advanced Refractory Technologies, Inc. (Buffalo, NY). They were single crystals and primarily in the β-phase form. They were 0.5–1.5 μm in diameter, with an aspect ratio of 10–25. Their density was 3.21 g/cm^3. The copper powder used was supplied by GTE Products Corporation (Towanda, PA); the mean particle size was 3.3 μm. The zinc powder used in conjunction with copper to form brass was also supplied by GTE; the mean particle size was 4 μm.

As described [1] and [2], Cu/SiCw composites containing 0–54 vol% SiC whiskers were fabricated by hot-pressing, using two different methods, namely the coated filler method (using Cu coated SiC whiskers without the addition of Cu powder) and the admixture method (using a mixture of Cu powder and SiC whiskers). In the coated filler method, a coating process developed by the authors was used to prepare Cu coated SiC whiskers. In this coating process, the surface of the SiC whiskers was metallized by electroless plating with Cu and subsequently electroplated with Cu to obtain the desired volume fraction of Cu in the Cu coated SiC whiskers. The SiC whiskers were uniformly and completely covered by the Cu coating. For the sake of comparison with the conventional powder metallurgy method, the admixture method was used. In the admixture method, mixtures of Cu powder and SiC whiskers were prepared at the same corresponding compositions by weight as the composites made by the coated filler method. Mixing was performed in the ball mill with alumina cylinders (13 mm × 13 mm) as the grinding medium.

Brass (Cu-Zn)/SiCw composites containing 0–50 vol% SiC whiskers were prepared also by the coated filler method and the admixture method. In the coated filler method, copper coated SiC whiskers (with 57.5 vol% SiC), obtained by electroless plating and subsequent electroplating of copper on the SiC whiskers, were mixed with different amounts of copper and zinc powders, such that the ratio of copper to zinc in the entire mixture (including the copper deposited on the whiskers) was 80:20 by weight. In the admixture method, SiC whiskers (without coating) were mixed with different amounts of copper and zinc powders, such that the ratio of copper to zinc was 80:20 by weight.

In this paper, the SiC whisker volume fraction is the quantity used to describe the composition of the composites. It should be noted that this is a nominal volume fraction, i.e., only metal matrix and SiC whiskers were considered; the volume fraction of porosity was not taken into account. The actual SiC whisker volume fraction is less than the nominal volume fraction due to the porosity.

Before composite fabrication, the coated whiskers (or a mixture of bare whiskers and metal powder(s)) was reduced in purging hydrogen gas at 250 °C for 60 min. The composite fabrication involved cold compaction of the coated whiskers (or the mixture) in a graphite die at 155 MPa to form a cylindrical green compact (0.5 in. or 12.7 mm in diameter). The green compact was then heated and hot pressed in the same die in purging nitrogen gas at 900 °C and 116 MPa for 25 min. During heating, the pressure was kept at 77 MPa until the temperature reached 900 °C. During heating, the zinc powder (melting point = 420 °C) in the compact melted and then diffused into the copper to form solid brass. Due to the molten zinc, a liquid phase was transiently present during sintering. The sintering temperature of 900 °C is below the solidus temperature of Cu-20Zn (~980 °C).

Composite testing involved measurements of the density, hardness (Brinell), compressive yield strength, volume electrical resistivity, coefficient of thermal expansion (CTE) and thermal conductivity.

The density of composites was measured by using the buoyancy (Archimedes) method (ASTM B328-92). The hardness measurement was performed using a Brinell Hardness Tester (Detroit Testing Machine Co., Model HB-2) at a load of 1000 kg. Compressive testing was conducted on a flat face of a cylindrical specimen (0.5 in. or 12.7 mm in diameter, 0.5 in. or 12.7 mm in height), using an MTS hydraulic mechanical testing system.

For measurement of the volume electrical resistivity, the four-probe method was used. Silver paint was used for electrical contacts. The CTE was determined by using a Perkin-Elmer TMA-7 thermal mechanical analyzer, with the temperature scanned from 25 to 100 °C at a rate of 3 °C/min.

The thermal conductivity (K) was determined by the equation

$$K = \alpha \rho C_p \tag{1}$$

where α, ρ and C_p are the thermal diffusivity, density and specific heat respectively of the sample. For obtaining the thermal conductivity, the thermal diffusivity was measured by the laser flash method (Nd glass laser, 10–15 J energy, 0.4 ms/pulse) [3], while the specific heat was measured by differential scanning calorimetry (Perkin-Elmer DSC-7).

X-ray diffraction was conducted to identify the phases in the composites which had been ground into powders. A powder diffractometer with CuKα radiation was used. X-ray spectroscopy was conducted using a scanning electron microscope (SEM) to analyse the elemental composition of the brass-matrix composite made by the coated filler method and containing 20 vol% SiC whiskers.

3. Results and discussion

3.1. X-ray diffraction and X-ray spectroscopy

The phases in brass-matrix composites made by both the coated filler method and the admixture method were analyzed by powder X-ray diffraction (Fig. 1). Fig. 1a and c show the presence of metallic zinc prior to sintering. After sintering, the absence of metallic zinc in both the composites made by the admixture method and the coated filler method (Fig. 1b and d) indicates that zinc had been dissolved into copper to form a copper-based solid solution, i.e., brass. The zinc dissolution is also supported by X-ray spectroscopy of a brass-matrix composite made by the coated filler method and containing 20 vol% SiC whiskers. X-ray spectroscopy showed peaks associated with Cu, Zn and Si (Si from SiC), such that the weight proportions of these three elements are 80.3:17.1:2.6 (i.e., the weight proportions of Cu to Zn are 82.4:17.6). The ratio of Cu to Zn is quite close to the ratio 80:20 in the mixture prior to sintering, though the amount of Zn relative to that of copper was less than that prior to sintering due to the evaporation of zinc during sintering.

The grain sizes of the copper in the mixture or the copper coated whiskers prior to sintering and of the brass matrix in the composites after sintering were

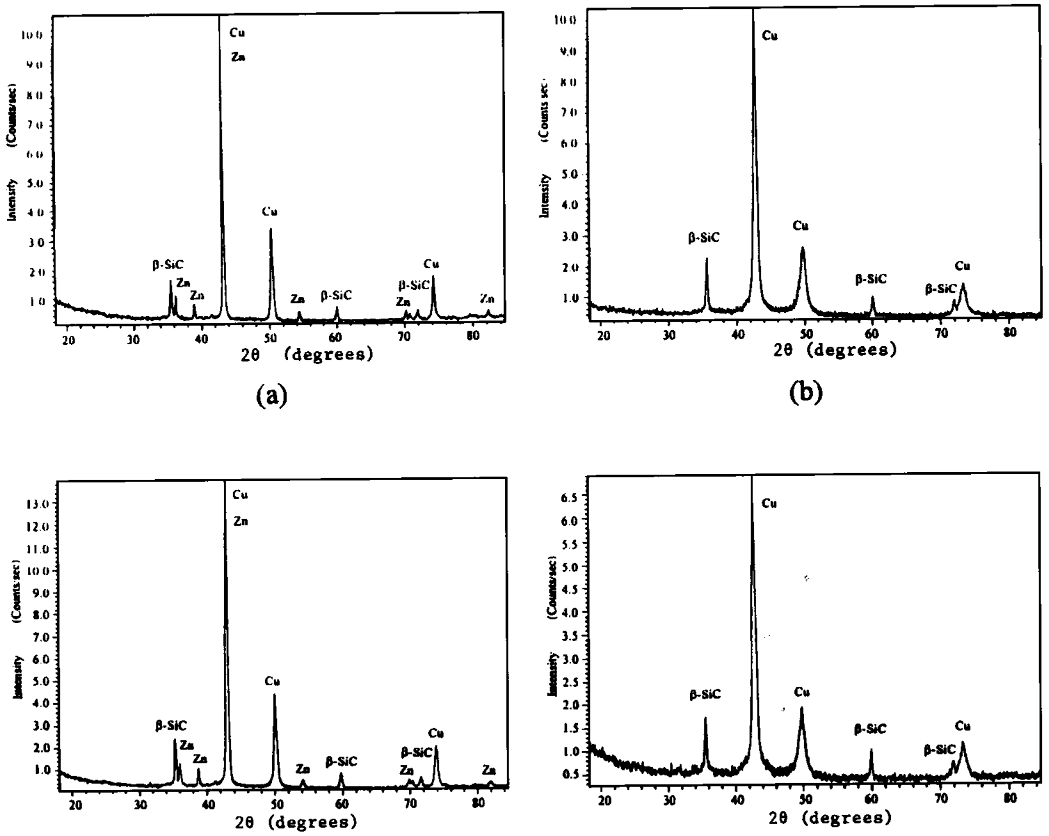

Figure 1 Powder X-ray diffraction patterns of brass-matrix composites containing 44 vol% SiC whiskers made by the coated filler method and the admixture method. (a) Admixture method – prior to sintering. (b) Admixture method – after sintering. (c) Coated filler method – prior to sintering. (d) Coated filler method – after sintering.

measured by X-ray diffraction using the method described in [4]. The results show that, prior to sintering, the grain size of the copper powder in the mixture was larger than 0.1 μm and the copper coating on the whiskers had a fine grain size of 0.025 μm; after sintering, the grain sizes of the brass matrix in the composites were even finer–0.016 μm for the composite made by the coated filler method and 0.018 μm for the composite made by the admixture method.

3.2. Porosity

The porosity can be determined by the equation

$$f_p = 1 - \rho/\rho_0, \qquad (2)$$

where f_p is the pore volume fraction, ρ the measured density, and ρ_0 the theoretical density.

The porosities (Fig. 2) of the brass-matrix composites at a given composition and made by the coated filler method and the admixture method were close, such that the former was slightly lower than the latter when the SiCw content exceeded 46 vol%. However, the porosity of the copper-matrix composites made by the admixture method was much higher than that of copper-matrix composites made by the coated filler method at the same SiCw volume fraction when the SiCw volume fraction exceeded 30%. These differences are because the fabrication of the copper-matrix composites involved no liquid phase, whereas that of the brass-matrix composites involved a liquid phase, and the advantage of the coated filler method over the admixture method was more significant when the sintering involved no liquid phase present.

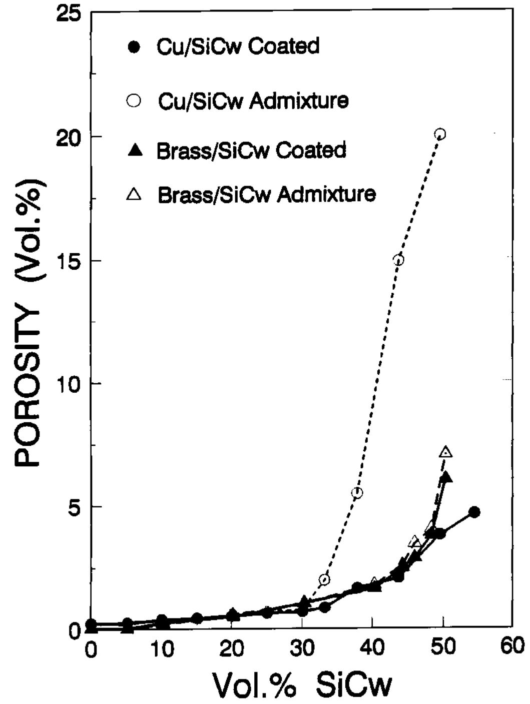

Figure 2 Variation of porosity with SiC whisker volume fraction in copper-matrix and brass-matrix composites made by the coated filler method and the admixture method.

3.3. Mechanical properties

The hardness (Fig. 3) and compressive yield strength (Fig. 4) were both higher for brass-matrix composites made by the coated filler method than for those of the same SiC whisker volume fraction and made by the admixture method for all whisker volume fractions exceeding 10%. The maximum hardness and maximum compressive yield strength for brass-matrix composites made by either method were both attained at 45 vol% SiC whiskers. In contrast, the maximum hardness and maximum compressive yield strength for copper-matrix composites made by the coated filler method were attained at 50 vol% SiC whiskers. Brass-matrix composites made by both methods exhibited higher hardness and compressive yield strength than copper-matrix composites at the same SiC whisker volume fraction and made by the coated filler method when the whisker volume fraction was 30% or less, and exhibited higher hardness and compressive yield strength than copper-matrix composites at the same whisker volume fraction and made by the admixture method at all whisker volume fractions.

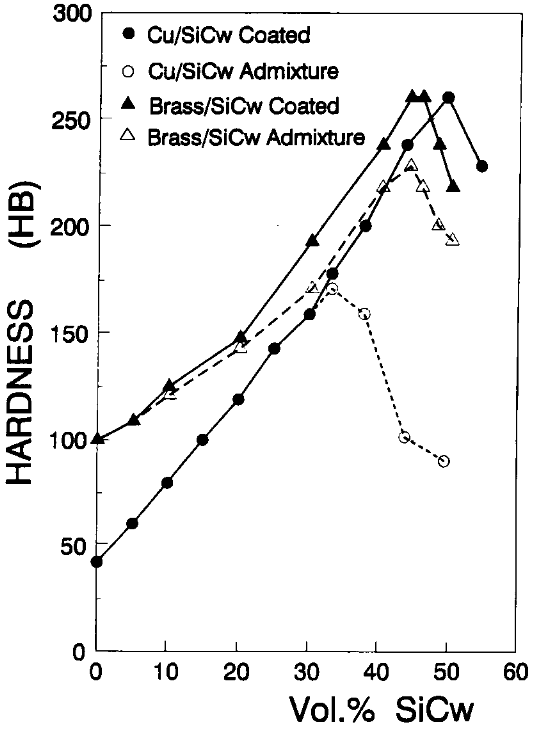

Figure 3 Variation of hardness with SiC whisker volume fraction in copper-matrix and brass-matrix composites made by the coated filler method and the admixture method.

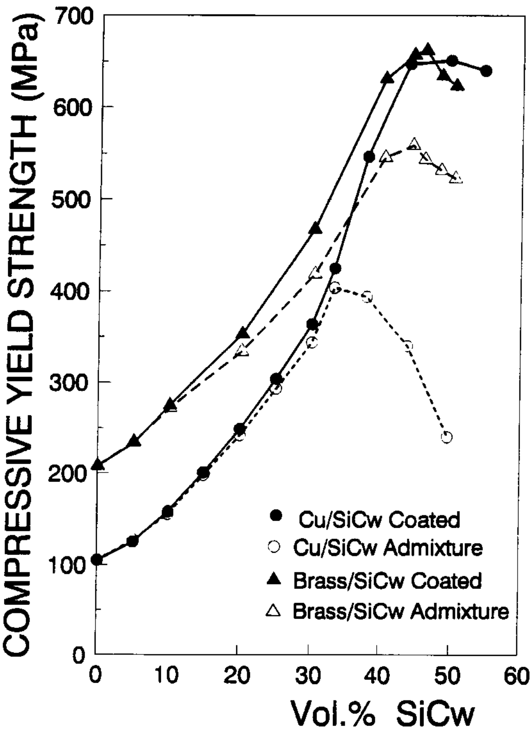

Figure 4 Variation of compressive yield strength with SiC whisker volume fraction in copper-matrix and brass-matrix composites made by the coated filler method and the admixture method.

The superior mechanical properties of the brass-matrix composites compared to the copper-matrix composites at low whisker volume fractions are not due to the difference in porosity, as the porosity was no different (Fig. 2), but are probably due to the higher strength of the brass matrix compared to the copper matrix. At high whisker volume fractions, the mechanical properties are dominated by the whiskers rather than the matrix, so brass-matrix and copper-matrix composites of the same whisker volume fraction and with similarly low porosity (both made by the coated filler method) exhibited similar mechanical properties at high whisker volume fractions. The superior mechanical properties of brass-matrix composites than copper-matrix composites, both made by the admixture method and both at the same whisker volume fraction, are attributed to the higher strength of the brass matrix compared to the copper matrix when the whisker volume fraction was less than 33% and to the lower porosity of the brass-matrix composites compared to the copper-matrix composites when the whisker volume fraction was greater than 33%.

For brass-matrix composites, the superior mechanical properties of composites made by the coated filler method compared to those made by the admixture method are not due to the difference in porosity, as the porosity was essentially the same, but are attributed to the better filler-matrix bonding provided by the coated filler method than the admixture method. For the copper-matrix composites, the superior mechanical properties of composites made by the coated filler method compared to those made by the admixture method are attributed to the difference in porosity.

3.4. Coefficient of thermal expansion

Fig. 5 shows that the CTE was lower for brass-matrix composites than copper-matrix composites of the same whisker volume fraction when the whisker volume fraction was high (>40% when compared to copper-matrix composites made by the coated filler method, and >33% when compared to copper-matrix composites made by the admixture method). This is not due to differences in porosity (Fig. 2), but is probably due to the stronger filler-matrix bonding in the brass-matrix composites than the copper-matrix composites. (Zinc is a well-known adhesion promotor). It is useful practically (say for electronic packaging) that a CTE as low as 8.8×10^{-6}/°C was attained in a brass-matrix

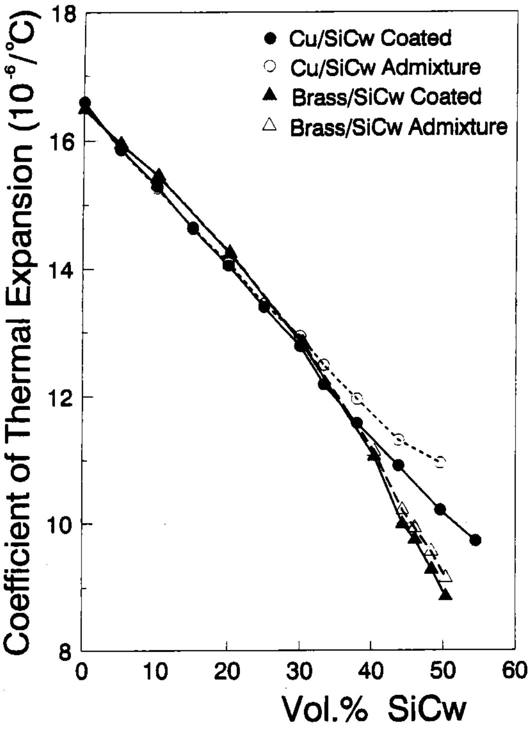

Figure 5 Variation of coefficient of thermal expansion with SiC whisker volume fraction in copper-matrix and brass-matrix composites made by the coated filler method and the admixture method.

composite made by the coated filler method and containing 50 vol% SiC whiskers.

3.5. Thermal conductivity

As shown in Fig. 6, the thermal conductivity was higher for copper-matrix composites than brass-matrix composites, except for copper-matrix composites made by the admixture method and containing more than 42 vol% SiC whiskers. This is attributed to the low thermal conductivity of the brass matrix compared to the copper matrix. For both brass-matrix and copper-matrix composites, the thermal conductivity was higher for the composite made by the coated filler method than that at the same SiC whisker volume fraction and made by the admixture method, such that the difference increased with increasing SiC whisker volume fraction and was larger for the copper-matrix composites than the brass-matrix composites. This is attributed to the better filler-matrix bonding in composites made by the coated filler method than those made by the admixture method, as porosity (Fig. 2) cannot explain it. The coated whiskers may render the composites with clean (less impurities such as oxides or other contaminants) and better bonding between the whiskers and the copper matrix which leads to a lower thermal contact resistivity at the filler-matrix interface. At 50 vol% SiCw, brass-matrix and copper-matrix composites, both made by the coated filler method, exhibited the same thermal conductivity.

3.6. Electrical resistivity

The electrical resistivity (Fig. 7) was higher for brass-matrix composites made by either method than copper-matrix composites at the same SiCw volume fraction at all SiCw volume fractions, except that copper-matrix composites made by the admixture method and containing >33 vol% SiCw were highest in electrical resistivity. This is attributed to the high electrical resistivity of the brass matrix compared to the copper matrix and the high porosity of copper-matrix composites made by the admixture method and containing >33 vol% SiCw.

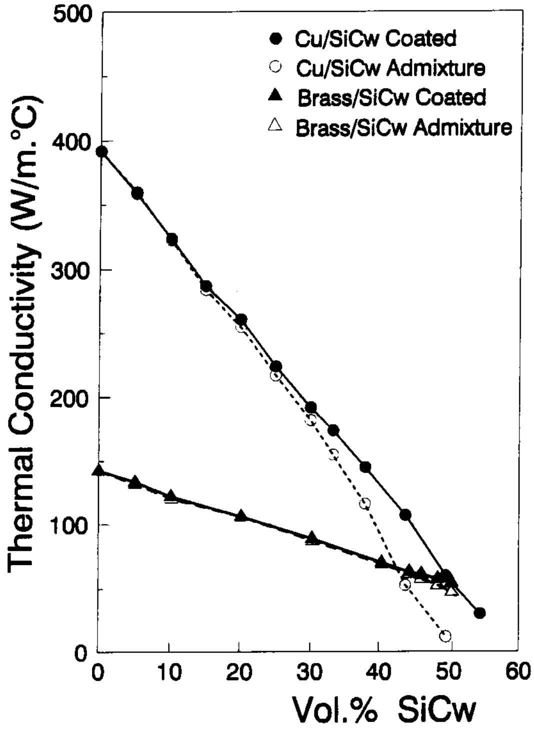

Figure 6 Variation of thermal conductivity with SiC whisker volume fraction in copper-matrix and brass-matrix composites made by the coated filler method and the admixture method.

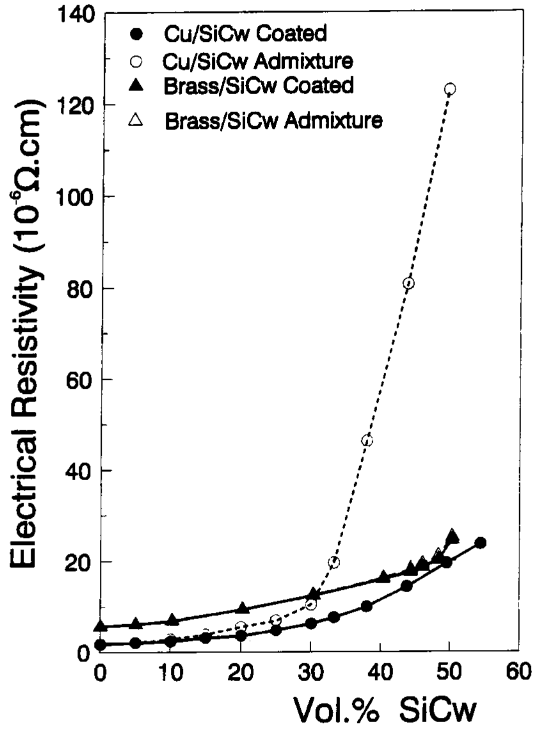

Figure 7 Variation of electrical resistivity with SiC whisker volume fraction in copper-matrix and brass-matrix composites made by the coated filler method and the admixture method.

For both copper-matrix and brass-matrix composites, the coated filler method gave composites with lower resistivity than the admixture method, though the difference was small for the brass-matrix composites.

3.7. Applications requiring high thermal conductivity and low CTE

Applications requiring both high thermal conductivity and low CTE ($<10 \times 10^{-6}/°C$) include substrates, lids, heat sinks and housings in electronic packaging. For such applications, the brass-matrix composite fabricated by the coated filler method and containing 50 vol% SiCw is recommended. Its CTE is lower and its thermal conductivity is higher than the copper-matrix composite fabricated by the coated filler method and containing 55 vol% SiCw.

3.8. Applications requiring high thermal conductivity and high strength

Applications requiring high thermal conductivity (>200 W/m °C) and moderately high strength include heat exchangers. For such applications, copper-matrix composites made by either coated filler method or admixture method and containing <25 vol% SiCw are recommended. For applications requiring high strength (>650 MPa in compressive yield strength) and moderately high thermal conductivity, the brass-matrix composite fabricated by the coated filler method and containing 47 vol% SiCw is recommended, although almost as good is the copper-matrix composite fabricated by the coated filler method and containing 50 vol% SiCw.

3.9. Applications requiring low electrical resistivity and high strength

For applications requiring low electrical resistivity ($<10 \times 10^{-6}\ \Omega\cdot$cm) and high strength, such as welding electrodes, the copper-matrix composite made by the coated filler method and containing 38 vol% SiCw is recommended. For applications requiring low resistivity ($<16 \times 10^{-6}\ \Omega\cdot$cm) and high strength, the copper-matrix composite made by the coated filler method and containing 44 vol% SiCw is recommended. For applications requiring low resistivity ($<20 \times 10^{-6}\ \Omega\cdot$cm) and high strength, the brass-matrix composite made by the coated filler method and containing 47 vol% SiCw is recommended.

4. Conclusion

Brass (Cu-18 Zn)-matrix and copper-matrix composites containing 0–54 vol% SiCw were fabricated by powder metallurgy, using both the admixture method and the coated filler method. The fabrication of the copper-matrix composites involved no liquid phase, whereas the fabrication of the brass-matrix composites involved a transient liquid phase (zinc). The coated filler method gave composites with lower porosity, greater hardness, higher compressive yield strength, lower CTE, higher thermal conductivity and lower electrical resistivity than the admixture method, but the difference between composites at the same volume fraction but made by different methods was much larger for copper-matrix composites than brass-matrix composites. The sintering was more effective (lower porosity and/or better filler-matrix bonding) in the coated filler method than the admixture method. The liquid phase helped the effectiveness of the sintering, so that, when a liquid phase was present, the improvement obtained by using the coated filler method instead of the admixture method was relatively small. Nevertheless, the highest hardness in brass-matrix composites was increased from 225 to 262 (Brinell) and the highest compressive yield strength in brass-matrix composites was increased from 560 to 660 MPa when the composites were made by the coated filler method instead of the admixture method.

The brass-matrix composites and copper-matrix composites, both made by the coated filler method, were similar in both hardness and compressive yield strength at >35 vol% SiCw, but the former exhibited higher such properties than the latter at <35 vol% SiCw. The CTE was lower for the brass-matrix composites than the copper-matrix composites at >35 vol% SiCw. The thermal conductivity was lower and the electrical resistivity was higher in brass-matrix composites than copper-matrix composites, both made by the coated filler method, except that the thermal conductivity at >50 vol% SiCw was similar or lower for the brass-matrix composites than the copper-matrix composites.

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