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Silicon carbide whisker copper–matrix composites fabricated by hot pressing copper coated whiskers

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Copper–matrix SiC whisker composites containing 33–54 vol % SiC whiskers and with < 5 vol % porosity were fabricated by hot pressing SiC whiskers that had been coated with copper by electroless plating followed by electroplating. The highest Brinell hardness of 260 was attained at 50 vol % SiC whiskers. The lowest coefficient of thermal expansion (CTE) of $9.6 \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$ (at 25–150 °C) was attained at 54 vol % SiC whiskers. The composites exhibited lower porosity, higher hardness, higher compressive yield strength, lower CTE, lower electrical resistivity and higher thermal conductivity than the corresponding composites made by hot pressing mixtures of copper powder and bare SiC whiskers.

1. Introduction

Silicon carbide whiskers, exhibit a large aspect ratio as well as many important properties, which include high strength and modulus, high melting point, high hardness, low coefficient of thermal expansion (CTE), low density and excellent resistance to chemical attack under extreme conditions. Table I lists typical properties of SiC whiskers [1, 2].

In recent years, SiC whiskers ($\mathrm{SiC_w}$) have attracted much attention as a reinforcement in metal–matrix composites not only for structural applications, but also for electronic packaging and other applications, since whisker composites, compared to continuous fibre composites, are easier to fabricate, cost less and provide more isotropic property improvements [3, 4]. Up to now, most whisker metal–matrix composites use aluminum or its alloys as matrices and have found wide applications in aerospace and automotive industries [3, 5–19].

Copper is one of the most important materials in thermal and electrical applications. Compared to aluminum, copper has higher electrical and thermal conductivities and a higher melting point. These characteristics make copper more attractive in electronic packaging applications than aluminum. However, just like aluminum, copper suffers from its high thermal expansion and softness. On the other hand, copper has a higher density than aluminum. The incorporation of SiC whiskers in copper was found in this work to provide composites with many advantages, namely high electrical and thermal conductivities, low CTE, greatly increased mechanical strength and reduced density. The high thermal conductivity and low CTE are especially relevant to electronic packaging applications. No previous work had been reported on whisker Cu–matrix composites, whether the whiskers were SiC or not.

Due to the shape of the whiskers, the proximity among the whiskers in the composites limits the whisker volume fraction to a maximum of 30–40 %. Dense composites (of low porosity) with a higher whisker volume fraction had not been reported, whether the matrix was copper or aluminum, and whether the composites were fabricated by powder metallurgy or liquid metal infiltration. A high whisker volume fraction, however, is desirable for lowering the CTE and increasing the mechanical strength.

This work achieved a composite containing a whisker volume fraction up to 54 % (with porosity < 5 vol %) by using an unconventional powder metallurgy (P/M) method. In this method, copper coated whiskers, instead of a mixture of copper powder and bare whiskers, were hot pressed to form a copper–matrix composite. Such a coated filler P/M method (for making composites with any metal matrix and any discontinuous reinforcement) had been previously used on particles [20, 21], but not on whiskers. The particles were copper or silver coated graphite particles for making metal–graphite brush materials [20], and copper coated molybdenum for making low CTE thermal conductors for electronic packaging [21]. Both [20] and [21] reported that the coated particles gave composites of lower electrical resistivity than the corresponding composites made by conventional P/M. Furthermore, [21] reported that the coated particles gave composites of higher thermal conductivity, lower CTE, higher hardness, higher compressive yield strength and lower porosity than the corresponding composites made by conventional P/M. The above mentioned use of coated particles, such that the coating serves as the matrix, should be distinguished from the use of coated particles, such that the coating serves to alloy with the matrix [22, 23] or to modify the filler–matrix interface [24].

TABLE I Typical properties of SiC whiskers [1, 2]

Property	Value
Chemistry	Stoichiometric SiC
Crystallographic structure	α- or β-phase SiC
Diameter, μm	0.1–1.5
Aspect ratio	10–25
Density, $g\,cm^{-3}$	3.20–3.26
Young's modulus, GPa	400–500
Poisson's ratio	0.17
Tensile strength, GPa	> 3.2
CTE, $10^{-6}\,°C^{-1}$	4.0
Thermal conductivity, $W\,m^{-1}\,K^{-1}$	> 16

Due to the extraordinarily high whisker volume fraction, this work provides composites of exceptionally high hardness compared to any copper alloy or copper–matrix composites. In particular, with 49.5 vol % SiC whiskers, a copper–matrix composite with Brinell hardness 260 was achieved. This hardness is even higher than the value of 238 for the alloy Monel (66 Ni–29 Cu–3 Al). The attraction of this composite is not just in the high hardness, but in the combination of high hardness, low electrical resistivity ($5.4 \times 10^{-5}\,\Omega\,cm^{-1}$, compared to a value of $6.4 \times 10^{-5}\,\Omega\,cm^{-1}$, for Monel), and low CTE ($10.2 \times 10^{-6}\,°C^{-1}$, compared to a value of $13.5 \times 10^{-6}\,°C^{-1}$ for Monel).

2. Experimental procedure

In this paper, the SiC whiskers used were from Advanced Refractory Technologies, Inc. (Buffalo, NY). They were single crystals and primarily in β-phase form. They were 0.5–1.5 μm in diameter, with an aspect ratio of 10–25. Their densities were $3.21\,g\,cm^{-3}$. The copper powder used was from GTE Products Corporation (Towanda, PA). Their average particle size was 3.3 μm.

Cu–SiC$_w$ composites containing 33–54 vol % (15–30 wt %) 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, the Cu coated SiC whiskers were prepared by electroless plating of Cu to metallize the surface of the SiC whiskers and subsequent electroplating of Cu to obtain the desired volume fraction of Cu in the Cu coated SiC whiskers. The SiC whiskers were uniformly and completely covered by Cu (Fig. 1). 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 × 13 mm) as the grinding medium. Scanning electron microscope (SEM) photographs of Cu coated SiC whiskers and a mixture of Cu powder and SiC whiskers at the same composition are shown in Fig. 2.

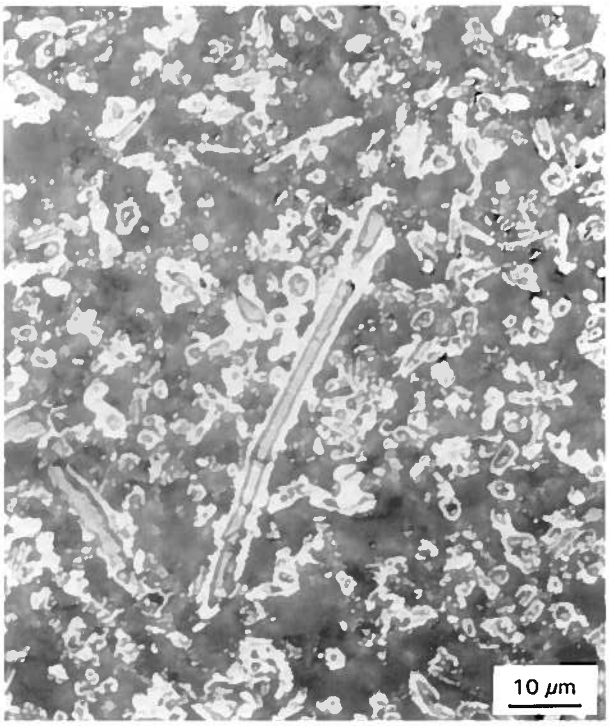

Figure 1 Optical micrograph showing the Cu coating on the SiC whiskers prior to compaction.

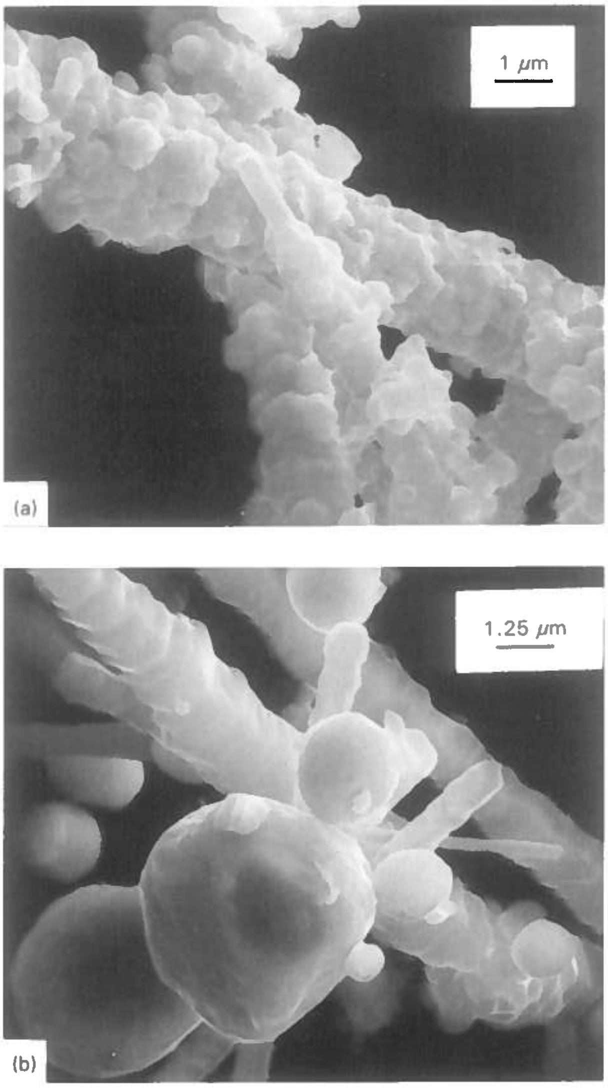

Figure 2 SEM micrographs showing (a) Cu coated SiC whiskers, and (b) a mixture of Cu powder and SiC whiskers.

In this paper, the SiC whisker volume fraction is the quantity used to describe the composition of the Cu–SiC_w composites. It should be noted that this is a nominal volume fraction, i.e. only Cu and SiC whiskers were considered; the volume fraction of porosity was not taken into account.

Before composite fabrication, the coated whiskers (or a mixture of bare whiskers and copper powder) was reduced in purging hydrogen gas at 300 °C for 120 min. The composite fabrication involved cold pressing the coated whiskers (or the mixture) in a graphite die at 155 MPa to form a cylindrical green compact (12.7 mm in diameter). The green compact was then heated and hot pressed in the same die in purging nitrogen gas at 950 °C and 116 MPa for 25 min. During heating, the pressure was kept at 77 MPa until the temperature reached 950 °C. The route for both methods is illustrated in Fig. 3.

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

The density of Cu–SiC_w 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 cylindrical specimen (12.7 mm in diameter and 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 value of the CTE was obtained by using a Perkin–Elmer TMA-7 thermal mechanical analyser, with the temperature scanned from 25 to 150 °C at a rate of 3 °C $\min^{-1}$.

The thermal conductivity, K, was determined by the equation

$$K = \alpha \rho C_p \qquad (1)$$

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^{-1}), while the specific heat was measured by differential scanning calorimetry (Perkin–Elmer DSC-7).

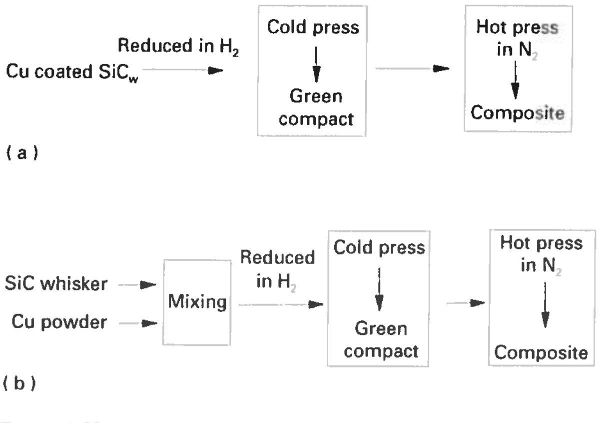

Figure 3 Hot press route using the two P/M methods for fabrication of Cu–SiC_w composites: (a) the coated filler method, and (b) the admixture method.

3. Results and discussion

3.1. Microstructure

Optical microscopy was used to examine the microstructure of polished sections of the Cu–SiC_w composites made by the two methods. Fig. 4 shows a dense composite containing 54.4 vol % SiC whiskers and without apparent pores, as obtained by using the coated filler method; in contrast, with the same high content of SiC whiskers, only a porous composite can be obtained by using the admixture method. Fig. 5 shows that the SiC whiskers were distributed uniformly in the Cu–SiC_w composites made by both methods. At a high content of SiC whiskers, e.g. 49.5 vol %, the composite made by the admixture method (Fig. 5c) had much higher porosity than that made by the coated filler method (Fig. 5a). In the case of a lower content of SiC whiskers, e.g. 33.3 vol %, dense composites can be made by using both methods and there is no apparent difference in the microstructure between the composites made by the two methods (Fig. 5b and d).

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.

Fig. 6 shows that, compared to the composites made by the coated filler method, all the composites, i.e. > 30 vol % SiC_w, made by the admixture method had relatively high porosity, which increased markedly with increasing whisker volume fraction. When the volume fraction of the whiskers exceeded 38 %, porous composites resulted from the admixture method. For the composites made by the coated filler method, although the porosity increased with increasing whisker content, the porosity remained low, even

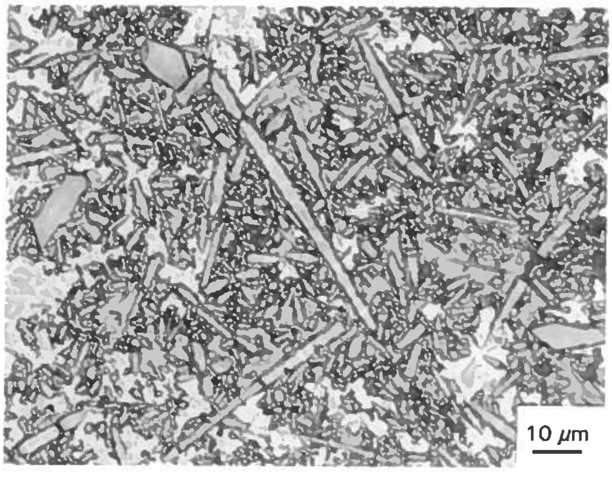

Figure 4 Optical micrograph showing the microstructure of the Cu–SiC_w composite containing 54.4 vol % SiC_w and made by the coated filler method.

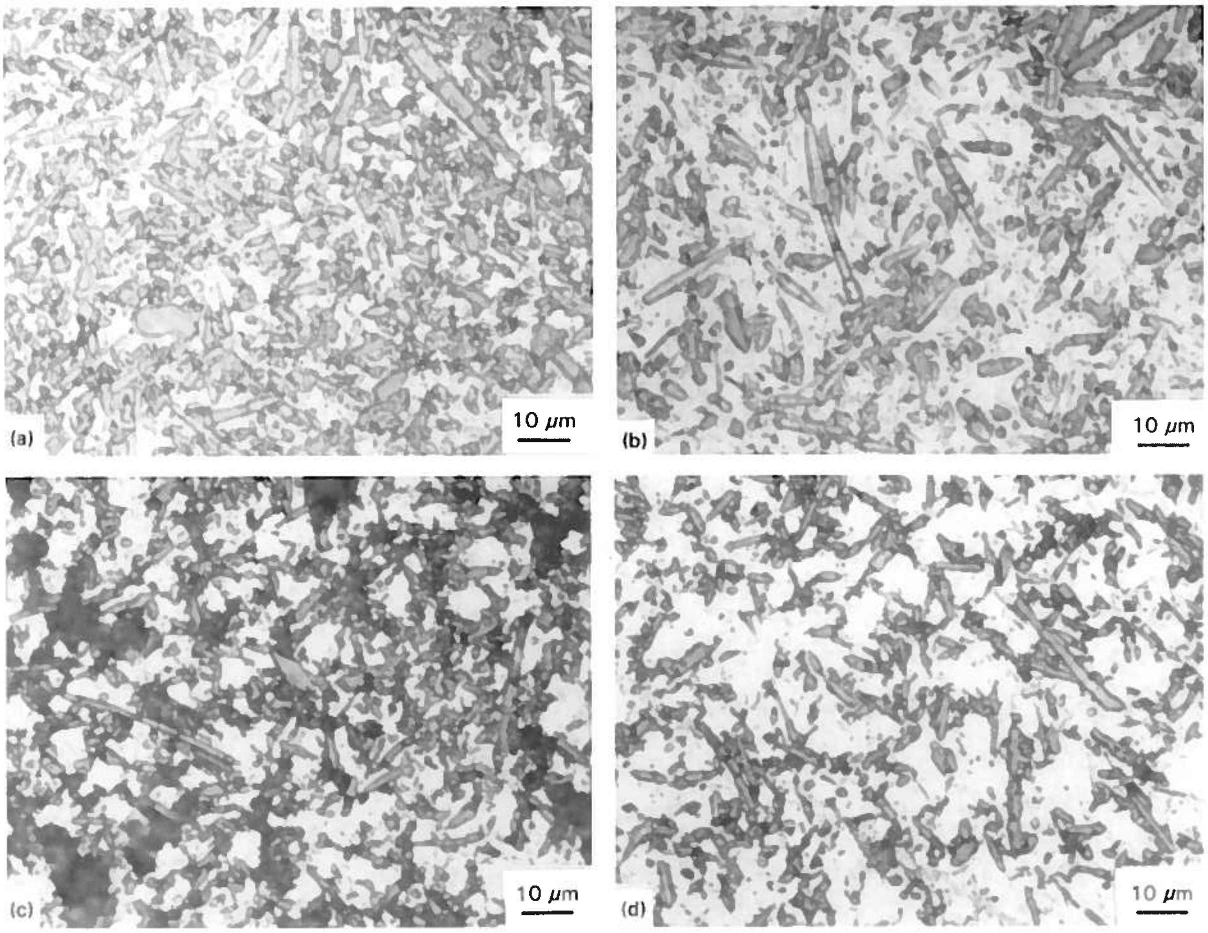

Figure 5 Optical micrographs showing the microstructure of Cu–SiC$_w$ composites made by the two P/M methods: (a) 49.5 vol % SiC$_w$, coated filler method; (b) 33.3 vol % SiC$_w$, coated filler method; (c) 49.5 vol % SiC$_w$, admixture method; and (d) 33.3 vol % SiC$_w$, admixture method.

up to a whisker volume fraction of 54.4 %. Fig. 7 shows optical micrographs (at a lower magnification than Fig. 5) of polished samples of composites containing 49.5 vol % SiC$_w$ made by the two methods. The composite made by the admixture method (Fig. 7b) contained a large amount of pores, with most of the pores ranging in size from 3 to 50 μm. Some large pores with sizes ranging from 100 to 200 μm are not shown in Fig. 7b. However, no apparent pore was observed in the composite made by the coated filler method (Fig. 7a).

Fig. 2 can be used to describe the situation for the composites made by the two methods. The admixture method requires a rather large amount of copper particles (usually > 65 vol %) in the mixture of copper powder and SiC whiskers (Fig. 2b) in order to make a dense composite. In the case of high volume fraction of SiC whiskers, since there are not enough copper particles to surround the SiC whiskers, during hot pressing (with the processing temperature below the melting point of Cu) the softened copper particles cannot thoroughly flow and fill the interstices between the SiC whiskers (the interstices are substantial in size due to the stiffness of the whiskers and the resulting hindrance to compaction), thus resulting in high porosity. In the coated filler method, the situation is different. Since the Cu coatings separate the adjacent SiC whiskers, even a small amount of copper is sufficient to join the whiskers together, thus resulting in a dense composite with a high whisker content.

3.3. Properties

The effects of the SiC whisker volume fraction and the composite fabrication method on the measured properties, namely the Brinell hardness, compressive yield strength, volume electrical resistivity, CTE and thermal conductivity, *K*, are shown in Figs. 8–12, respectively.

Figs 8 and 9 show that the hardness and compressive yield strength of the composites made by the coated filler method are higher than those of the corresponding composites made by the admixture method, which increase with increasing SiC whisker volume fraction up to 49.5 % and slightly decrease, though still high, at 54.4 vol % SiC$_w$. In contrast, the hardness and compressive yield strength of the composites made by the admixture method decrease dramatically with increasing SiC whisker volume fraction from 33.3 and 49.5 %. These differences are due to the difference in porosity of the composites made by the two different methods (Fig. 6). The differences in hardness and compressive yield strength between the composites made by the two different methods increase as the SiC whisker volume fraction increases, since the difference in porosity also increases. The electrical

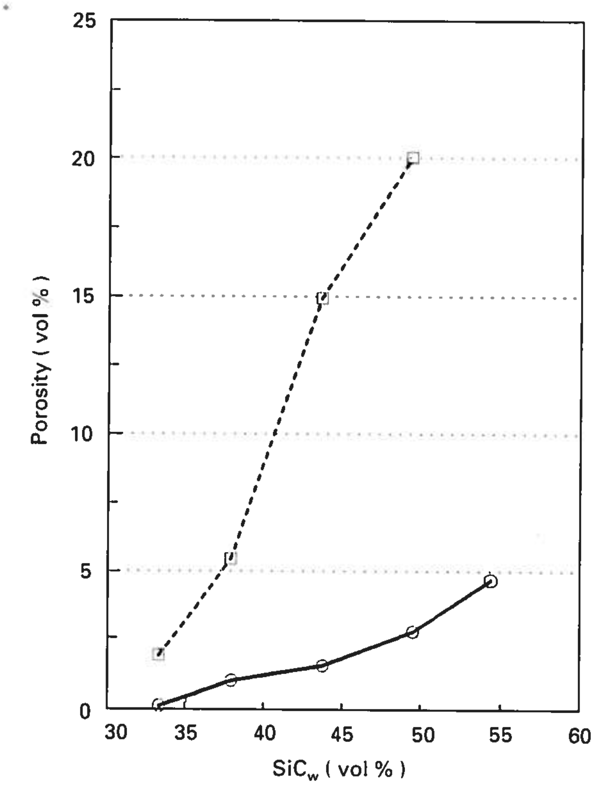

Figure 6 Porosity as a function of vol % SiC whiskers for the composites made by the two methods: (○) coated, (□) admixture.

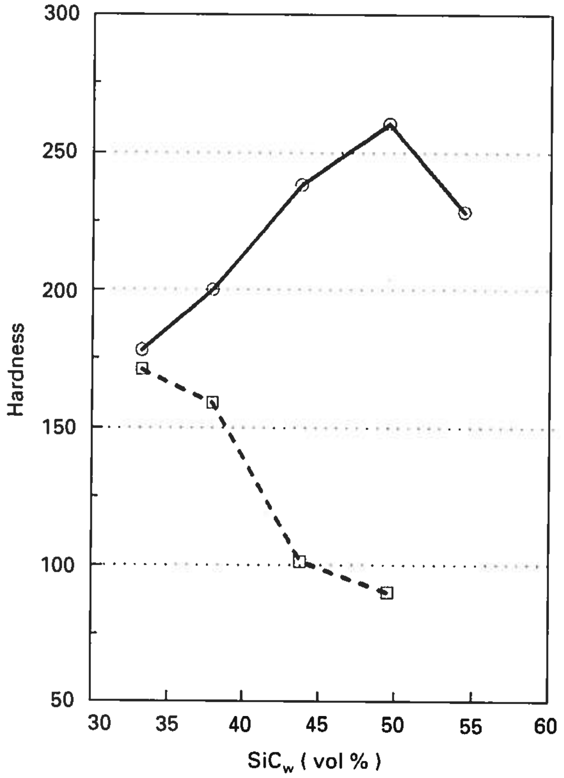

Figure 8 Brinell hardness as a function of SiC whisker volume fraction for the Cu–SiC$_w$ composites made by the two methods: (○) coated, (□) admixture.

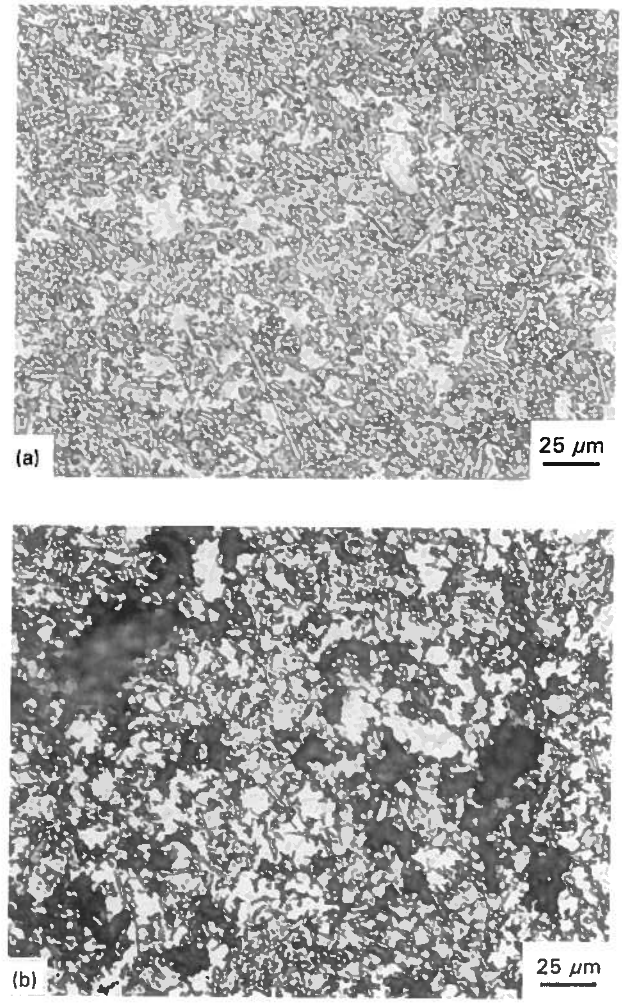

Figure 7 Optical micrographs of Cu–SiC$_w$ composites made by the two methods: (a) 49.5 vol % SiC$_w$, coated filler method; and (b) 49.5 vol % SiC$_w$, admixture method.

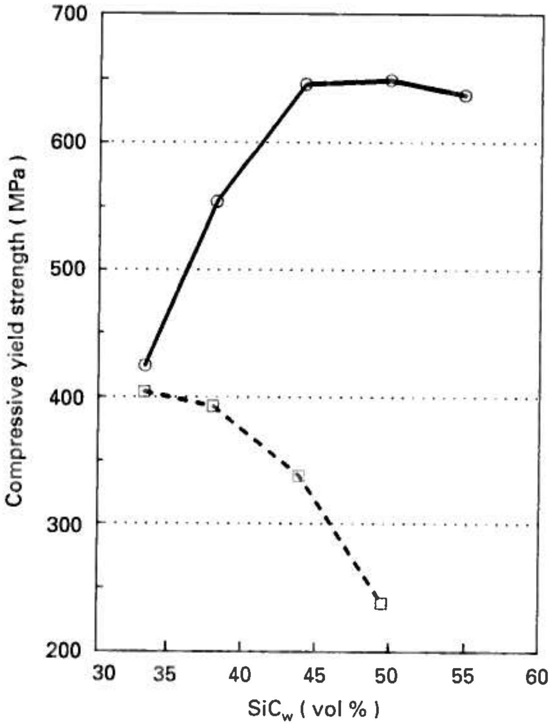

Figure 9 Compressive yield strength as a function of SiC whisker volume fraction for the Cu–SiC$_w$ composites made by the two methods: (○) coated, (□) admixture.

resistivity of the composites made by the coated filler method was lower than that of the composites made by the admixture method and the difference also became larger as the SiC whisker volume fraction increased (Fig. 10).

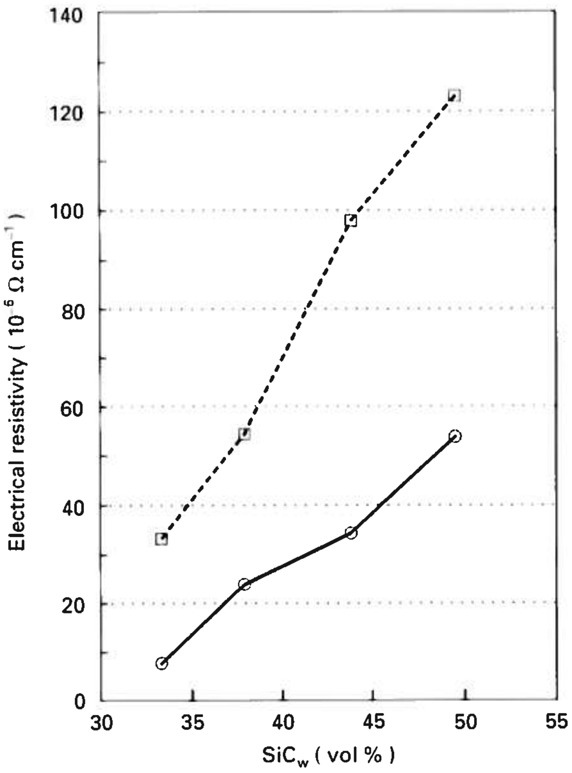

Figure 10 Volume electrical resistivity as a function of SiC whisker volume fraction for the Cu–SiC$_w$ composites made by the two methods: (○) coated, (□) admixture.

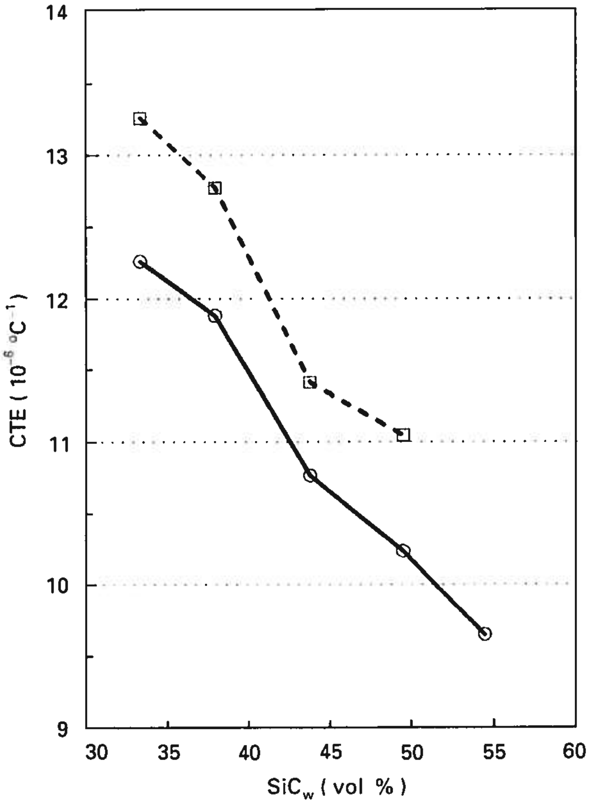

Figure 11 Coefficient of thermal expansion (CTE) as a function of SiC whisker volume fraction for the Cu–SiC$_w$ made by the two methods: (○) coated, (□) admixture.

Figs 11 and 12 show that the composites made by the coated filler method had lower CTE and much higher thermal conductivity than the corresponding composites made by the admixture method. Unlike the properties discussed above, the differences in the CTE and thermal conductivity between the composites made by the two methods did not increase with increasing whisker volume fraction, as if they were not governed by the difference in porosity, which increased with increasing SiC whisker volume fraction. Since the bonding between the reinforcement and the matrix is important to the CTE and the thermal conductivity, the differences in CTE and thermal conductivity between composites made by the two methods may be due to the difference in bonding between the composites made by the two methods. Since the electroless and electroplating of Cu on the SiC whiskers involve the deposition of Cu atoms one by one on the whisker surface, better Cu–SiC$_w$ bonding can probably be achieved in the composites made by using the Cu coated SiC whiskers than that in composites made by using mixtures of Cu powder and SiC whiskers. As a result, a lower CTE and a higher thermal conductivity were exhibited by the composites made using the Cu coated SiC whiskers.

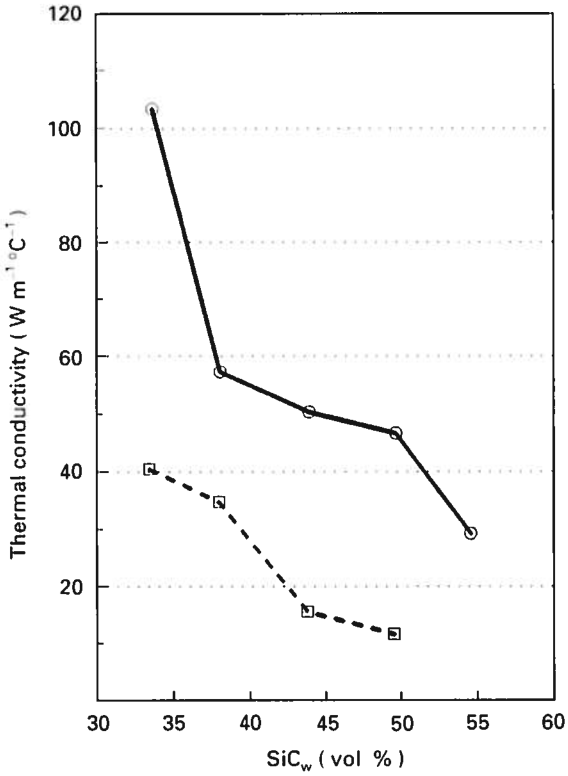

Figure 12 Thermal conductivity as a function of SiC whisker volume fraction for the Cu–SiC$_w$ composites made by the two methods: (○) coated, (□) admixture.

The composite of the highest hardness was that containing 49.5 vol % SiC whiskers and made by the coated filler method. The Brinell hardness was 260, compared to a value of 238 which was obtained in the same measuring condition for the alloy Monel (66 Ni–29 Cu–3 Al), and compared to a value of 174 for an aluminum–matrix composite containing 55 vol % SiC particles, and a value of 200 for an aluminum–matrix composite containing 60 vol % AlN particles [25]. The Brinell hardness of 260 obtained in this work seems to be higher than that of any previously reported copper–matrix composite, aluminum–matrix composite or copper alloy.

TABLE II Comparison between Cu–SiC$_w$ and Cu–Mo composites and Monel alloy (data of different materials were obtained in the same way by the authors)

	Cu–SiC$_w$[a]		Cu–Mo[b]	Monel[c]
	Vol % SiC$_w$		Vol % Mo	
	49.5	54.4	69.6	
Hardness, Brinell	260	228	193	238
Compressive yield strength, MPa	651	640	647	730
CTE, 10^{-6} °C^{-1} At 25–150 °C	10.2	9.6	7.3	13.45
Electrical resistivity, 10^{-6} Ω cm^{-1}	35	54	3.87	64.4

[a] Made by the coated filler method.
[b] From [21].
[c] K-Monel, 66 Ni–29 Cu–3 Al.

Table II shows the comparison between Monel and selected composites of this work. Although the 49.5 vol % SiC whisker composite exhibited higher hardness than Monel, it exhibited lower compressive yield strength than Monel. On the other hand, it exhibited much lower CTE and lower electrical resistivity than Monel. The lower electrical resistivity suggests higher thermal conductivity.

Table II also shows the comparison between a Cu–matrix Mo particle composite (from [21]) and selected Cu–SiC$_w$ composites of this work. In spite of the lower filler volume fraction in Cu–SiC$_w$ than Cu–Mo, the hardness was higher in Cu–SiC$_w$. However, Cu–Mo has the advantage of a lower CTE and a lower electrical resistivity compared to Cu–SiC$_w$. The low CTE of Cu–Mo is due to the high Mo volume fraction, whereas the low electrical resistivity of Cu–Mo is due to the metallic nature of Mo. For electronic packaging, which requires low CTE and high thermal conductivity and does not require high hardness, Cu–Mo is more attractive than Cu–SiC$_w$. However, for applications requiring high hardness, low CTE as well as high conductivity, e.g. sliding contacts and brushes for large currents, Cu–SiC$_w$ is more attractive.

4. Conclusions

SiC whisker copper–matrix composites containing up to 54.4 vol % SiC whiskers were fabricated by hot pressing, using two methods. One method, called the admixture method (conventional method), used a mixture of Cu powder and SiC whiskers. The other method, called the coated filler method, used Cu coated SiC whiskers. Dense composites with high contents (up to 54.4 vol %) of SiC whiskers were obtained by using the coated filler method, whereas only porous composites could be made by using the admixture method, when the nominal volume fraction of SiC whiskers exceeded 38 %. The composites made by the coated filler method exhibited lower porosity, higher Brinell hardness, higher compressive yield strength, lower volume electrical resistivity, lower coefficient of thermal expansion and higher thermal conductivity than the corresponding composites made by the admixture method.

The differences in the Brinell hardness, compressive yield strength and electrical resistivity between the composites made by the two methods increased with increasing SiC whisker content, as resulting from the difference in porosity, which also increased with increasing SiC whisker content, especially at a high whisker volume fraction. In the case of a high content of SiC whiskers (> 30 vol %), since the amount of Cu particles was not sufficient to surround the whiskers in the mixture and during hot pressing the softened Cu particles could not thoroughly flow and fill the interstices among the whiskers, a high level of porosity was present in the composites made by the admixture method. For the composites made by the coated filler method, since the Cu coating separated the adjacent whiskers from one another, even a small amount of Cu was sufficient to join the whiskers together by hot pressing the Cu coated whiskers, thus leading to a dense composite with a high whisker volume fraction. The composites made by the coated filler method probably had better bonding at the Cu–SiC$_w$ interface than the composites made by the admixture method, thus leading to a lower CTE and a higher thermal conductivity.

This work provides composites of exceptionally high Brinell hardness, in addition to new composites in the form of Cu–SiC$_w$. Furthermore, this work provides whisker metal–matrix composites of exceptionally high whisker volume fraction.

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