# A comparative study of the coated filler method and the admixture method of powder metallurgy for making metal-matrix composites

# PAY YIH, D. D. L. CHUNG

Composite Materials Research Laboratory, State University of New York at Buffalo, Buffalo, NY 14260-4400, USA

Copper-matrix composites were made by powder metallurgy (PM). The reinforcements were molybdenum particles, silicon carbide whiskers and titanium diboride platelets. The coated filler method, which involves a reinforcement coated with the matrix metal, was used. In contrast, conventional PM uses the admixture method, which involves a mixture of matrix powder and reinforcement. For all the composite systems, the coated filler method was found to be superior to the admixture method in providing composites with lower porosity, greater hardness, higher compressive yield strength, lower coefficient of thermal expansion (CTE), higher thermal conductivity and lower electrical resistivity, though the degree of superiority was greater for high than low reinforcement contents. In the coated filler method, the coating on the reinforcement separated reinforcement units from one another and provided a cleaner interface and stronger bond between reinforcement and matrix than the admixture method could provide. The highest reinforcement content attained in dense composites ( <5% porosity) made by the coated filler method was 70 vol % Mo, 60 vol % TiB<sub>2</sub> and 54 vol % SiC. The critical reinforcement volume fraction above which the porosity of composites made by the admixture method increases abruptly is 60% Mo, 42% TiB<sub>2</sub> and 33% SiC. This fraction increases with decreasing aspect ratio of the reinforcement. Among Cu/Mo, Cu/TiB<sub>2</sub> and Cu/SiC at the same reinforcement volume fraction (50%), Cu/Mo gave the lowest CTE, highest thermal conductivity and lowest electrical resistivity, while Cu/SiC gave the greatest hardness and Cu/TiB<sub>2</sub> and Cu/SiC gave the highest compressive yield strength. Compared to Cu/SiC, Cu/TiB<sub>2</sub> exhibited much higher thermal conductivity and much lower electrical resistivity.

## 1. Introduction

Powder metallurgy, a conventional method of metal processing, is a common method for making metal-matrix composites. For composites with matrices that are relatively high (>1000 °C) in melting temperature, powder metallurgy is particularly attractive, as the competing method of liquid metal infiltration required melting of the matrix metal. Powder metallurgical fabrication of a metal-matrix composite conventionally involves mixing the discontinuous reinforcement and matrix metal powder and subsequent sintering. This conventional method of powder metallurgy is called the admixture method. A less conventional method of powder metallurgy is the coated filler method, which involves coating the discontinuous reinforcement with the matrix metal and subsequent sintering, such that the use of the matrix metal powder is optional. The coated filler method is more effective than the admixture method when the reinforcement volume fraction in the composite is high [1-3]. This is because a high reinforcement volume fraction corresponds to a low matrix

0022-2461 © 1997 Chapman & Hall

volume fraction and, at a low matrix volume fraction, the distribution of matrix metal is more uniform when the matrix metal is coated on the reinforcement than when the matrix metal is in the form of particles. The more uniform distribution of the matrix metal results in less direct contact between one reinforcement unit and another, thus promoting sintering and reducing the porosity in the resulting composite. As a result, a metal-matrix composite with a high volume fraction of a reinforcement having a high hardness, a low coefficient of thermal expansion (CTE), a high electrical resistivity and a low thermal conductivity exhibits lower porosity, higher hardness, higher compressive yield strength, lower CTE, lower electrical resistivity and higher thermal conductivity if it is made by the coated filler method rather than the admixture method [1-3]. At a low volume fraction of the reinforcement, the two methods give composites of similar quality. The reinforcement volume fraction above which the admixture method gives composites of high porosity is hereby called the critical volume fraction. Although previous work has shown the superiority of

the coated filler method over the admixture method at a high reinforcement volume fraction, little attention has been given to the critical volume fraction. Due to the practical importance of knowing the critical volume fraction, an objective of this paper is to determine the critical volume fraction for various reinforcements and investigate the dependence of the critical volume fraction on the reinforcement aspect ratio. Moreover, previous work did not provide a systematic comparison of the coated filler method and the admixture method for various reinforcements over a wide range of reinforcement volume fraction. Such a systematic comparison will lead to a better understanding of the origin of the superiority of one method over the other. This comparison constitutes the second objective of this paper. Although previous work has compared composites with various reinforcements and made with the coated filler method, comparison was not made at the same reinforcement volume fraction. A third objective of this paper is to compare at the same reinforcement volume fraction over a wide range of reinforcement volume fraction so as to understand the effect of the reinforcement type. The reinforcements chosen for this study are molybdenum particles, silicon carbide whiskers and titanium diboride platelets, which have aspect ratio 1, 10 and 3, respectively. The matrix chosen for this study is copper.

### 2. Experimental procedure

The coated filler method was applied to three types of fillers, namely TiB<sub>2</sub> platelets (3–5  $\mu$ m size, ~3 aspect ratio, from Union Carbide Advanced Ceramics, Cleveland, OH), Mo particles (3.5-5.5 µm size, from GTE Sylvania, Towanda, PA) and SiC whiskers (primarily  $\beta$  phase, 0.5–1.5  $\mu$ m in diameter, 10–25 aspect ratio, from Advanced Refractory Technologies, Inc., Buffalo, NY). In order to make copper-matrix composites, copper was coated on these fillers using a coating process developed by the authors. The coating was performed by electroplating in the case of Mo particles (electrically conducting) and by electroless plating followed by electroplating in the case of SiC whiskers and TiB<sub>2</sub> platelets. Refer to Fig. 1 of Ref. 3 for optical micrographs of the coated fillers. The Cu coating was uniform and continuous on the filler units. In the case of SiC whisker composites, the filler volume fraction in the resulting composite was controlled by varying the copper coating thickness; no copper powder was used. In the case of Mo particles and TiB<sub>2</sub> platelets, the filler volume fraction was varied by adding different proportions of copper powder (3.3 µm mean size, from GTE Products Corp., Towanda, PA) to the coated filler, which had a fixed copper content. Mixing of the coated filler and the copper powder was conducted in a ball mill. In all cases, the coated filler (optionally mixed with copper powder) was reduced in hydrogen at 300 °C for 60 min prior to compaction and subsequent sintering by hot pressing. Compaction was conducted by cold pressing in a graphite die to form a cylindrical green compact of diameter 12.7 mm and height 12.7 mm. The pressure during cold pressing was 155 MPa. Subsequent hot pressing was conducted in the same die in purging nitrogen at 1000 °C for 25 min in the case of Mo particles, 1000 °C for 20 min in the case of TiB<sub>2</sub> platelets and 950 °C for 25 min in the case of SiC whiskers. The pressure during hot pressing was 116 MPa. During heating prior to hot pressing, the pressure was kept at 77 MPa until the hot-pressing temperature was reached. For comparison, the corresponding composites made by the admixture method were fabricated under the same processing conditions. The processes for various composites were selected such that, at a low filler volume fraction, dense composites with low porosity could be made by both methods under the same processing conditions.

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

The density of the sintered composites was measured using the buoyancy (Archimedes') method (ASTM B328-92). The porosity of the composite was determined by

$$V_{\rm p} = 1 - \rho/\rho_{\rm o} \tag{1}$$

where  $V_p$  is the pore volume fraction,  $\rho$  the measured density, and  $\rho_0$  is the theoretical density. Hardness was determined 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 using an hydraulic mechanical testing system (MTS Systems Corp., Marblehead, MA, USA).

For measurement of the volume electrical resistivity, the four-probe method was used; silver paint was used for electrical contacts. The CTE was measured by using a Perkin-Elmer DMA-7 thermomechanical analyser, with the temperature scanned from 25 to  $150 \,^{\circ}\text{C}$  at a rate of  $5 \,^{\circ}\text{C}\,\text{min}^{-1}$ .

The thermal conductivity (*K*) was determined by

$$K = \alpha \rho C_{\rm p} \tag{2}$$

where  $\alpha$ ,  $\rho$  and  $C_p$  are the thermal diffusivity, density and specific heat, respectively, of the sample. To obtain the thermal conductivity, the thermal diffusivity was measured by the laser flash method (Nd glass laser, 10 ~15 J energy, 0.4 ms/pulse), and the specific heat was measured by differential scanning calorimetry (Perkin-Elmer DSC-7).

## 3. Results

Refer to Figs 3 and 4 of Ref. 3 for optical micrographs of polished sections of the composites made by the coated filler method and the admixture method. At a low filler content (15 vol % TiB<sub>2</sub>, 30 vol % Mo and 15 vol % SiC), there is no apparent difference in microstructure between the composites made by the coated filler method and admixture method for all types of fillers; the composites made by either method are nearly pore free with the filler distributed in the matrix uniformly. At a high filler content (60 vol % TiB<sub>2</sub>, 70 vol % Mo and 50 vol % SiC), the composites made by the two methods are different in microstructure. For Cu/TiB<sub>2</sub>, the microstructure of the



Figure 1 Variation of porosity, hardness and compressive yield strength with Mo particle volume fraction in Cu/Mo composites made by the coated filler method ( $\bullet$ ) and the admixture method ( $\triangle$ ).



Figure 2 Variation of porosity, hardness and compressive yield strength with SiC whisker volume fraction in Cu/SiC whisker composites made by the coated filler method ( $\bullet$ ) and the admixture method ( $\triangle$ ).

corresponding composites made by the two methods differs mainly in that the composites made by the admixture method have higher porosity. For Cu/Mo, the microstructure of the corresponding composites made by the two methods differs mainly in that direct Mo–Mo contacts (Mo clustering) are far more prevalent in the composite made by the admixture method. The presence of Mo clustering is due to the higher filler volume fraction (70 vol % Mo) in Cu/Mo than in



Figure 3 Variation of porosity, hardness and compressive yield strength with  $TiB_2$  platelet volume fraction in Cu/TiB<sub>2</sub> platelet composites made by the coated filler method ( $\bullet$ ) and the admixture method ( $\triangle$ ).

Cu/TiB<sub>2</sub> or Cu/SiCw; thus, the proportion of contacting Mo particles in the mixture becomes severe at a high filler content. The spherical shape of the Mo particles allows a higher maximum filler volume fraction than the whisker and platelet shapes of the SiC whiskers and TiB<sub>2</sub> platelets, since it is relatively easy for spherical particles to move to fill the interstices during sintering.

Figs 1–3 show the porosity, hardness and compressive yield strength as functions of the volume fraction of reinforcement for Cu/Mo, Cu/SiC and Cu/TiB<sub>2</sub> composites, respectively. When the Mo content exceeds 60 vol %, the SiC content exceeds 33 vol % and the TiB<sub>2</sub> content exceeds 42 vol %, the composites made by the admixture method have higher porosity than the corresponding composites made by the coated filler method, so the hardness and the compressive yield strength of the former are lower than those of the latter.

Figs 4–6 show that, when the reinforcement content exceeds 60 vol % Mo, 33 vol % SiC and 42 vol % TiB<sub>2</sub> for Cu/Mo, Cu/SiC and Cu/TiB<sub>2</sub> composites, respectively, these composites exhibit lower thermal conductivity and higher electrical resistivity than the composites made by the coated filler method, partly because of the higher porosity in the composites made by the admixture method.

#### 4. Discussion

Except for the CTE, the porosity affects almost all properties of composites. The critical value of the porosity above which the mechanical properties of the composites made by the admixture method degrade abruptly varies slightly among the different composite



Figure 4 Variation of porosity, CTE, electrical resistivity and thermal conductivity with Mo particle volume fraction in Cu/Mo composites made by the coated filler method ( $\bullet$ ) and the admixture method ( $\triangle$ ).



Figure 5 Variation of porosity, CTE, electrical resistivity and thermal conductivity with SiC whisker volume fraction in Cu/SiC whisker composites made by the coated filler method ( $\bullet$ ) and the admixture method ( $\triangle$ ).

systems, as shown in Table I. The volume fraction of the reinforcement at which the critical porosity value is reached corresponds to the reinforcement content maximum for the composites made by the conventional admixture method to remain effectively strengthened. This reinforcement content limitation is



Figure 6 Variation of porosity, CTE, electrical resistivity and thermal conductivity with TiB<sub>2</sub> platelet volume fraction in Cu/TiB<sub>2</sub> platelet composites made by the coated filler method ( $\bullet$ ) and the admixture method ( $\Delta$ ).

TABLE I Critical volume fraction and critical porosity for various composites made by the admixture method

Composite	Cu/Mo	$Cu/TiB_2$	Cu/SiC
Reinforcement aspect ratio	1	3	10
Critical volume fraction(%)	60	42	33
Critical porosity (vol. %)	1.5	2.0	2.0
Minimum volume fraction (%)	41	37	23

called the critical volume fraction. Although this fraction was determined from the measured mechanical properties of the composites of this work, it also can be estimated by using percolation theory. Models had been developed to estimate the minimum volume fraction for filler–filler contact for equiaxed particles [4], whiskers [5] and short fibres [6]. This minimum volume fraction is called the percolation threshold. It decreases with increasing aspect ratio. Table I lists the minimum volume fraction obtained using the twodimensional model of Ref. [5] for the aspect ratios shown. Although the critical volume fraction is higher than the minimum volume fraction, both volume fractions decrease with increasing aspect ratio.

When the porosity exceeds the critical value, increasing the porosity level remarkably degrades the properties (except CTE) of the composites. In contrast is the situation below the critical value. Figs 1–6 show that, for all the copper–matrix composite systems studied, at a low volume fraction of reinforcement

(<50 vol % Mo for Cu/Mo composites, <30 vol %SiC for Cu/SiC whisker composites and <35 vol % for Cu/TiB<sub>2</sub> platelet composites), although the composites made by the two methods are at similar porosity levels, the composites made by the coated filler method have, to various extents, higher hardness, higher compressive yield strength, higher thermal conductivity and lower electrical resistivity. These differences in the properties between the composites made by the two methods cannot be simply explained by the porosity alone, since the composites made by the two methods are at similar porosity levels. Moreover, there exists a difference in CTE, to a certain extent, between corresponding composites made by the two methods, though the CTE is known to be not affected by the porosity. Therefore, there must exist factors other than the porosity which affect the properties of the composites made by the different methods, although their effects are small, compared to the porosity effect on the properties of the composites at high reinforcement contents. These other factors are discussed below.

For composites containing reinforcements with a spherical shape, such as the Cu/Mo particle composites, the composites made by the admixture method tend to have reinforcement particle clustering due to the direct contact among the reinforcement particles, especially at a high Mo content, whereas the tendency to cluster is greatly reduced in the composites made by the coated filler method, even at a similarly high Mo content, since the matrix coating on the reinforcements substantially separates them from one another. The reinforcement particle clustering may degrade the properties of the composites in two ways. Firstly, a particle cluster can be considered to be equivalent to a reinforcement of a large size. Based on the dislocation and subgrain strengthening mechanisms for discontinuously reinforced metalmatrix composites, a larger particle size leads to less strengthening. Secondly, the contacted Mo particles within a Mo cluster, as present in the Cu/Mo composites made by the admixture method, cannot be effectively sintered together at such a low sintering temperature (1000 °C). This results in weak bonding among the contacted Mo particles in the Mo cluster, in contrast to the good bonding between a Mo particle and the Cu matrix. This insufficient sintering will weaken the mechanical properties and degrade other properties of the composites.

For composites reinforced by reinforcements that are not equiaxed, such as the Cu/SiC whisker composites and the Cu/TiB<sub>2</sub> platelet composites, no apparent reinforcement clustering was observed throughout the whole range of reinforcement content. Therefore, reinforcement clustering is not a factor influencing the properties of the composites. For these composites, the reinforcement/matrix interface is believed to be a factor. In a metal-matrix composite, the interface between the reinforcement and the matrix is important for the properties of the composite. For the mechanical properties, good or strong bonding will allow effective transfer of the external load from the soft matrix to the reinforcement and will yield more dislocations due to the thermal misfit strain associated with the CTE mismatch between matrix and reinforcement. For the thermal and electrical properties, a good or clean interface between the reinforcement and matrix will cause less thermal barrier and lower electrical contact resistance, thereby resulting in higher thermal and electrical conductivities for the composites. For the CTE, a good bond will allow the low CTE reinforcement to contribute its fullest to reducing the CTE of the composite.

In this work, the commercially provided reinforcements could not be very clean and pure on the surface and the powder metallurgy route adopted in this work was under similar processing conditions as used for common applications and could not be controlled so strictly and completely as to avoid any oxidation. Thus, during the fabrication of the composites made by the admixture method, some contaminants (including oxidation products, foreign impurities, etc.) may be introduced to the interface between the reinforcement and the matrix and will weaken the bonding, form a thermal barrier and increase the electrical contact resistance between the reinforcement and the matrix. This negative effect will increase with increasing reinforcement surface area. For the composites made by the coated filler method, the coating process (including electroless and electroplating) may provide the matrix coated reinforcement with a cleaner interface between the reinforcement and the matrix coating. Furthermore, the reinforcement, having been already protected by the matrix coating, has a reduced chance of oxidation at the interface during fabrication of the composites. Therefore, better bonding, less thermal barrier and lower electrical resistance between the reinforcement and the matrix in the composites made by the coated filler method could be achieved. This reinforcement/matrix interface effect may partly explain why the composites made by the coated filler method are superior to the composites made by the conventional admixture method in all properties (including CTE), even at a low reinforcement volume fraction and at similar porosity levels. However, among the factors of porosity, microstructure and the reinforcement/matrix interface, porosity is the dominant factor which affects the properties (except CTE) of the composites made by the two methods, especially at a high reinforcement volume fraction.

Fig. 7 shows the difference in porosity  $\Delta V_{\rm p}$ , which is defined as  $V_p$  (coated)  $-V_p$  (admixture), where  $V_p$ (coated) and  $V_p$  (admixture) are the porosities of corresponding composites made by the coated filler method and the admixture method, respectively. Note that  $\Delta V_{\rm p}$  is negative for all the composite systems studied, since  $V_{p}$  (coated) is less than  $V_{p}$  (admixture). Compared to the admixture method, the coated filler method is more effective in reducing the porosity for all the composite systems, especially when the reinforcement volume fraction exceeds a certain value, which varies from one composite system to another (60 vol% Mo for Cu/Mo particle composites, 42 vol% TiB<sub>2</sub> for Cu/TiB<sub>2</sub> platelet composites and 30 vol% SiC for Cu/SiC whisker composites). These values correspond to the limitation of the reinforcement



*Figure 7* Variation of difference in porosity with reinforcement volume fraction between the corresponding composites made by the coated filler method and the admixture method  $(\Delta V_p = V_p (\text{coated}) - V_p (\text{admixture})).$ 

content (i.e. critical volume fraction) for composites made by the admixture method. They are in the order of Cu/Mo particle composite > Cu/TiB<sub>2</sub> platelet composite > Cu/SiC whisker composite, because the aspect ratios of the reinforcement are in the reverse order, i.e. SiC whiskers > TiB<sub>2</sub> platelet > Mo sphere particles. The greater the aspect ratio, the less effective is the admixture method at a high reinforcement content.

Fig. 8 shows the difference in hardness  $\Delta H_{\rm B}$ , which is defined as  $H_{\rm B}$  (coated) –  $H_{\rm B}$  (admixture), where  $H_{\rm B}$  (coated) and  $H_{\rm B}$  (admixture) are the Brinell hardness of corresponding composites made by the coated filler method and the admixture method, respectively. Note that  $\Delta H_{\rm B}$  is positive for all composites. The coated filler method is particularly effective for attaining high hardness when the reinforcement content is high. This is due to its effectiveness in reducing the porosity of the composites at high reinforcement contents (Fig. 7). The coated filler method showed its effectiveness in increasing the hardness of the composites even at relatively low reinforcement contents (as low as 30 vol% Mo for Cu/Mo composites, 25 vol% SiC whiskers for Cu/SiC whisker composites and 15 vol% TiB<sub>2</sub> platelets for Cu/TiB<sub>2</sub> platelet composites), although its effectiveness is not as remarkable as at high reinforcement contents. Since, at low reinforcement contents, the composites made by the two methods are similarly low in porosity, the effectiveness at low reinforcement contents may be due to the better reinforcement/matrix interface or stronger bonding in the composites made by the coated filler method.

Fig. 9 shows that the coated filler method has similar effectiveness trends in relation to both hardness and compressive yield strength. The effectiveness



*Figure 8* Variation of difference in hardness with reinforcement volume fraction between the corresponding composites made by the coated filler method and the admixture method  $(\Delta H_{\rm B} = H_{\rm B} ({\rm coated}) - H_{\rm B} ({\rm admixture})).$ 



Figure 9 Variation of difference in compressive yield strength with reinforcement volume fraction between the corresponding composites made by the coated filler method and the admixture method  $(\Delta \sigma_{ey} = \sigma_{ey}(\text{coated}) - \sigma_{ey}(\text{admixture})).$ 

of the coated filler method, compared to the admixture method, in improving the mechanical properties (hardness and compressive yield strength) of the composites is in the order: Cu/SiC whisker composites > Cu/TiB<sub>2</sub> platelet composites > Cu/Mo particle composites. This effectiveness order of the coated filler



*Figure 10* Variation of difference in electrical resistivity with reinforcement volume fraction between the corresponding composites made by the coated filler method and the admixture method.

method, compared to the admixture method, in improving the mechanical properties is related to its effectiveness order in reducing the porosity of the composites.

Fig. 10 shows the difference in electrical resistivity between corresponding composites made by the two methods. The difference is defined as the resistivity of the composite made by the coated filler method minus that of the composite made by the admixture method. For all the composite systems, this difference is negative. Note that the vertical scale is different for the different curves in Fig. 10. At a high reinforcement content ( > 33 vol% for Cu/SiC whisker composites, > 30 vol%for Cu/Mo particle composites, > 50 vol% for Cu/TiB<sub>2</sub> platelet composites), the coated filler method, compared to the admixture method, exhibits significant effectiveness in decreasing the electrical resistivity of the composites. This effectiveness is in the order: Cu/SiC whisker composites  $> Cu/TiB_2$  platelet composites > Cu/Mo particle composites. This is related to the difference in effectiveness for reducing the porosity, with the greatest effectiveness for Cu/SiC whisker composites (Fig. 7).

Fig. 11 shows that the effectiveness of the coated filler method in improving the thermal conductivity of various composite systems is similar in trend to that of the electrical conductivity, except that, at relatively low reinforcement contents, the thermal conductivity is still considerably higher for composites made by the coated filler method than those made by the admixture method. This indicates that the thermal conductivity is more sensitive to the state of reinforcement/matrix interface than the electrical conductivity is. In other words, the thermal barrier formed at the reinforcement/matrix interface greatly influences the



Figure 11 Variation of difference in thermal conductivity with reinforcement volume fraction between the corresponding composites made by the coated filler method and the admixture method  $(\Delta K = K \text{ (coated)}-K(\text{admixture})).$ 



*Figure 12* Variation of difference in CTE with reinforcement volume fraction between the corresponding composites made by the coated filler method and the admixture method ( $\Delta$ CTE = CTE(coated) – CTE(admixture)).

thermal conductivity of the composites, and the coated filler method is believed to be able to provide a cleaner interface or less thermal resistance between the reinforcement and the matrix.

Fig. 12 (with a negative vertical scale) indicates that at a high reinforcement content, the coated filler method is more effective than the admixture method



Figure 13 Variation of fractional decrease in CTE with reinforcement volume fraction of various composites made by the coated filler method. ( $\Box$ ) Cu/SiC<sub>w</sub>; ( $\triangle$ ) Cu/TiB<sub>2</sub>; ( $\bigcirc$ ) Cu/Mo.



Figure 14 Variation of fractional increase in porosity with reinforcement volume fraction of various composites made by the coated filler method. ( $\Box$ ) Cu/SiC<sub>w</sub>; ( $\triangle$ ) Cu/TiB<sub>2</sub>; ( $\circ$ ) Cu/Mo.

in decreasing the CTE of various composites. These results appeared at first to be due to the porosity at a high reinforcement content. Since the porosity itself has no effect on the CTE of the composite, the observed effect on the CTE is not due to the porosity, but is due to the bonding or interface between the reinforcement and the matrix. Since the amount of inter-



Figure 15 Variation of fractional increase in hardness with reinforcement volume fraction of various composites made by the coated filler method. ( $\Box$ ) Cu/SiC<sub>w</sub>; ( $\triangle$ ) Cu/TiB<sub>2</sub>; ( $\circ$ ) Cu/Mo.



Figure 16 Variation of fractional increase in compressive yield strength with reinforcement volume fraction of various composites made by the coated filler method. ( $\Box$ ) Cu/SiC<sub>w</sub>; ( $\Delta$ ) Cu/TiB<sub>2</sub>; ( $\circ$ ) Cu/Mo.

face area increases with increasing reinforcement content, the effectiveness of the coated filler method in improving the CTE increases with increasing reinforcement content of the composite, as indicated in Fig. 12.

Figs 13–18 show the effect of the reinforcement type on the properties of copper–matrix composites made by the coated filler method. This effect is expressed in



Figure 17 Variation of fractional decrease in thermal conductivity with reinforcement volume fraction of various composites made by the coated filler method. ( $\Box$ ) Cu/SiC<sub>w</sub>; ( $\Delta$ ) Cu/TiB<sub>2</sub>; ( $\circ$ ) Cu/Mo.



Figure 18 Variation of fractional increase in electrical resistivity with reinforcement volume fraction of various composites made by the coated filler method. ( $\Box$ ) Cu/SiC<sub>w</sub>; ( $\Delta$ ) Cu/TiB<sub>2</sub>; ( $\circ$ ) Cu/Mo.

terms of fractional change in a property relative to the property of copper. Cu/Mo composites are best for high thermal and electrical conductivities, low CTE and low porosity; Cu/SiC composites are best for good mechanical properties but worst for thermal

TABLE II Comparison of the properties of the composites made by the coated filler method at essentially the same reinforcement volume fraction

Composite	Cu/Mo	Cu/TiB <sub>2</sub>	Cu/SiC
Vol% reinforcement	$50 \pm 1$	$48 \pm 1$	$50 \pm 1$
CTE (10 <sup>-6</sup> °C <sup>-1</sup> )	$9.5\pm0.1$	$10.2\pm0.1$	$10.2\pm0.1$
Thermal conductivity $(W m^{-1} \circ C^{-1})$	221 ± 5	$176 \pm 3$	$60 \pm 2$
Electrical resistivity $(10^{-6} \Omega \text{ cm})$	$2.9\pm0.1$	3.4 ± 0.1	$19.5\pm0.7$
Hardness $(H_{\rm B})$	$159\pm 5$	$218 \pm 10$	$260 \pm 12$
Compressive yield strength (MPa)	472 ± 14	659 ± 15	$651 \pm 18$

TABLE III Properties of Mo, SiC whisker and  $\mathrm{TiB}_2$  platelet [7–10]

Material	Mo	TiB <sub>2</sub>	SiC
Density (g cm <sup>-3</sup> )	10.22	4.50	3.21
Particle size or diameter (µm)	3.5-5.5	3–5	0.5–1.5
Aspect ratio	1	~ 3	10-25
Electrical resistivity $(\Omega \text{ cm})$	$5.17 \times 10^{-6}$	10-30 × 10 <sup>-6</sup>	$4 \times 10^{13}$
Thermal conductivity $(Wm^{-1} \circ C^{-1})$	145	~ 100	> 16
CTE (10 <sup>-6</sup> °C <sup>-1</sup> )	4.90	8.1	4.0
Elastic modulus (GPa)	324	350–570	450
Poisson's ratio	0.293	0.13-0.19	0.17

and electrical conductivities;  $Cu/TiB_2$  composites are intermediate in thermal and electrical conductivities and have good mechanical properties.

Table II shows the comparison of the properties of various composites made by the coated filler method at the same reinforcement volume fraction (48-50%). Since the CTE of SiC whiskers is lower than those of Mo and  $TiB_2$  (Table III), the measured CTE values indicate that, at least at 50 vol% reinforcement, Cu/Mo and Cu/TiB<sub>2</sub> composites have stronger reinforcement/matrix bonding than Cu/SiC whisker composite. Since the CTE of Mo is lower than that of  $TiB_2$ (Table III), the measured CTE value of Cu/Mo is lower than that of Cu/TiB<sub>2</sub>. The thermal and electrical conductivities are in the order of Cu/Mo >  $Cu/TiB_2 > Cu/SiC$ , because they are in the same order for Mo, TiB<sub>2</sub> and SiC themselves (Table III). Table II shows that Cu/TiB<sub>2</sub> and Cu/SiC composites have similarly good mechanical properties, which are much better than those of Cu/Mo. This is because TiB<sub>2</sub> platelets and SiC whiskers are stiffer than Mo particles (Table III), and have larger aspect ratio than Mo particles (Table III).

## 5. Conclusions

Copper-matrix composites were fabricated by solidstate sintering using the coated filler method (an unconventional powder metallurgy process using matrix-metal-coated reinforcement without (or optionally with) matrix metal powder) and the admixture method (a conventional powder metallurgy process using a mixture of reinforcement and matrix metal powder). The coated filler method is highly effective for the fabrication of high-performance discontinuously reinforced copper-matrix composites with various types of reinforcement, including metal (Mo) and ceramics (SiC and TiB<sub>2</sub>) with different morphologies (particles, whiskers and platelets). Compared to the admixture method, the coated filler method can provide composites with a cleaner reinforcement/matrix interface, better reinforcement-matrix bonding and less reinforcement clustering (associated with direct particle-particle contact). Therefore, the composites made by the coated filler method have lower porosity, improved microstructure, superior mechanical properties (higher hardness and compressive yield strength) and improved physical properties (higher thermal conductivity, lower CTE and lower electrical resistivity) than the composites made by the admixture method.

Porosity is the dominant factor which affects almost all properties (except CTE) of the composites. The critical porosity value above which the mechanical properties of the composites made by the admixture method degrade abruptly varies among different composite systems. The critical porosity value is 1.5 vol%(corresponding to 60 vol% Mo) for the Cu/Mo particle composite system, 2.0 vol% (corresponding to 33 vol% SiC) for the Cu/SiC whisker composite system and 2.0 vol% (corresponding to 42 vol% TiB<sub>2</sub>) for Cu/TiB<sub>2</sub> platelet composite system.

The coated filler method (as compared to the admixture method) is very effective in reducing the porosity of the composites, especially at a high reinforcement content. This is because the matrix coating separates the reinforcement units from one another. Even at a high reinforcement content, a small amount of metal matrix is sufficient to join the reinforcement units together to form a dense composite. For the same reason, reinforcement clustering is greatly reduced in Cu/Mo particle composites made by the coated filler method at high reinforcement contents.

Among Cu/Mo, Cu/TiB<sub>2</sub> and Cu/SiC at the same reinforcement volume fraction (50%), Cu/Mo gave the lowest CTE, highest thermal conductivity and lowest electrical resistivity, while Cu/SiC gave the greatest hardness and Cu/TiB<sub>2</sub> and Cu/SiC gave the highest compressive yield strength. Compared to Cu/SiC, Cu/TiB<sub>2</sub> exhibited much higher thermal conductivity and much lower electrical resistivity.

#### Acknowledgement

This work was supported by the Defense Advanced Research Projects Agency of the US Department of Defense and the Center for Electronic and Electro-Optic Materials of the State University of New York at Buffalo.

#### References

- 1. PAY YIH and D.D.L. CHUNG, J. Electron. Mater. 24 (1995) 841.
- 2. Idem., J. Mater. Sci. 31 (1996) 399.
- 3. Idem., Int. J. Powder Metall. 31 (1995) 335.
- J.J. LICARI, "Electronic packaging and interconnection", edited by C.A. Harper (McGraw-Hill, New York, 1991) p. 7.
- 5. E.A. HOLM and M.J. CIMA, J. Amer. Ceram. Soc. 72 (1989) 303.
- 6. Y.H. LEE, J. Mater. Sci. 30 (1995) 3033.
- 7. ROBERT B. ROSS, "Metallic materials specification handbook", Fourth edition (Chapman & Hall, New York, 1992).
- T.W. CLYNE and P.J. WITHERS, "An introduction to metal matrix composites", edited by E.A. Davis and I.M. Ward (Cambridge University Press, New York, 1993) p. 479.
- 9. "Compilation of titanium diboride properties", Advanced Ceramics Corporation, Cleveland, OH.
- T.M. MOORE and R.G. McKENNA, "Characterization of integrated circuit packaging materials" (Butterworth-Heinemann, Boston, 1993) p. 193.

Received 2 July and accepted 13 November 1996