Copper-Matrix Molybdenum Particle Composites Made from Copper Coated Molybdenum Powder

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Copper-matrix molybdenum particle composites containing 33 ~ 73 wt.% Mo were fabricated by hot pressing copper coated molybdenum powder. For comparison, corresponding composites fabricated by hot pressing a mixture of copper and molybdenum powders were also made. The former method gave composites of lower porosity, higher hardness, higher compressive yield strength, lower coefficient of thermal expansion, lower electrical resistivity and higher thermal conductivity than the latter method. These differences are partly due to the separation of the molybdenum particles by the copper coating in the former case. In contrast, molybdenum particle clustering occurred in the latter case when the Mo content exceeded 53 wt.%.

INTRODUCTION

Thermal conductors with low thermal expansion are needed in electronic packaging for substrates, heat sinks, lids, housings, and constraining cores in printed circuit boards. The low thermal expansion is necessitated by
- the low thermal expansion of the semiconductor and of its carrier, which is often ceramic, and
- the thermal cycling encountered by the electronic package during use.

The high thermal conductivity is necessitated by the need for the package to dissipate heat—a need which is increasingly critical as the package is more miniaturized and the power is increased.

Thermal conductors with low thermal expansion include metal-matrix composites (usually with aluminum or copper as the thermally conducting matrix), polymer-matrix composites (with carbon fibers,

boron nitride particles or even diamond particles as the thermally conducting filler), and carbons (carbon-carbon composites, pyrolytic graphite, etc.). The low thermal conductivity of polymers gives the polymer-matrix composites a disadvantage, especially when the thermal contact resistance is considered. Carbons that are high in thermal conductivity tend to be very expensive, though they can be even more thermally conductive than copper. On the other hand, metals are low in cost and high in thermal conductivity, making metal-matrix composites highly attractive in both cost and performance. This paper is focused on copper-matrix composites because of the high thermal conductivity of copper.

Although the metal matrix in a metal-matrix composite is a good thermal conductor, the filler is preferably also of good thermal conductivity in order to maximize the conductivity of the composite. Moreover, the filler must have a low coefficient of thermal expansion (CTE), since the metal matrix has a high CTE and the composite is required to have a low CTE.

Table I. Physical Properties of Some Engineering Metals[1]

Metal	Density (g/cm³)	Melting Point (°C)	Thermal Conductivity (W/m °C)	CTE (×10⁻⁶) (20–100°C)	Electrical Resistivity (10⁻⁶ Ω·cm)	Young's Modulus (GPa)
Al	2.7	658	210	24	2.76	68.3
Cu	8.96	1083	385	16.4	1.7	110
Fe	7.9	1535	76.2	12.2	8.9	197
Mo	10.22	2620	145	4.9	5.17	324
Ni	8.88	1455	60.7	13.1	6.4	207
W	19.3	3370	163.3	4.4	5.65	345

Fig. 1. Optical micrograph showing the Cu coating (bright ring) on Mo particles.

These requirements point to the choice of a low CTE metal (as opposed to a ceramic) as the filler. Table I gives the physical properties of some commonly used engineering metals. Molybdenum and tungsten are particularly attractive due to their low CTE. Although tungsten is similar to molybdenum in thermal conductivity, CTE, electrical resistivity and Young's modulus, it suffers from a high density. Molybdenum particles were thus chosen as the filler in the copper-matrix composites of this work.

Even with a filler of low CTE, a sufficiently low CTE (<10 × 10⁻⁶ °C⁻¹) in the composite cannot be attained unless the filler content is sufficiently high (e.g., >50 vol.% Mo). The fabrication of metal-matrix composites with a high filler volume fraction (as high as 75%) can be achieved by liquid metal infiltration.[2] However, achieving this by conventional powder metallurgy (P/M) is difficult. Dense composites made by P/M all tend to have relatively low filler volume fractions (<40%); at high filler volume fractions, they

tend to be porous. As the melting point of copper is high compared to that of aluminum, the liquid metal infiltration technique is simpler for aluminum-matrix composites than copper-matrix composites. Moreover, powder metallurgy is a more widely used metal processing technique than liquid metal infiltration. For these reasons, this paper focuses on fabricating by powder metallurgy copper-matrix composites with high filler volume fractions (up to 70%).

In order to achieve metal-matrix composites of high filler volume fractions by powder metallurgy, an unconventional P/M method was used in this work. This method involves sintering a coated powder which consists of the matrix metal coated on individual filler particles; it is called the coated filler method in this paper. In contrast, conventional P/M technology involves sintering a mixture of the matrix metal powder and the filler particles; it is called the admixture method in this paper. The coated filler method has been previously used to make copper-matrix or silver-matrix graphite particle composites for use as brushes; it gave composites of lower electrical resistivity than the corresponding composites made by conventional P/M.[3] In recent years, the coated filler method was used by the Specialty Metal Products Division of Ametek Inc. to prepare Cu/Mo composite products with high Mo contents and low porosity. However, systematic research work involving the comparison between the composites made by the two methods in terms of the thermal conductivity, electrical resistivity, CTE, porosity, and mechanical properties has not been previously made. The objective of this paper is to provide comparison in all these aspects between the composites made by the two methods. 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[4,5] or to modify the filler-matrix interface.[6]

For the sake of comparison, a Cu/Mo composite made by the admixture method (Sumitomo Electric Industries, Ltd., Japan) and a Cu/Mo composite made by the coated filler method (Ametek Inc., Wallingford, CT) were examined in this work. Both were made by powder metallurgy for electronic packaging applications, such as substrates, heat sinks, thermal spreaders, mother boards, and housings.

The attractive properties of Cu/Mo composites for electronic packaging applications include low ther-

mal expansion compared to Cu, Ni, or Fe and high thermal conductivity compared to SiC or Al_2O_3. Cu/Mo composites are attractive not only for electronic packaging, but also for sliding electrical contacts, motor brushes, and resistance welding electrodes, because of their hardness and electrical conductivity.

EXPERIMENTAL

Cu/Mo composites containing 33–73 wt.% (30–70 vol.%) Mo were fabricated by two powder metallurgical methods, namely the coated filler method (using Cu coated Mo powder, optionally mixed with Cu powder) and the admixture method (using a mixture of Cu powder and Mo powder). In the coated filler method, the Cu coated Mo powder (70 vol.% Mo in particles after coating) was prepared by an electroplating process developed by the authors. The composition of the coated particles were determined using the method described in the Appendix. The Mo particles were uniformly and continuously covered by the coating (Fig. 1). The Cu/Mo composite at 73 wt.% Mo was made from the Cu coated Mo powder without the addition of Cu powder. Composites at lower Mo contents were made from a mixture of the Cu coated Mo powder and "bare" Cu powder in a proportion required to achieve a particular Mo weight fraction in the composites. For comparison with the admixture method, mixtures of Cu powder and Mo powder were prepared at the same corresponding compositions by weight to the composites made by using the coated filler method. The Cu and Mo powders used were of mean size of 3.3 and 4.5 µm, respectively, and were from GTE Products Corporation (Towanda, PA). Mixing was performed in a ball mill with alumina cylinders (13 × 13 mm) as the grinding medium.

Before composite fabrication, the appropriate powder or powder mixture was reduced in purging hydrogen gas at 300°C for 120 min. Composite fabrication involved cold pressing the appropriate powder or powder mixture in a graphite die at 156 MPa to form a cylindrical green compact (0.5" dia. × 0.5" high), which was then hot pressed by using the same die in purging nitrogen gas at 1000°C and 117 MPa for 25 min. During heating, the pressure was kept at 77 MPa. The P/M route for both methods is shown in Fig. 2.

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

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

$$Vp = 1 - \rho/\rho_o, \qquad (1)$$

where Vp is the pore volume fraction, ρ the measured density, and ρ_o the theoretical density.

The hardness measurement was performed using a Brinell Hardness Tester (Detroit Testing Machine Co., Model HB-2) at a load of 1000 kg for the Brinell

hardness test and a Rockwell Hardness Tester (Page-Wilson Co., Model 3JR) for the Rockwell B scale hardness test. Compressive testing was conducted on a cylindrical specimen, 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 DMA-7 thermal mechanical analyzer, with the temperature scanned from 25 to 150 °C at a rate of 5°C/min.

The thermal conductivity (K) was determined by using the equation

$$K = \alpha\rho C_p, \qquad (2)$$

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),[7] while the specific heat was measured by differential scanning calorimetry (Perkin-Elmer DSC-7).

Optical microscopy was used to examine the microstructure of the Cu/Mo composites made by the two P/M methods. For quantitatively analyzing the microstructure of the Cu/Mo composites, quantitative metallography was used to examine the degree of contact, or the contiguity, of Mo particles in the composite, which can be determined by the equation[8]

$$C_t = 2N_{L\alpha\alpha}/(N_{L\alpha\beta} + 2N_{L\alpha\alpha}), \qquad (3)$$

where C_t is the contiguity ratio of Mo particles, $N_{L\alpha\alpha}$ and $N_{L\alpha\beta}$ are the numbers of intersections per unit length of a random line with α–α (Mo-Mo) and α–β (Mo-Cu) interface traces, respectively.

RESULTS AND DISCUSSION

Microstructure

Figure 3 shows the optical micrographs of polished and etched (with copper preferentially etched) sections of the Cu/Mo composites made by the two P/M methods. It was thus found that the composites with
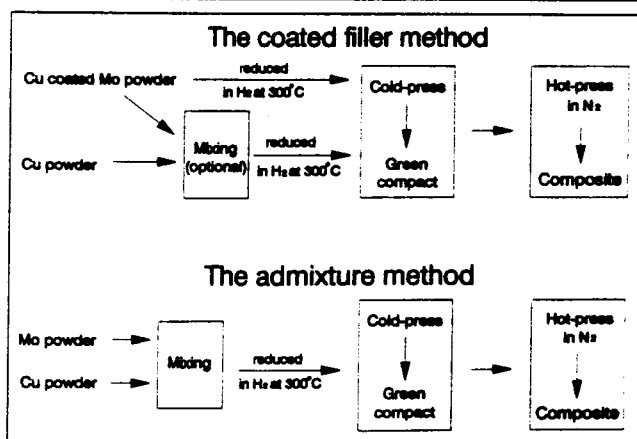

Fig. 2. Powder metallurgy route for the two methods utilized in the preparation of Cu/Mo composites.
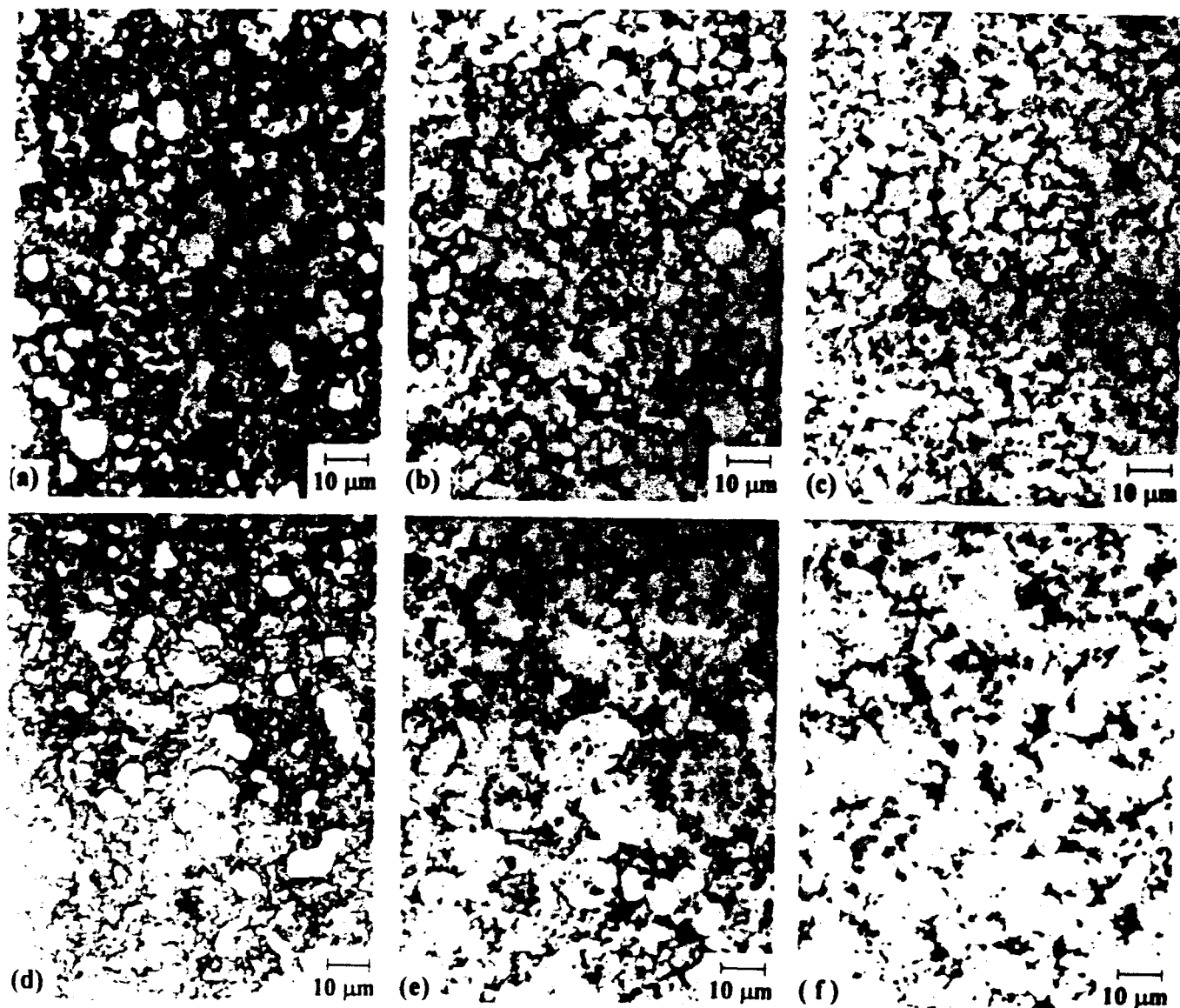
Fig. 3. Optical micrographs showing the microstructure of the Cu/Mo composites made by the two P/M methods with the Cu matrix (dark area) preferentially etched: (a) 33 wt.% Mo. coated filler method; (b) 63 wt.% Mo. coated filler method; (c) 73 wt.% Mo, coated filler method; (d) 33 wt.% Mo, admixture method; (e) 63 wt.% Mo, admixture method; and (f) 73 wt.% Mo. admixture method.

high Mo contents of 63 and 73 wt.% Mo, for example, made by the coated filler method had the adjacent Mo particles substantially separated from one another by the Cu matrix (Figs. 3b and 3c), whereas the corresponding composites made by the admixture method had the adjacent Mo particles contacting each other to form Mo agglomerates. (Figs. 3e and 3f). The extent of Mo particle contacts increased with increasing Mo content among the composites made by the admixture method. However, in the case of a low Mo content (33 wt.% Mo, for example), the microscopic observation showed no apparent difference in the microstructure between the composites made by the two methods (Figs. 3a and 3d). Table II lists the contiguity ratio of Mo in the Cu/Mo composite samples corresponding to Fig. 3.

The fabrication of composites by the P/M route involves solid-state flow of the lower melting matrix.

In this work, the hot pressing temperature was 1000°C, which is below the melting point of copper (1083°C) and is much lower than the melting point of molybdenum (2617°C). During hot pressing, the composite formed through the flow of the softened Cu, with the rigid Mo particles dispersed in the Cu matrix. For the composites made by the admixture method, the degree of Mo contact increased with increasing Mo content, since it was difficult for the small amount of softened Cu particles to flow through the contacted rigid Mo particles in a random Cu/Mo mixture. However, for the composites made by the coated filler method, the Cu coating separated the Mo particles, thereby greatly reducing the degree of contact between the Mo particles, even though the Cu content was low. In the case of composites containing a low volume fraction of Mo, since there was a sufficient amount of Cu particles surrounding the Mo particles

for the composites made by the admixture method, there was no apparent difference in the microstructure between the composites made by the two methods.

Porosity

Figure 4 shows that, at Mo contents below 50 wt.%, the composites made by the two P/M methods had almost the same low level of porosity. At Mo contents exceeding about 60 wt.%, the porosity of the composites made by the admixture method increased dramatically, especially at 73 wt.% Mo, whereas the porosity of the composites made by the coated filler method remained at a relatively low level and increased only slightly when the Mo content was increased to 73 wt.%. This is supported by optical micrographs obtained after polishing but no etching, as shown in Fig. 5 for the 73 wt.% Mo composites made by the two methods.

At a high Mo content, as discussed previously, the high porosity of the composites made by the admixture method was due to the small amount of Cu particles, which could not flow thoroughly through the contacted rigid Mo particles to fill up the interstices. Since the hot pressing temperature was much lower than the melting point of Mo, the contacted Mo particles could not be effectively sintered, thus resulting in high porosity. Figure 5b shows that most pores were present among the contacted Mo particles. For the composites made by the coated filler method, however, even at high Mo contents, the Cu coating separated the Mo particles from one another, thus resulting in low porosity. At Mo contents below 50 wt.%, even for the composites made by the admixture method, there was a sufficient amount of Cu particles to surround the Mo particles, so the porosity of the composites made by both methods was low.

Physical Properties

The effects of the Mo weight fraction and the com-

Table II. Contiguity Ratio (C_i) of Mo in Cu/Mo Composites

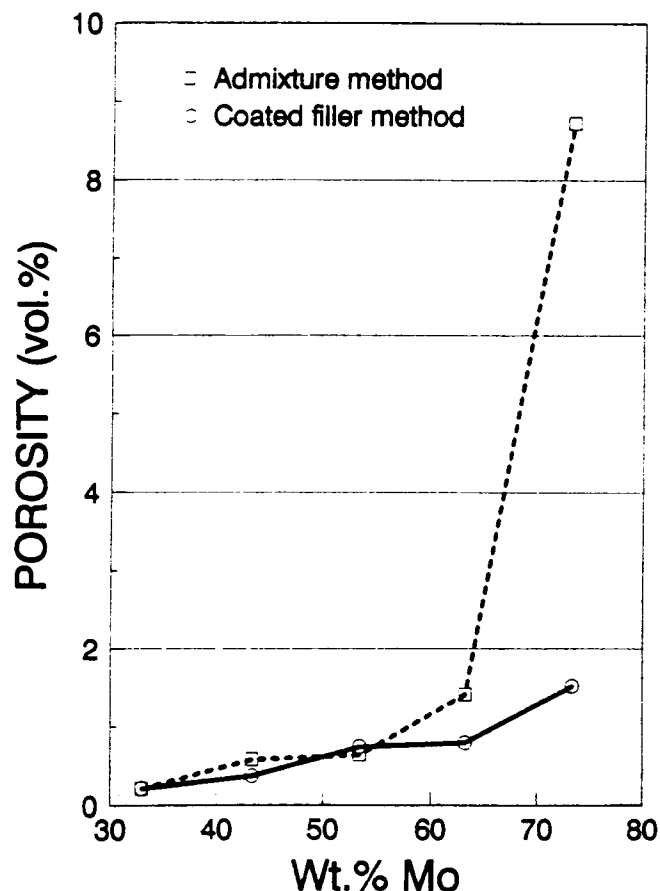| Sample Method	Adm.	Coated	Adm.	Coated	Adm.	Coated
Wt% Mo	33	33	63	63	73	73
C_i	0.07	0.07	0.58	0.19	0.78	0.26

Fig. 4. Porosity as a function of weight percent Mo for the Cu/Mo composites made by the two P/M methods.
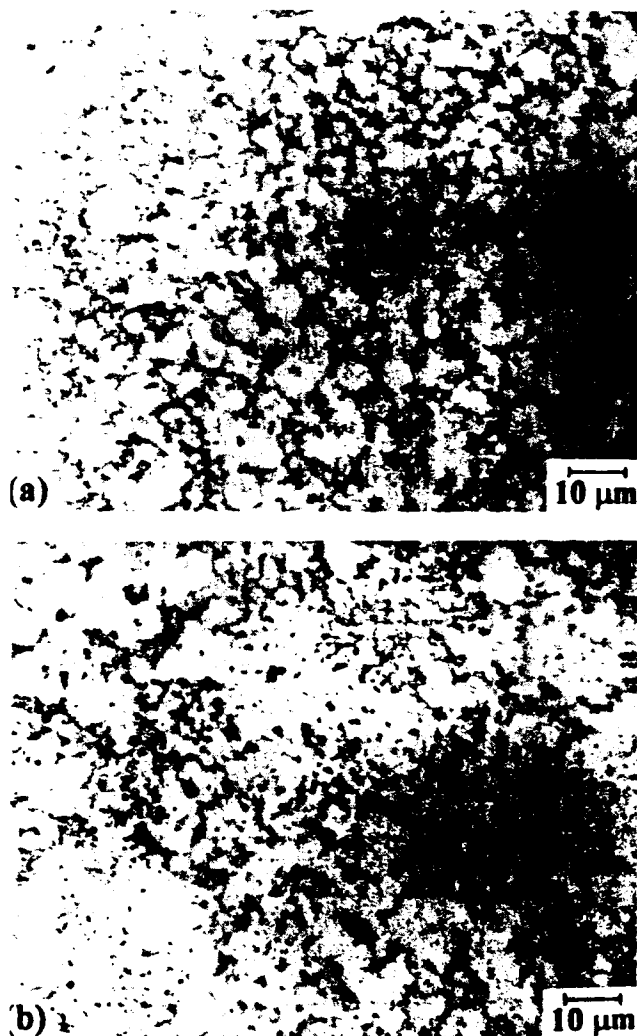

Fig. 5. Optical micrographs showing pores in the Cu/Mo composites made by the two P/M methods. The samples were polished but not etched: (a) 73 wt.% Mo, coated filler method; and (b) 73 wt.% Mo, admixture method.
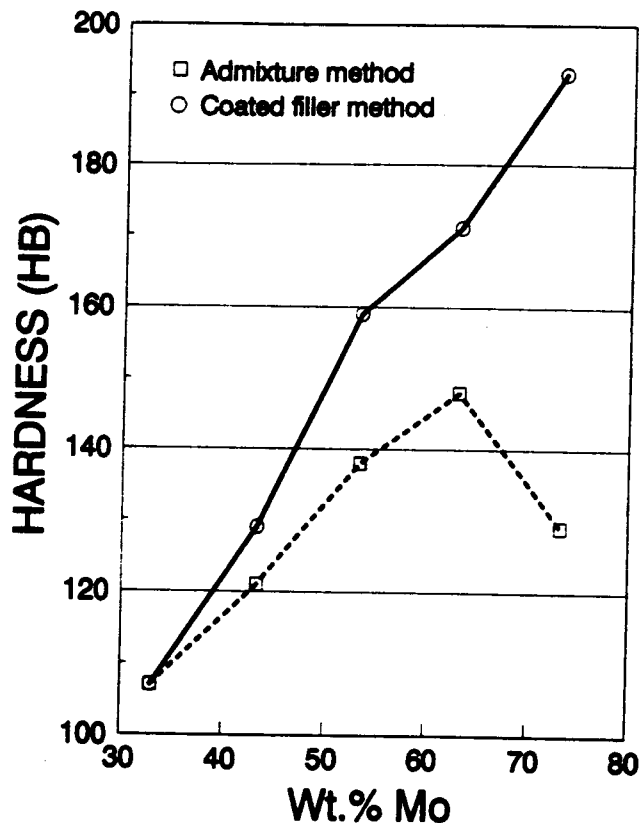
Fig. 6. Brinell hardness as a function of weight percent Mo for the Cu/Mo composites made by the two P/M methods.
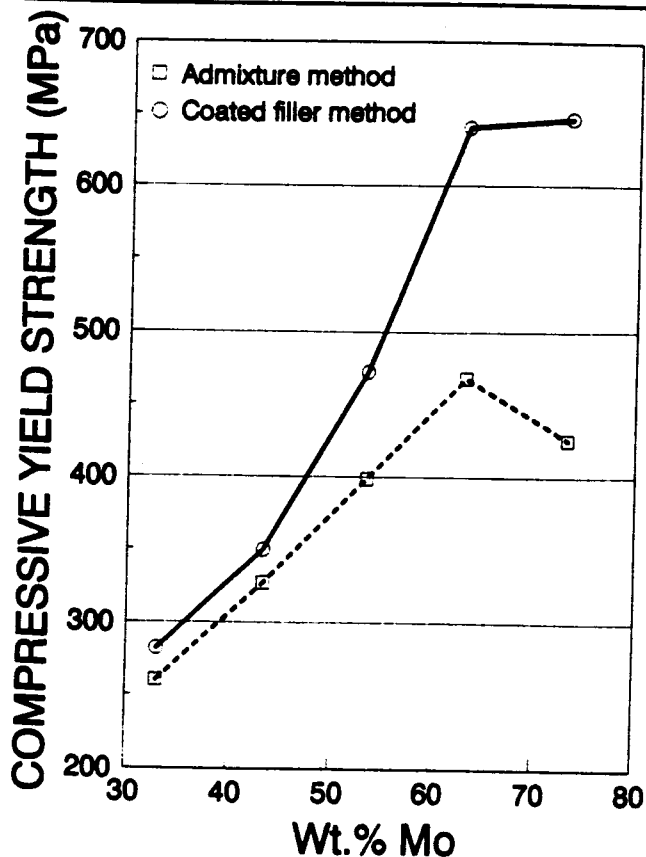

Fig. 7. Compressive yield strength as a function of weight percent Mo for the Cu/Mo composites made by the two P/M methods.
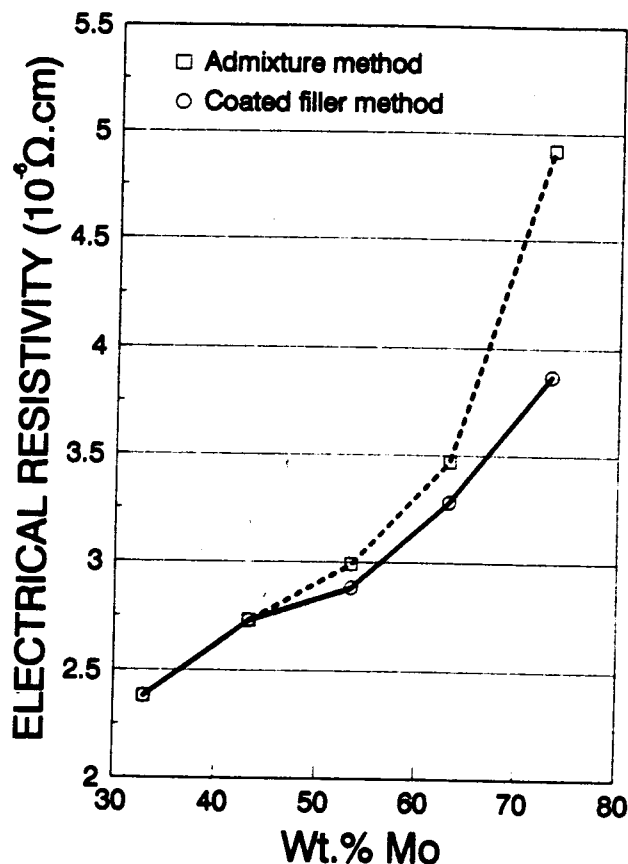

Fig. 8. Electrical resistivity as a function of weight percent Mo for the Cu/Mo composites made by the two P/M methods.

posite fabrication method on the measured properties, such as hardness, compressive yield strength, volume electrical resistivity, CTE, and K, are shown in Figs. 6–10, respectively.

Hardness and Compressive Yield Strength

Figures 6 and 7 show that the hardness and compressive yield strength of the composites made by the coated filler method were higher than those of the corresponding composites made by the admixture method. The differences between the composites made by the two methods increased with increasing Mo content, especially at high Mo contents (>53.4 wt.%). At Mo contents exceeding 63 wt.%, both the Brinell hardness and compressive yield strength of composites made by the admixture method decreased abruptly, whereas, for the composites made by the coated filler method, the hardness continued to increase while the compressive yield strength remained high.

Electrical Resistivity

Figure 8 shows that, at high Mo contents (>63 wt.%), the electrical resistivity of the composites made by the admixture method increased more markedly with increasing Mo content than that of the composites made by the coated filler method.

All the difference in the properties mentioned above between the composites made by the two methods are

attributed, at least partly, to the higher porosity of the composites made by the admixture method. Moreover, the insufficient sintering of the contacted Mo particles in the Mo particle agglomerates contributes to the degradation of properties of the composites made by the admixture method. Table III shows the effect of the porosity and Mo particle agglomerates (expressed in contiguity ratio C_t) on measured properties of the Cu/Mo composites made by the two methods at high contents of Mo (63 and 73 wt.% Mo).

Thermal Conductivity and Coefficient of Thermal Expansion

Figures 9 and 10 show that the composites made by the coated filler method exhibited lower CTE and higher thermal conductivity than the composites made by the admixture method at Mo contents from 33 to 73 wt.%. The differences increased with increasing Mo content. The CTE and thermal conductivity are substantially linear with Mo content and are not as sensitive to the porosity as the hardness, compressive yield strength, and electrical resistivity are.

At low Mo contents, there was little porosity difference (Fig. 4, <53 wt.% Mo) and no apparent difference in microstructure (Figs. 3a and 3d, at 33 wt.% Mo) between the composites made by the two methods. Nevertheless, all the properties showed a difference between the composites made by the two methods at all Mo contents from 33 to 73 wt.%, such that the difference increased with increasing Mo content. Therefore, the porosity and the microstructure cannot explain fully the difference in the properties between the composites made by the two methods.

Due to the very limited solid solubility of Cu and Mo in the Cu-Mo system[9] and the processing parameters in this work (1000°C, 117 MPa, 25 min), mechanical bonding[10] of Cu to Mo due to the differential thermal
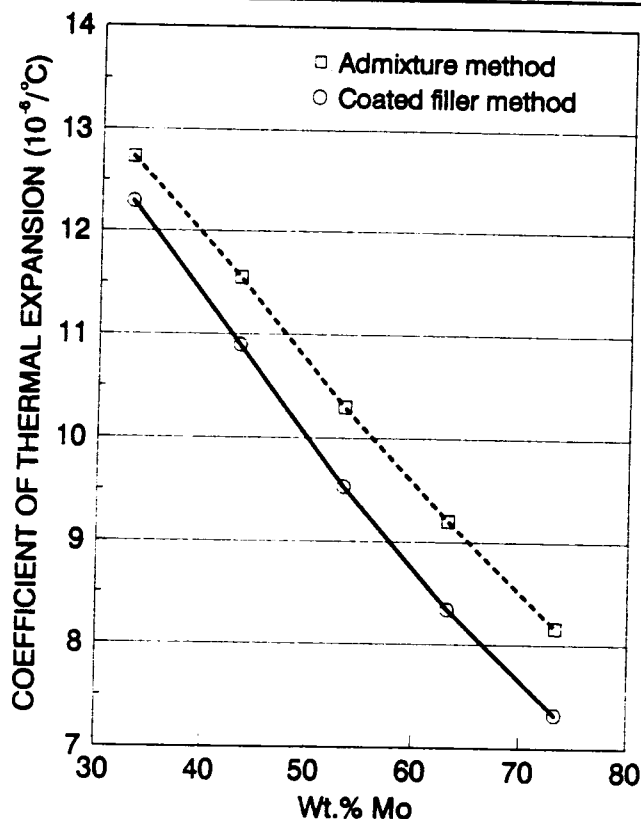

Fig. 9. Coefficient of thermal expansion as a function of weight percent Mo for the Cu/Mo composites made by the two P/M methods.
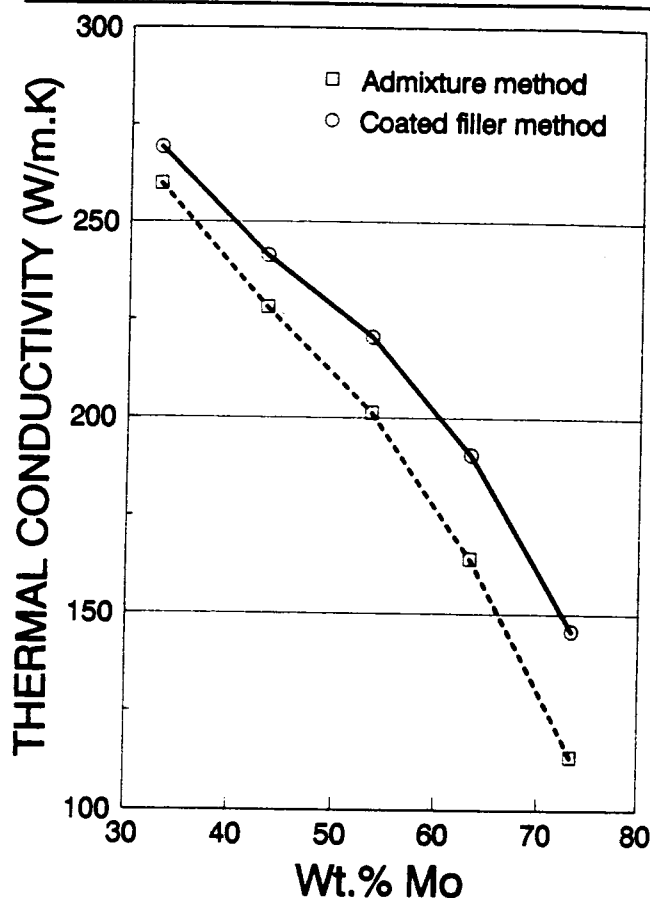

Fig. 10. Thermal conductivity as a function of weight percent Mo for the Cu/Mo composites made by the two P/M methods.

Table III. Measured Properties vs Porosity (V_p) and Contiguity Ratio (C_t) of Cu/Mo Composites

Sample Method	Wt.% Mo	V_p (%)	C_t	Hardness (HB)	Compressive Yield Strength (MPa)	Electrical Resistivity ($10^{-6}\Omega$·cm)
Admixture	63	1.4	0.58	148	468	3.47
Coated	63	0.8	0.19	171	641	3.28
Admixture	73	8.7	0.78	129	425	4.92
Coated	73	1.5	0.26	193	647	3.87

Table IV. Comparison of Cu/Mo Composites of this Work, Sumitomo, and Ametek with Kovar

Sample Method	This Work		Sumitomo	Ametek	Kovar[11] (Fe-27%Ni-7%Co)
	Admixture	Coated			
Mo particle size (μm)	4.5	4.5	4.0	85	/
Wt.% Mo	73.3	73.3	80*	75*	/
Porosity (vol.%)	8.7	1.5	4.7	0.8	/
Density (g/cm³)	8.99	9.70	9.47	9.82	8.3*
Hardness (R_B)	76	97	42	82	/
Compressive yield strength (MPa)	425	647	/	/	/
CTE (10^{-6}/°C) (25–150°C)	8.2	7.3	8.0*	7.7*	5.3*
Electrical resistivity (10^{-6} Ω·cm)	4.92	3.87	5.62	4.4	50*
Thermal conductivity (W/m.K)	114	141	/	185*	17*

Note: Values with * are published values. Values without * are measured values obtained in this work.
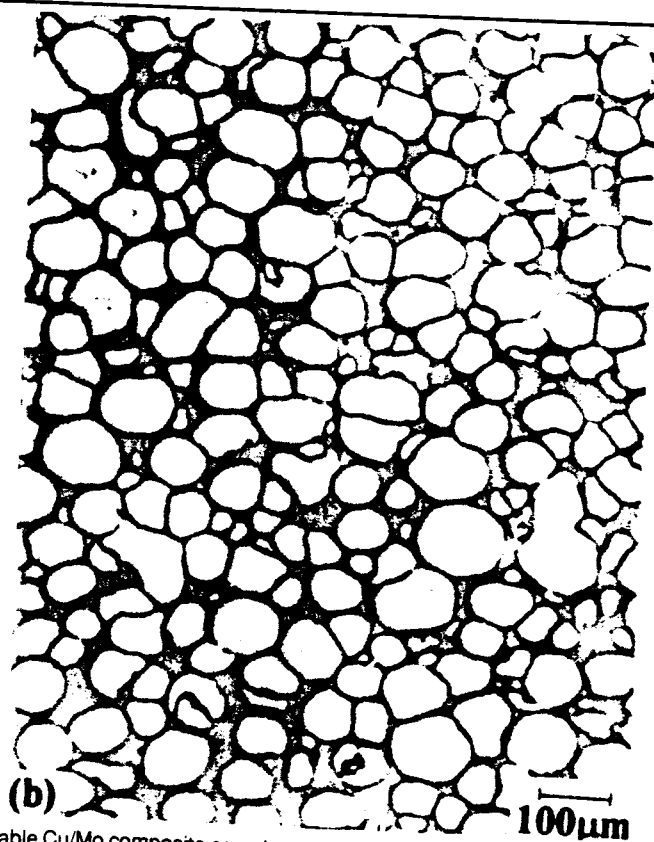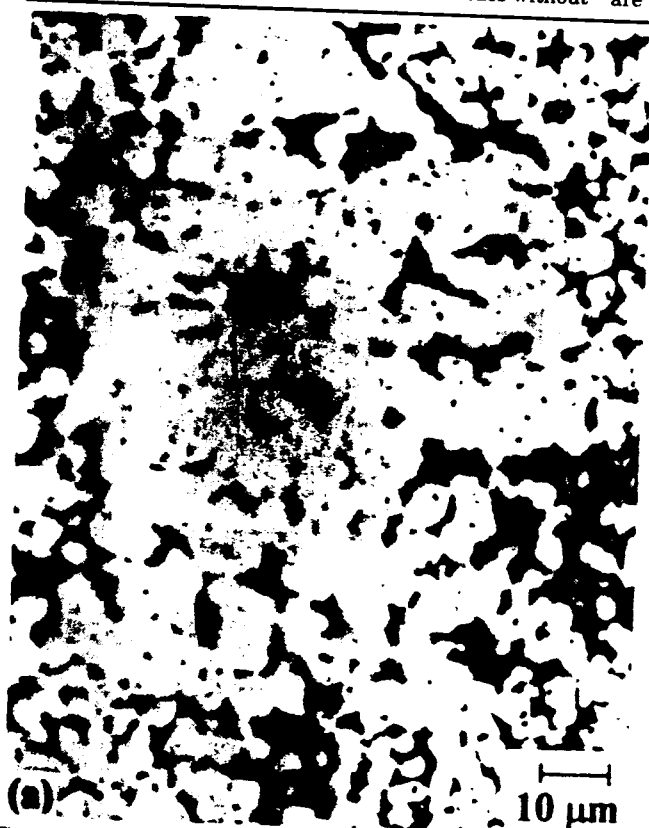

Fig. 11. Optical micrograph showing the microstructure of commercially available Cu/Mo composite samples: (a) Sumitomo sample containing 80 wt.% Mo; and (b) Ametek sample containing 75 wt.% Mo.

contraction is expected to be dominant, though other types of bonding (such as dissolution and wetting bondin)[10] may occur to a limited degree. The quality of both types of bonding is affected by how tightly the Cu and the Mo are joined together. Since the electroplating of Cu on Mo involves the discharge of Cu ions and deposition of Cu atoms one by one on the surface of Mo particles, good bonding in atomic scale between the Cu coating (matrix material) and the Mo (reinforcement) in a Cu coated Mo particle had already been formed before the fabrication of the composite. Obviously, stronger Cu/Mo bonding is expected by using Cu coated Mo particles than that obtained by using a mixture of Cu and Mo powders in which some defects (such as impurities, oxides, etc.) may be introduced to the interface between Cu and Mo after the same hot-press processing.

In Cu/Mo composites, because of the different CTEs of the two components (high for Cu and low for Mo), the free thermal expansion of the Cu matrix is con-

strained by the Mo particles through the bonding between Cu and Mo. Thus, the CTE of the composite is affected by the bonding between the Cu matrix and the Mo particles. Weaker bonding leads to a higher CTE. The interface between the two components affects heat conduction, so better bonding between Cu and Mo leads to a higher thermal conductivity in the composite. Since the effect of bonding on the properties depends on the total amount of interface between Cu and Mo in the composite, differences in the properties between the composites made by the two methods increased with increasing Mo content. Compared to the effect of porosity on hardness, compressive yield strength, and electrical resistivity, the effect of the bonding on these properties was not significant in this work, especially at low contents of Mo (<53 wt.%).

Comparison with Commercial Cu/Mo Composites

For the sake of comparison, commercial samples of a Cu/Mo composite containing 80 wt.% Mo, known as CMSH (admixture method) from Sumitomo Electric Industries, Ltd., Japan, and a Cu/Mo composite containing 75 wt.% Mo, known as AMC 7525 (coated filler method) from Specialty Metal Products Division of Ametek Inc., Wallingford, CT, were examined in this work. Their properties are listed in Table IV, together with those of the Cu/Mo composites fabricated in this work. Optical microscopy (Fig. 11a) showed that the Sumitomo composite sample contained Mo particle agglomerates—similar to the microstructure of 63 and 73 wt.% Mo composites (Figs. 3e and 3f) fabricated by the admixture method in this work. Therefore, its properties were inferior to the 73.3 wt.% Mo composite made by the coated filler method, even though the Mo content of CMSH was higher. Figure 11b shows that the Ametek sample had Mo particles substantially separated by the Cu matrix—similar to the microstructure of Cu/Mo composites (Figs. 3b and 3c) fabricated by the coated filler method in this work. Therefore, its properties were superior to the Sumitomo composite sample and the 73.3 wt.% Mo composite made by the admixture method in this work. Compared to the 73.3 wt.% Mo composite made by the coated filler method in this work, the Ametek sample had lower porosity and higher thermal conductivity, but lower hardness, higher CTE, and higher electrical resistivity (Table IV). It also can be noticed that the Ametek sample had a much larger Mo particle size (85 μm) than that (4.5 μm) of Cu/Mo composites fabricated in this work. In general, at high Mo contents, the properties of Cu/Mo composites made by the coated filler method (whether the composites made in this work or the Ametek sample) are superior to those of the composites made by the admixture method (whether the composites made in this work or the Sumitomo sample).

Kovar is a low CTE Fe-Ni-Co alloy used in the electronic industry. As shown in Table IV, it has lower CTE than Cu/Mo composites, but its thermal and electrical conductivities are much lower.

Since some of the values listed in Table IV are published values and some are values measured in this work, comparison should be more reliable between measured values than between published and measured values.

CONCLUSION

Copper-matrix molybdenum particle composites containing up to 70 vol.% Mo were fabricated by powder metallurgy using two methods. One method, called the admixture method (conventional method), used a mixture of Cu and Mo powders. The other method, called the coated filler method, used Cu coated Mo particles (70 vol.% Mo) with Cu powder mixed in optionally for varying the composition of the composite.

The composites made by the coated filler method exhibited lower porosity, higher hardness, higher compressive yield strength, lower coefficient of thermal expansion, lower electrical resistivity, and higher thermal conductivity than the corresponding composites made by the admixture method.

The difference between the composites made by the two methods increased with increasing Mo content. The microstructure of the two types of composites differed only at high Mo contents (>53 wt.%). The difference was that Mo particle agglomeration occurred in the composites made by the admixture method, but not in those made by the coated filler method. Inside a Mo particle agglomerate, sintering was inefficient at 1000°C, so the bonding was poor between contacted Mo particles and the electrical/thermal contact resistance between adjacent Mo particles was high. Moreover, the clustering made the Mo particles a less effective reinforcement.

A possible cause of the property differences observed at all Mo contents between composites made by the two methods is related to the better Cu/Mo bonding obtained by using Cu coated Mo particles than that obtained by using a mixture of Cu and Mo powders after the same hot-press processing.

REFERENCES

1. Robert B. Ross, *Metallic Materials Specification Handbook*, Fourth Ed., (New York: Chapman & Hall, 1992), pp. 1, 94, 181, 226, 229 and 606.
2. Shy-Wen Lai and D.D.L. Chung, *J. Mater. Sci.* 29, 3128 (1994).
3. Pang-Kai Lee, *IEEE Trans. Components, Hybrids, Manuf. Tech.* CHMT-3(1), 4 (1980).
4. A.K. Jha, S.V. Prasad and G.S. Upadhyaya, *Powder Metall.* 32, 309 (1989).
5. Shiro Kohara and Kiyohiko Tatsuzawa, *J. Jpn. Soc. Powder Metall.* 35, 6 (1988).
6. Velidandla V. Bhanuprasad, Radhakrishna B.V. Bhat, Anjilivelil K. Kuruilla, Konduri S. Prasad, Awadh B. Panedy and Yashwant R. Mahajan, *Inter. J. Powder Metal.* 27, 227

(1991).

7. W.J. Parker, R.J. Jenkins, C.P. Butler and G.L. Abbott, *J. Appl. Phys.* 1, 1679 (1961).

8. J. Gurland, *Quantitative Microscopy*, eds. Robert T. DeHoff and Frederick N. Rhines, (New York: McGraw-Hill, 1968), p. 278.

9. P.R. Subramanian and D.E. Laughlin, *Binary Alloy Phase Diagrams*, ed.-in-chief, Thaddeus B. Massalski, eds. Hiroaki Okamoto, P.R. Subramanian and Linda Kacprzak, (Materials Park, OH: ASM Intl., 1990), p. 1435.

10. Arthur G. Metcalfe, *Interfaces in Metal Matrix Composites*, ed. Arthur G. Metcalfe, (New York: Academic Press, 1974), p. 1.

11. James J. Licari, *Electronic Packaging and Interconnection*, ed.-in-chief Charles A. Harper, (New York: McGraw-Hill, Inc., 1991), p. 7.

APPENDIX: METHOD FOR MEASURING THE COMPOSITION OF METAL COATED PARTICLES

Since standard methods for measuring the composition of the metal coated particles are not available, a method was developed for this measurement.

CONDITIONS FOR USING THIS METHOD

The conditions for using this method are:

- the metal coated particles can be used (optionally in conjunction with the coating material in powder form) to make a sound composite which serves as a test vehicle, and
- during the fabrication of the composite, the metal coating does not alloy or have any chemical reaction with the base particles.

THE CONCEPT

This method involves making two types of composite with nearly the same composition (proportions of the matrix and the particulate reinforcement). One type is Composite A, which is made from matrix-coated particles (the very particles the composition of which is to be determined), optionally in conjunction with matrix particles. The other type is Composite B, which is made from a mixture of matrix particles and base particles (without coating) and the composition of which can be exactly attained. Since the composition of the metal coated particles is unknown (quantity to be determined), the composition of Composite A can be made close to that of Composite B by trial and error through adjusting the proportion of matrix powder used along with the metal coated particles in making Composite A. Provided that

- Composites A and B are properly fabricated at suitable and similar composite compositions,
- their porosities are at equally low levels, and
- the variation of porosity is small within a limited composite composition range, the assumption that the porosity is the same for Composites A and B can be made.

The porosity of Composite B can be determined by measuring its density, since the composition (hence the theoretical density) of this composite is exactly known. With the porosity and the proportion of matrix powder used in making Composite A known and the density of Composite A measured, the composi-

tion of metal coated particles can be calculated.

EQUATIONS

The equations used in this method are as follows:

$$V_p = 1 - \rho/\rho_o \qquad (1)$$

where V_p, ρ, and ρ_o are the porosity, measured density, and the theoretical density of the composite (Composite A or B), respectively;

$$V_b = [\rho - \rho_m (1 - V_p)] / (\rho_b - \rho_m) \qquad (2)$$

where V_b is the volume fraction of the base particles in composite A, and ρ_b, and ρ_m are the densities of base particle and metal coating materials, respectively;

$$W_b = \rho_b [\rho - \rho_m (1 - V_p)]/[\rho (\rho_b - \rho_m] \qquad (3)$$

where W_b is the weight fraction of the base particles in Composite A;

$$W = (1 + R) \rho_b [\rho - \rho_m (1 - V_p)]/[\rho(\rho_b - \rho_m)] \qquad (4)$$

where W is the weight fraction of the base particles in the metal coated particles and R is the weight ratio of matrix powder (which is the same as the coating material) to the metal coated particles used in making Composite A and

$$V = \rho_m W/[\rho_b - W(\rho_b - \rho_m)] \qquad (5)$$

where V is the volume fraction of the base particles in the metal coated particles.

In the equations mentioned above, Eq. (1) is well known. Equations (2) to (5) were derived based on the relations among density, weight and volume, and the rule of mixtures.

PROCEDURE

From Eqs. (1) to (5), only V_p and ρ are unknown and need to be measured to determine W or V, i.e., the composition (in weight or volume fraction) of the metal coated particles. The following procedure is used to determine the composition of the metal coated particles.

Method for Fabrication of Composites A and B

A suitable method (such as powder metallurgy or liquid metal infiltration) should be used to fabricate Composites A and B with low levels of porosity. In this work, hot pressing was used.

Preparation of Composite B

The fabrication process and the composition of Composite B should be selected to make a composite with a low level of porosity. The filler content of Composite B should not be greater than the base particle content in the metal coated particles. The porosity (V_p) of Composite B can be determined from Eq. (1), since the theoretical density (ρ_o) of Composite B is known and the density (ρ) of Composite B can be measured by using the buoyancy (Archimedes) method (ASTM B328-92).

In this work, Composite B (with Cu as the matrix and Mo particles as the filler) was made by the

admixture method. In the composition range 15–25 vol.% Mo, the porosities of Composites A and B were low (<0.003) and the difference in porosity between Composites A and B at the same composition was very small (<0.0005). Thus, a composition of 20 vol.% Mo was selected for Composite B and the assumption that V_p is the same for Composites A and B is valid.

Preparation of Composite A

Composite A was fabricated by using the coated filler method, i.e. using metal coated particles, optionally together with matrix powder. The same process conditions as those used for the fabrication of Composite B should be used in the fabrication of Composite A. The composition of Composite A should be as close as possible to that of Composite B.

Procedure for Measurement of the Composition of Metal Coated Particles

The procedure consists of the following steps:

Step 1

Fabricate Composite B, measure its density and calculate its porosity by using Eq. (1).

Step 2

Estimate the composition of the metal coated particles. Form a mixture of metal coated particles (assumed to be at the estimated composition) and matrix powder, such that the mixture has the same composition as Composite B. Use this mixture to fabricate Composite A. Measure the density of Composite A. Use the measured density of Composite A and the porosity of Composite B (determined in Step 1) to calculate the composition of Composite A by using either Eq. (2) or equation (3). Calculate the composition of the metal coated particles by using Eq. (4) and Eq. (5). Compare the composition of Composite A with that of Composite B. If the compositions of Composites A and B are very close (usually, the difference in composition should be less than 0.5 vol.% filler or base particles), the value of the composition of the metal coated particles determined in this step can be taken as the final result. If the compositions of Composites A and B are not close enough, go to Step 3.

Step 3

Repeat Step 2, except that the composition of the metal coated particles determined in Step 2 is used as a more accurate estimated value to make another Composite A. The composition of Composite A made in this step should be very close to that of Composite B. If necessary, repeat Step 3 to make yet another Composite A. Each time use the composition of the metal coated particles determined by using the last Composite A as the more accurate estimated value to make the next Composite A, until the composition of Composite A is very close to that of Composite B. Take the composition of the metal coated particles determined by using the last Composite A as the final result.

MEASUREMENT ACCURACY

If the porosity is low and the porosities of Composites A and B at the same composition are almost the same, the value of the composition of metal coated particles measured by this method should be reliable. The accuracy of the result depends on the accuracy of measuring the density of the composites A and B.