POWDER METALLURGY FABRICATION OF METAL MATRIX COMPOSITES USING COATED FILLERS

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At high filler volume fractions, the use of matrix-coated fillers to make metal-matrix composites by powder metallurgy was found to yield superior composites than the use of a mixture of filler and matrix powder. The superiority encompassed lower porosity, increased hardness, higher compressive yield strength, lower coefficient of thermal expansion (CTE), lower electrical resistivity and higher thermal conductivity. These differences are due primarily to the metal coating separating the filler units from one another. The coating effectively prevented direct filler-filler contact and distributed the matrix metal uniformly around each filler unit, thereby promoting sintering and low porosity.

INTRODUCTION

Metal-matrix composites fabricated by conventional powder metallurgy (P/M) techniques using a mixture of filler and metal matrix powder have been restricted to a low filler contents (< 40v/o), because of the increasing proportion of direct filler-filler contact as the filler volume fraction increases. The direct filler-filler contacts degrade the quality of sintering at the processing temperature, because the filler usually has a melting point higher than the matrix and the sintering temperature is below the melting point of the matrix. Excessive filler-filler contacts lead to a composite of inferior properties due to ineffective filler-filler sintering at the relatively low processing temperature (lower than that required for filler-filler sintering). The ineffectively sintered filler constitutes defects in the composite. Furthermore, excessive filler-filler contacts lead to a composite of high porosity, since the filler-filler contacts hinder the solid-state flow of the softened metal matrix through the filler units to fill the interstices during sintering. To circumvent the problem, this paper describes the use of matrix-coated fillers to eliminate the possibility of direct filler-filler contacts even at high filler volume fractions, thus resulting in composites of high filler volume fraction and low porosity.

The matrix-coated filler has been previously used (a method hereby called the coated filler method) to make copper-matrix or silver-matrix graphite particle composites for use as brushes.[1] The composites thus obtained were lower in electrical resistivity than the corresponding composites obtained by using a mixture of matrix powder and filler (hereby called the admixture method).[1] In recent years, the coated filler method has been used by the Specialty Metal Products Division of AMETEK Inc. to make Cu/Mo composite products containing a high Mo content and low porosity by using wrought P/M technology. However, comparison of the composites made by the two methods has not been made in terms of behavior other than the electrical properties. Though the coated filler method is an effective P/M method for making composites with a high filler content, there has been little research on the coated filler method. Using both the coated filler method and the admixture method, copper-matrix composites with fillers of various shapes, i.e., particles (Mo), platelets (TiB_2) and whiskers (SiC), and various material types,

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i.e., metal (Mo) and ceramics (TiB_2 and SiC) were fabricated and evaluated. The properties of the corresponding composites made by the two methods were compared. It was found that, at a high filler volume fraction, the composites with all types of fillers made by the coated filler method were superior (higher strength and hardness, lower thermal expansion, higher thermal conductivity and lower electrical resistivity) to the corresponding composites made by the admixture method.

SiC whiskers, due to their whiskers form, are one of the most effective reinforcements in metal-matrix composites. However, these composites have been limited to whiskers volume fractions below 0.4, whether they are made by P/M[2,3] or by liquid metal infiltration.[4] In this work, SiC whiskers were used in the coated filler method for the first time and resulted in metal-matrix composites with whisker volume fractions up to 0.55 and low porosity (< 5v/o). The high whisker volume fraction resulted in a Brinell hardness of 260 in a composite containing 50v/o SiC whiskers and made by the coated filler method. This hardness value is high compared to that of aluminum-matrix or copper-matrix composites reported previously. For example, an Al-matrix SiC particle composite containing 55v/o SiC had a Brinell hardness of 174; an Al-matrix AlN particle composite containing 60v/o AlN had a Brinell hardness of 200.[5]

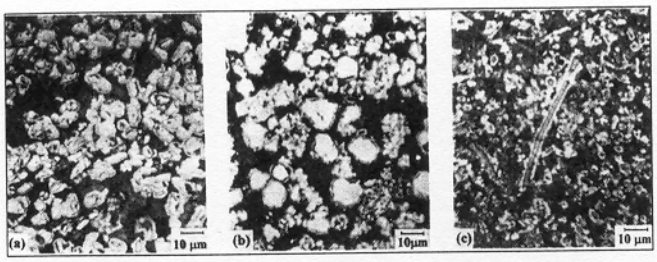

Figure 1. Optical micrographs of the copper coated fillers prior to compaction. (a) Cu coated TiB_2 platelets, (b) Cu coated Mo particles, (c) Cu coated SiC whiskers.

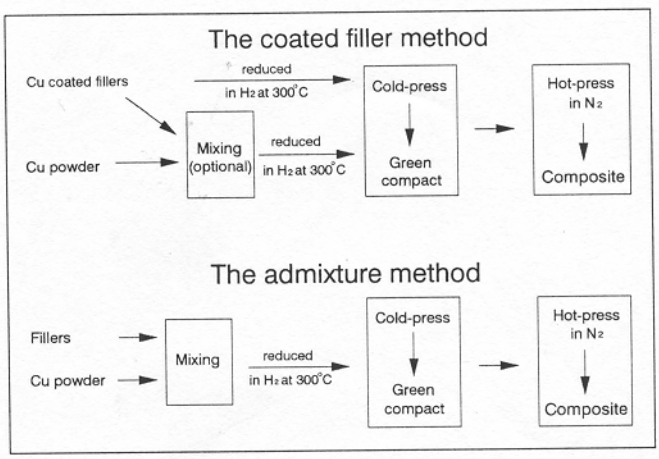

Figure 2. P/M illustrating the coated filler and the admixture methods.

EXPERIMENTAL

The coated filler P/M method was applied to three types of fillers, namely TiB_2 platelets (3 - 5μm size, ~3 aspect ratio, from Union Carbide Advanced Ceramics, Cleveland, OH), Mo particles (3.5 - 5.5μm size, from GTE Sylvania, Towanda, PA) and SiC whiskers (primarily β phase, 0.5 - 1.5μm 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 possesses 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_2 platelets. Figure 1 shows optical micrographs of the coated fillers. Note that 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_2 platelets, the filler volume fraction was varied by adding different proportions of copper powder (3.3μm 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 60min 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 0.5in (12.7mm) and height 0.5in (12.7mm). The pressure during cold pressing was 155MPa. Subsequent hot pressing was conducted in the same die in purging nitrogen at 1000°C for 25min in the case of Mo particles, 1000°C for 20 min in the case of TiB_2 platelets, and 950°C for 25min in the case of SiC whiskers. The pressure during hot pressing was 116MPa. During heating prior to hot pressing, the pressure was kept at 77MPa until the hot pressing temperaturewas reached. For comparison, the corresponding composites made by the admixture method were fabricated under the same processing conditions. The P/M route for both methods is shown in Figure 2. The P/M 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 den-

sity, hardness (Brinell), compressive yield strength, volume electrical resistivity, coefficient of thermal expansion (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:

$$V_p = 1 - \rho/\rho_o, \quad (1)$$

where V_p is the pore volume fraction, ρ the measured density, and ρ_o 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 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 coefficient of thermal expansion (CTE) was obtained by using a Perkin-Elmer DMA-7 thermomechanical analyzer, with the temperature scanned from 25 to 150°C at a rate of 5°C/min.

The thermal conductivity (K) was determined by:

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

where α, ρ 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, 10~15J energy, 0.4ms/pulse),[6] and the specific heat was measured by differential scanning calorimetry (Perkin-Elmer DSC-7).

The microstructures of the composites made by the two P/M methods, were characterized by means of optical microscopy.

RESULTS AND DISCUSSION

Composites with a Low Filler Content

Figure 3 shows optical micrographs of polished sections of Cu/TiB_2 platelet composites (15v/o TiB_2), Cu/Mo particle composites (30v/o Mo) and Cu/SiC whisker composites (15v/o SiCw) made by the coated filler method and the admixture method. It is seen that, at a low filler content, there is no apparent difference in microstructure between the composites made by the coated filler method and admixture method for all types of fillers. Figure 3 also shows that , for the P/M processes used in this study, the composites made by either the coated filler method or the admixture method are nearly pore free with the fillers distributed in the matrix uniformly. Table I gives the measured properties of the composites. It shows that the physical and mechanical properties of the composites made by the two methods are almost the same. Therefore, there is no apparent superiority of the coated method to the conventional admixture method for fabrication of the composites with a low filler content.

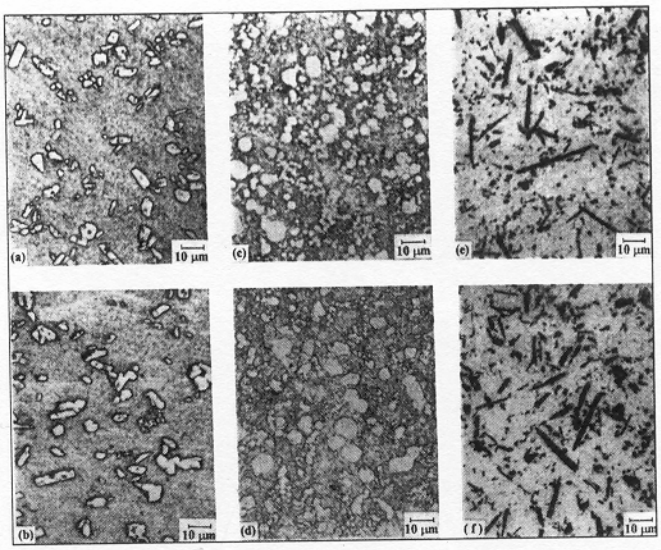

Figure 3. Optical micrographs of polished sections of composites with a low filler content: (a) Cu/TiB_2 (15v/o TiB_2), coated filler method; (b) Cu/TiB_2 (15v/o TiB_2), admixture method; (c) Cu/Mo (30v/o Mo), coated filler method; (d) Cu/Mo (30v/o Mo), admixture method; (e) Cu/SiC (15v/o SiCw), coated filler method; (f) Cu/SiC (15v/o SiCw), admixture method.

Composites with a High Filler Content

Figure 4 shows optical micrographs of polished sections of Cu/TiB_2 platelet composites (60v/o TiB_2), Cu/Mo particle composites (70v/o Mo) and Cu/SiC whisker composites (50v/o SiCw) made by the coated filler method and the admixture method. For Cu/TiB_2 (Figures 4(a) and 4(b)) and Cu/SiCw (Figures 4(e) and 4(f)), the microstructure of the corresponding composites made by the two methods differs mainly in that the composites made by the admixture method had higher porosity. For Cu/Mo (Figures 4(c) and 4(d)), the microstructure of the corresponding composites made by the two methods differs mainly in that direct Mo-Mo contacts (Mo clustering) were far more prevalent in the composite made by the admixture method. The presence of Mo clustering is due to the higher filler volume fraction (70v/o Mo) in Cu/Mo than in Cu/TiB_2 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 allowed a higher maximum filler volume fraction than the whisker and

Table I. Properties of Copper-Matrix Composites (Low Filler Content)

Composite	Cu/TiB_2 platelets (15v/o TiB_2)		Cu/Mo particles (30v/o Mo)		Cu/SiC whiskers (15v/o SiCw)	
Method	Admixture	Coated	Admixture	Coated	Admixture	Coated
Porosity (v/o)	0.27	0.15	0.21	0.21	0.39	0.43
Hardness (Brinell)	76.8	76.8	107	107	100	100
Compressive yield strength (MPa)	145	145	260	282	204	205
CTE (10^{-6}/°C) (25-100°C)	14.5	14.4	12.7	12.3	14.7	14.6
Electrical resistivity (10^{-6} Ω.cm)	2.1	2.1	2.4	2.4	3.9	3.2
Thermal conductivity (W/(m.°C))	362	363	260	269	284	287

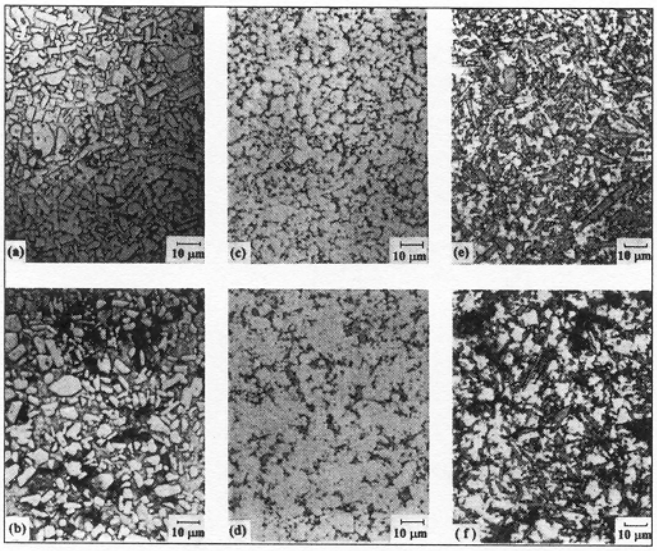

Figure 4. Optical micrographs of polished sections of composites with a high filler content: (a) Cu/TiB_2 (60v/o TiB_2), coated filler method, (b) Cu/TiB_2 (60v/o TiB_2), admixture method, (c) Cu/Mo (70v/o Mo), coated filler method, (d) Cu/Mo (70v/o Mo), admixture method, (e) Cu/SiC (50v/o SiCw), coated filler method, (f) Cu/SiC (50v/o SiCw), admixture method.

platelet shapes of the SiC whiskers and TiB_2 platelets, since it is relatively easy for spherical particles to move to fill the interstices during sintering. For all three types of fillers, the porosity was higher in the composites made by the admixture method than those made by the coated filler method, as shown in Table II. The lower porosity of the composites made by the coated filler method for all three types of fillers is due to the fact that the matrix coating around each filler unit separated the filler units from one another. In consequence, direct filler-filler contact was avoided and the matrix was distributed more evenly among the filler units. Thus, by using a matrix coated filler, the ineffective sintering between contacting filler units can be effectively reduced, yielding a composite with a low porosity even at a high filler volume fraction. As noted previously, a Cu/SiC composite containing 54.5v/o whiskers (well above the 40v/o limit for composites made by conventional methods) with less than 5v/o porosity was made by the coated filler method, as shown in Figure 5.

The measured properties of the various composites are shown in Table II. For all three types of fillers, the hardness and compressive yield strength were much higher for composites made by the coated filler method than the corresponding composites made by the admixture method. The poor mechanical properties of the composites made by the admixture method is due to the high porosity and ineffective sintering between the contacting filler units (which have a high melting point). In the case of the Cu/Mo composite made by the admixture method, the contacting filler units led to Mo clustering (Figure 4(d)). At the normal sintering temperature (1000°C) and time (25min), the contacting Mo particles

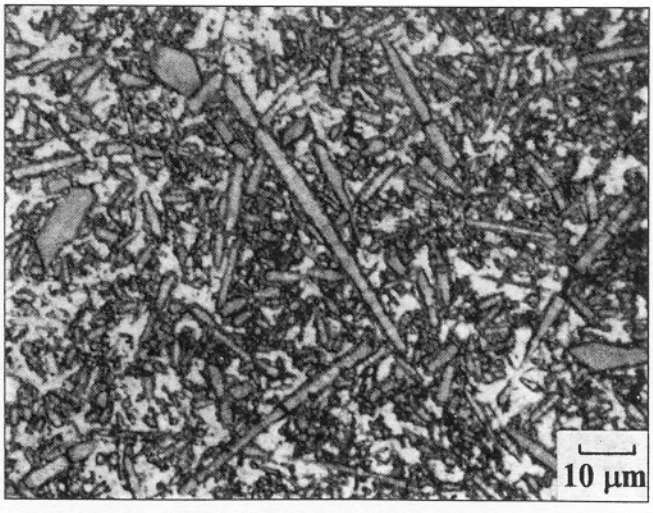

Figure 5. Optical micrograph of polished section of Cu/SiCw composite with 54.5v/o SiCw made by the coated filler method.

Table II. Properties of Copper-Matrix Composites (High Filler Content)

Composite	Cu/TiB_2 platelets (60v/o TiB_2)		Cu/Mo particles (70v/o Mo)		Cu/SiC whiskers (50v/o SiCw)	
Method	Admixture	Coated	Admixture	Coated	Admixture	Coated
Porosity (v/o)	17.6	11.0	8.7	1.5	20	2.8
Hardness (Brinell)	85	159	129	193	90	260
Compressive yield strength (MPa)	231	482	427	647	239	651
CTE (10^{-6}/ (C) (25-100 (C)	9.0	8.5	8.2	7.3	11.0	10.2
Electrical resistivity (10^{-6} Ω.cm)	37.9	7.7	4.9	2.9	123	20
Thermal conductivity (W/(m. C))	96	137	113	145	12	47

could not be effectively sintered together since Mo has a melting point of 2620°C. The ineffectively sintered Mo particles were actually defects in the composite. Although the SiC whisker composite had the lowest filler volume fraction among the composites in Table II, it exhibited the highest hardness and compressive yield strength, provided that the composite was made by the coated filler method. This is attributed to the high aspect ratio and stiffness of the SiC whiskers compared to the other fillers.

The CTE was lower for composites made by the coated filler method than the corresponding composites made by the admixture method. The coefficient of thermal expansion (CTE) of a composite is determined by both the matrix and filler components. Since the contribution of the filler to CTE manifests itself through the bonding between the matrix and filler, improved bonding leads to a lower CTE for the composite. For the composite made by the coated filler method, the matrix coated filler had already provided clean sound bonding between the matrix and filler during the coating process, thus avoiding possible contamination and impurities (such as oxides) introduced at the interface between the matrix and filler during subsequent sintering. Furthermore, the matrix coated filler promoted sintering between the filler units. Therefore, at a high filler content, the composite made by the coated filler method exhibited improved bonding between the matrix and filler than the composite made by the admixture method, thus resulting in a lower CTE.

The electrical resistivity was lower for composites made by the coated filler method than the corresponding composites made by the admixture method. The thermal conductivity was higher for composites made by the coated filler method than the corresponding composites made by the admixture method. When Mo was used as the filler, the thermal conductivity was particularly high. The lower electrical resistivity and higher thermal conductivity of the composites made by the coated filler method are due to lower porosity and improved bonding.

In summary, at a low filler content, the coated filler method gave composites with no apparent superiority to the admixture method. At a high filler content, for all three types of fillers used here, the composites made by the coated filler method were superior to the composites made by the admixture method in all respects. This is because the use of the matrix coated filler avoided direct filler-filler contact and helped distribute the matrix evenly among the filler units, thus effectively reducing ineffective filler-filler sintering, lowering the porosity and providing better bonding between the matrix and filler. The so-called "high filler volume fraction" in this work refers to a filler content at which there exists some apparent difference in properties between the composites made by the coated filler method and the admixture methods. The minimum value of the high filler volume fraction range depends on the matrix and filler type. For copper matrix composites, the minimum value is 35v/o for TiB_2 platelets, 45v/o for Mo particle and 25v/o for SiC whiskers. The difference in properties between the corresponding composites made by the two methods increases dramatically with increase in filler content within the high filler volume fraction range.

For electronic packaging applications which required low CTE and high thermal conductivity Cu/Mo composites are most attractive. For brushes which require hardness, wear resistance electrical and thermal conductivity and low CTE, Cu/SiC whisker composites are most attractive. Although the mechanical properties of Cu/TiB_2 are inferior to those of Cu/SiCw and Cu/Mo, the low cost, low CTE and high electrical and thermal conductivities of Cu/TiB_2 compared to Cu/SiCw and the low density of TiB_2 compared to Mo make Cu/TiB_2 attractive in certain situations.

CONCLUSIONS

The coated filler P/M method was found to be applic-

able to the fabrication of copper-matrix composites with metal or ceramic fillers, whether the filler was spherical, flake-like or whisker-like. This method is particularly valuable at high filler volume fractions. Compared to the corresponding composites made by the admixture method, composites made by the coated filler method exhibited lower porosity, greater hardness, higher compressive yielding strength, lower CTE, lower electrical resistivity and higher thermal conductivity. In contrast to the conventional admixture method, the coated filler method enabled the fabrication of composites with high filler content, low porosity and improved properties. By using a matrix coated filler, direct filler-filler contact can be avoided and the matrix can be distributed uniformly among the filler units, thus promoting sintering and reducing porosity. Furthermore, the matrix coated filler can provide enhanced bonding integrity between the matrix and the filler than the admixture method.

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