Titanium diboride copper-matrix composites

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Copper-matrix titanium diboride platelet (3-5 µm) composites containing 15-60 vol% TiB₂, were fabricated by powder metallurgy, using copper-coated TiB₂ (60 vol% TiB₂) and various amounts of copper powder. The porosity was ≤0.5% when TiB₂ was ≤48 vol%. Above 48 vol% TiB₂, the porosity increased abruptly with increasing TiB₂ content, reaching 6.7% at 60 vol% TiB₂. As a result, the hardness and compressive yield strength dropped precipitously with increasing TiB₂ volume fraction beyond 48%. At 48 vol% TiB₂, the thermal conductivity was 176 W m⁻¹ C⁻¹, the electrical resistivity was 3.42 x 10⁻⁸ Ωcm, the coefficient of thermal expansion (CTE) was 10.2 x 10⁻⁶ C⁻¹, the compressive yield strength was 659 MPa, and the Brinell hardness was 218. For composites made by conventional powder metallurgy, using a mixture of TiB₂ platelets (not coated) and copper powder, the porosity was ≤1.8% when TiB₂ was at ≤42 vol%; above 42 vol% TiB₂, the porosity increased abruptly and the hardness and compressive yield strength decreased abruptly. The electrical resistivity and thermal conductivity were also affected by the porosity, but less so than the mechanical properties. Composites made using copper-coated TiB₂ exhibited lower electrical resistivity, higher thermal conductivity, lower CTE, higher compressive yield strength, greater hardness, greater abrasive wear resistance, greater scratch resistance and lower porosity than the corresponding composites made from uncoated TiB₂.

1. Introduction
Titanium diboride (TiB₂) is well-known for its stiffness and hardness. Furthermore, in contrast to most ceramics, it is electrically and thermally conductive. Metals, on the other hand, are electrically and thermally conductive, but most of them exhibit a low coefficient of thermal expansion (CTE). The combination of low CTE and high thermal conductivity is particularly attractive for electronic packaging, such as heat sinks, housings, substrates, lids, etc. The combination of high electrical and thermal conductivity and hardness is particularly attractive for welding electrodes, motor brushes and sliding contacts. Owing to these attractive combinations of properties and the availability of TiB₂ in discontinuous forms (such as platelets), TiB₂ is an important reinforcement for composites. In particular, metal-matrix TiB₂ composites are attractive because metals usually have high CTE and limited stiffness and hardness. The TiB₂ addition greatly increases the stiffness, hardness and wear resistance and decreases the CTE, while reducing the electrical and thermal conductivity much less than the addition of most other ceramic reinforcements [1-10]. Metal matrices previously used for TiB₂ composites include aluminium [1-7], Al₂₃Fe₃Ti₄ [8], intermetallic compounds [9-12], iron [3, 13-14], nickel [14], copper [3, 15, 16], bronze [3] and titanium [17]. This work focuses on the use of copper as the matrix owing to its high electrical and thermal conductivities compared to most metals and the importance of these conductivities for numerous applications.

Previous work on copper-matrix TiB₂ composites includes TiB₂ in the form of a sintered porous block (which is impregnated with molten copper to form the composites) [3], and TiB₂ in the form of discontinuous platelets (which are hot pressed with copper below the melting point of copper in order to form the composite) [10]. In other works, the TiB₂ volume fraction is limited to 56.5% [3] and 15% and 60% [10]. The present work provides a systematic study of Cu-TiB₂ composites as function of the TiB₂ volume fraction, which includes 15%, 30%, 35%, 42%, 48%, 50%, and 60%. Because the CTE decreases and the hardness increases with increasing TiB₂ volume fraction, while the thermal and electrical conductivities decrease with increasing TiB₂ volume fraction, the optimal TiB₂ volume fraction depends on the particular combination of properties desired. As a result, a systematic study as a function of the TiB₂ volume fraction is necessary in order to optimize the TiB₂ volume fraction for a particular application.

The composite fabrication method of Viswanadham et al. [10] gave composites of much lower porosity than that of Joo et al. [3]. This work used the same method and the same TiB₂ platelets as Viswanadham et al. [10]. As in the latter work, both the admixture method and the coated filler method of powder metallurgy were used, though the latter gave composites of lower porosity than the former. The admixture method refers to the method in which the reinforcement and matrix powder are mixed and then sintered together. In the coated filler method the reinforcement
2. Experimental procedure

The TiB₂ platelets described in Table 1 were supplied by Union Carbide Advanced Ceramics (Cleveland, OH). The copper powder used was supplied by GTE Products Corporation (Towanda, PA); the mean particle size was 3.3 mm.

Cu/TiB₂ composites containing 15–60 vol % TiB₂ platelets were fabricated by hot-pressing, using the two methods, namely the coated filler method (using copper-coated TiB₂ platelets, optionally mixed with copper powder to obtain the desired composition), and the admixture method (using a mixture of copper powder and TiB₂ platelets). In the coated filler method, the surface of the TiB₂ platelets was metallized by electroless plating with copper and subsequently electroplated with copper to obtain copper-coated TiB₂ platelets containing 60 vol % TiB₂. In the admixture method, mixtures of copper powder and TiB₂ platelets were prepared at the same corresponding compositions by weight as the composites made by the coated filler method.

Before composite fabrication, the copper-coated TiB₂ platelets (or a mixture of copper-coated TiB₂ platelets and copper powder, for the coated filler method) and the mixture of TiB₂ platelets and copper powder (for the admixture method) were reduced in purging hydrogen gas at 250 °C for 60 min. The composite fabrication involved cold compaction of the coated platelets (or the mixture) in a graphite die at 155 MPa to form a cylindrical green compact (0.5 in or 12.7 mm diameter). The green compact was then heated and hot pressed in the same die in purging nitrogen gas at 950 °C and 116 MPa for 25 min. During heating, the pressure was kept at 77 MPa until the temperature reached the hot-pressing temperature.

Composite testing involved measurements of the density, hardness (Brinell), compressive yield strength, abrasive wear resistance, scratch resistance, volume electrical resistivity, coefficient of thermal expansion (CTE) and thermal conductivity. The density of Cu TiB₂ composites was measured by using the buoyancy (Archimedes) method (ASTM B328-92). The hardness measurement was performed using a Brinell Hardness Tester (Detroit Testing Machine Co., Model HB-2) at a load of 1000 kg. Compressive testing was conducted on a flat face of a cylindrical specimen (0.5 in or 12.7 mm diameter, 0.5 in or 12.7 mm high), using an MTS hydraulic mechanical testing system.

The abrasive wear test was conducted on a Teledyne Taber Model 503 standard abrasion tester. Fig. 1 shows the abrasive wear testing geometry. The cylindrical samples, 0.5 in (12.7 mm) diameter, were positioned in a disc-like sample holder. Two Crystalon (a clay composite impregnated with 180 grid SiC particles) grinding wheels were loaded by 1 kg weights in a perpendicular direction on the samples, which rotated with the sample holder in a horizontal plane. The rotating speed of the sample holder was constant at 72 rev min⁻¹. The number of cycles used for the test was 600,000. After the abrasive wear test, the weight loss of the sample was measured. The weight loss relates to the volume loss through the density. Because the weight loss depends on the wear conditions (such as load, rotating speed and the number of cycles), the relative wear under the same wear conditions was considered. Relative wear is defined as the volume loss of a sample due to wear divided by that of a standard sample. In this work, the composite made by the admixture method and containing 50 vol % TiB₂ was chosen as the standard sample.

The scratch resistance test was conducted on a Teledyne Taber Model 502 shear/scratch tester under a load of 1 kg. After testing, the scratch width on the surface of the sample was measured by optical microscopy. This width relates to the scratch resistance of the composites. Moreover, the greater the width, the lower was the shear strength.

For measurement of the volume electrical resistivity, the four-probe method was used. Silver paint was used for electrical contacts. The CTE was determined by using a Perkin–Elmer TMA-7 thermal mechanical

<table>
<thead>
<tr>
<th>TABLE 1 Properties of TiB₂ platelets</th>
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<tbody>
<tr>
<td>Density (g/cm³)</td>
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<tr>
<td>Particle size or diameter (µm)</td>
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<tr>
<td>Aspect ratio</td>
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<tr>
<td>Electrical resistivity (10⁻⁸ Ωcm)</td>
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<tr>
<td>Thermal conductivity (W/m°C)</td>
</tr>
<tr>
<td>CTE (10⁻⁶ °C⁻¹)</td>
</tr>
<tr>
<td>Elastic modulus (GPa)</td>
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<td>Poisson’s ratio</td>
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</table>

![Figure 1 Abrasive wear testing geometry.](image)
The thermal conductivity, $K$, was determined by the
equation

$$K = \alpha \rho C_p,$$  \hspace{1cm} (1)

where $\alpha$, $\rho$ 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 (neodymium glass laser, 10–15 J energy, 0.4 ms pulse$^{-1}$) [18], while the specific heat was measured by differential scanning calorimetry (Perkin-Elmer DSC-7).

After fabrication, the composite was cut into pieces using a diamond saw for testing. For density and hardness tests, one sample was measured three times for each test, whereas for the compressive test, two samples were used. For abrasive testing, one sample was used and weighed three times after testing. In the scratch test, one sample was tested three times, whereas in the thermal diffusivity test, one sample was measured five times. For specific heat testing, one sample was measured three times, and for CTE testing, one sample was measured ten times. Two samples were measured three times each for electrical resistivity measurement.

3. Results and discussion

3.1. Microstructure

Fig. 2 shows optical micrographs of polished sections of Cu/TiB$_2$ platelet composites made by the two methods. A low content of TiB$_2$ platelets (15 vol%), dense Cu/TiB$_2$ platelet composites were made by both the coated filler and the admixture methods and there was no apparent difference between the microstructures of the composites made by the two methods (Fig. 2a and b). At a high content of TiB$_2$ platelets (60 vol%), the composite made by the admixture method had a much higher porosity (Fig. 2d) than the composite made by the coated filler method (Fig. 2c). For all the composites made by the two methods, the TiB$_2$ platelets were distributed uniformly in the copper matrix (Fig. 2).

3.2. Porosity

Fig. 3 shows that the porosity of Cu/TiB$_2$ platelet composites made by the admixture method increased sharply with increasing TiB$_2$ volume fraction when the TiB$_2$ volume fraction exceeded 42%, but the porosity of the composites made by the coated filler method remained low up to 50 vol% TiB$_2$. The reason is that, in the coated filler method, by using copper-coated TiB$_2$ platelets, even at a high TiB$_2$ platelet content, the matrix copper coating separated the TiB$_2$ platelets from one another, thus making it possible to obtain a dense composite. This is supported by Fig. 4, which shows optical micrographs of Cu/TiB$_2$ composite containing 42 and 50 vol% TiB$_2$ and made by the two methods. Fig. 4a and b show that at a TiB$_2$ content of 42 vol%, dense composites can still be made by the two methods, but at the higher TiB$_2$ platelet content (50 vol%), many pores existed.

![Figure 2 Optical micrographs of the Cu/TiB$_2$ platelet composites made by the two methods: (a) 15 vol% TiB$_2$ coated filler method; (b) 15 vol% TiB$_2$ admixture method; (c) 60 vol% TiB$_2$, coated filler method; (d) 60 vol% TiB$_2$, admixture method.](image-url)
3.3. Properties of the composites

3.3.1. Mechanical properties

Fig. 5 shows that the hardness of the composites made by the coated filler method increased with increasing

**Figure 3** Variation of porosity with TiB$_2$ platelet volume fraction in copper-matrix composites made by (○) the coated filler method and (□) the admixture method. The vertical bar at each data point is an error bar.

**Figure 4** Optical micrographs of the Cu TiB$_2$ platelet composites made by the two methods: (a) 42 vol.% TiB$_2$ coated filler method; (b) 42 vol.% TiB$_2$, admixture method; (c) 50 vol.% TiB$_2$, coated filler method; (d) 50 vol.% TiB$_2$, admixture method.

**Figure 5** Variation of Brinell hardness with TiB$_2$ platelet volume fraction in copper-matrix composites made by (○) the coated filler method and (□) the admixture method. The vertical bar at each data point is an error bar.
TiB₂ content up to 48 vol % and reached the highest Brinell hardness value of 218. In contrast, for the composites made by the admixture method, the hardness level was lower than that of the composites made by the coated filler method at any TiB₂ platelet content exceeding 15 vol %, and dropped markedly when the TiB₂ content exceeded 42 vol %. Fig. 6 shows the compressive yield strength of the composites made by the two methods; the trend is similar to that of the hardness shown in Fig. 5.

Because the applications of Cu/TiB₂ platelet composites include electrical contacts and sliding contacts, the hardness, abrasive wear resistance and scratch resistance are important properties. Table II lists the measured hardness, abrasive wear resistance (in terms of the relative wear) and scratch resistance (in terms of the scratch width) of selected Cu/TiB₂ platelet composites.

Table II shows that at a TiB₂ content of 50 vol %, the composite made by the coated filler method had a much higher hardness, abrasive wear resistance and scratch resistance than those of the corresponding composite made by the admixture method. Even at a lower TiB₂ content (42 vol %), the composite made by the coated filler method was superior to the composite made by the admixture method at a higher TiB₂ content (50 vol %). The superiority of the composites made by the coated filler method in mechanical properties, especially at high TiB₂ contents (>42 vol %), to the composites made by the admixture method, is related to the difference in porosity (Fig. 3).

### 3.3.2. Thermal and electrical properties

Fig. 7 shows that the thermal conductivity of the composite made by the coated filler method was higher than that of the corresponding composite made by the admixture method, when the TiB₂ content exceeded 35 vol %. The thermal conductivity difference between the composites made by the two methods increased with increasing TiB₂ content. Fig. 8 shows that the coefficient of thermal expansion (CTE) was lower for the composites made by the coated filler method than the corresponding composites made by the admixture method when the TiB₂ content exceeded 15 vol %. As shown in Fig. 9, the electrical resistivity of the composites made by the coated filler method was slightly lower than that of the corresponding composites made by the admixture method, when the TiB₂ content exceeded 35 vol %. At a high TiB₂ content (>50 vol %), the electrical resistivity of the composite made by the admixture method increased sharply, while the electrical resistivity of the composite made by the coated filler method increased to a much smaller extent.

Porosity is an important factor which influences the thermal conductivity and electrical resistivity. However, at low TiB₂ contents (<35 vol %), although the porosity difference between the composites made by the two methods was small, there was still considerable differences in thermal conductivity and electrical resistivity between the composites made by the two methods. Therefore, porosity alone cannot explain these differences. Another possible reason is that a cleaner or less-contaminated (contaminants such as oxides or impurities) interface results in a lower thermal barrier and lower contact electrical resistivity, and this can be provided by using the coated filler method rather than the admixture method.

Because porosity has no effect on CTE [19], the low CTE of the composites made by the coated filler method compared to that of the composites made by the admixture method may be due to the stronger

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**Table II** Measured hardness, abrasive wear resistance and scratch resistance of selected Cu/TiB₂ composites made by the coated filler method and the admixture method

<table>
<thead>
<tr>
<th>Composite fabrication method</th>
<th>Admixture method</th>
<th>Coated filler method</th>
<th>Coated filler method</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiB₂ (vol %)</td>
<td>50 ± 1</td>
<td>50 ± 1</td>
<td>42 ± 1</td>
</tr>
<tr>
<td>Hardness (HB)</td>
<td>143 ± 5</td>
<td>208 ± 8</td>
<td>185 ± 7</td>
</tr>
<tr>
<td>Relative wear (%)</td>
<td>100</td>
<td>42 ± 1</td>
<td>74 ± 1</td>
</tr>
<tr>
<td>Scratch width (mm)</td>
<td>0.76 ± 0.01</td>
<td>0.41 ± 0.01</td>
<td>0.47 ± 0.01</td>
</tr>
</tbody>
</table>

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Figure 7 Variation of thermal conductivity with TiB<sub>2</sub> platelet volume fraction in copper-matrix composites made by (○) the coated filler method and (□) the admixture method. The vertical bar at each data point is an error bar.

Figure 8 Variation of coefficient of thermal expansion with TiB<sub>2</sub> platelet volume fraction in copper-matrix composites made by (○) the coated filler method and (□) the admixture method. The vertical bar at each data point is an error bar.

Figure 9 Variation of electrical resistivity with TiB<sub>2</sub> platelet volume fraction in copper-matrix composites made by (○) the coated filler method and (□) the admixture method. The vertical bar at each data point is an error bar.

...determined by the net effect of the strains (which are associated with the internal stresses produced by the CTE mismatch between elastically accommodated reinforcement and matrix) on the length of the composites in a given direction. Under an extreme condition of a composite with absolutely no bonding between the reinforcement and the matrix, because there is no possibility of an internal stress arising, the reinforcements dispersed in the matrix are akin to pores, and thus make no contribution to the low CTE reinforcement of the CTE of the composite. In contrast, at a given reinforcement content, a stronger bond between the reinforcement and the matrix gives a lower CTE for the composite.

3.4. Comparison with previous copper-matrix composites made by the coated filler method and other materials

Table III lists the properties of copper-matrix composites made by the coated filler method in this work and in previous work, together with those of two alloys [20, 21]. Although Monel alloy has good mechanical properties (with the highest compressive yield strength), it suffers from high electrical resistivity and low thermal conductivity. (In metals and alloys, a high electrical resistivity relates to a low thermal conductivity). Therefore, Monel does not meet the requirement for electronic packaging. Kovar alloy has been a common electronic packaging material due to its low CTE, but its poor electrical and thermal conductivities limit its application in high-power and high-density microelectronic packaging technology. Compared to Monel and Kovar alloys, all copper-matrix...
composites at any reinforcement content made by the coated filler method in this work and previous work have higher thermal and electrical conductivities. For the Cu-Mo composite at a high molybdenum content (70 vol%), its low CTE, relatively high electrical and thermal conductivities, together with its excellent mechanical properties, make it very attractive in applications related to electronic packaging, sliding electrical contacts, motor brushes and resistance welding electrodes. At a high SiC whisker content Cu/SiC whisker (50 vol% SiC)

* Mo particle composite from [21].
* SiC whisker composite from [20].
Volume fraction above which the porosity increased abruptly with increasing volume fraction.
# Ni-29 Cu-3 Al alloy.
# Fe-27 Ni-7 Co alloy.

electrical and thermal conductivities than Cu/SiC

References


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