The Influence of Technological Process on Dry Sliding Wear Behaviour of Titanium Carbide Reinforcement Copper Matrix Composites

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Two types of milled process are used in SPS to prepare TiC reinforcement Cu matrix composites: (a) Ti and C powders are milled together, and then mixed with Cu powders; (b) All the three kinds of powders are milled together. The microstructures of specimens were analyzed with XRD, SEM and TEM. The pin-disc wear test was carried. It was found that TiC reinforcement formed in sintering by direct reaction in the method (a). However, in method (b), diffused reaction mechanism has also been confirmed in TiC forming process. All the composites exhibit good wear resistance at 200N normal load with lowest wear lose $1.4 \times 10^{-5}$ mm$^3$/Nm (method (a)) and $1.12 \times 10^{-5}$ mm$^3$/Nm (method (b)) respectively. The composite sintered from the powders of the method (b) shows lower wear lose and a steadier friction coefficient at even normal load then the composites sintered from the other powders which show third body abrasion in wear test. [doi:10.2320/matertrans.M2010270]

Keywords: mechanical alloying, spark plasma sintering, wear behaviors

1. Introduction

Ductile copper is widely used in industrial products, however, the lower hardness, tensile strength and poor wear resistance limits its applications. Generally, there are two ways to improve the mechanical properties and wear resistance of copper, by an age hardening mechanism or by incorporation of a hard second phase. Many investigations have been carried out to prepared second hard phase reinforcement copper matrix composites. Mechanical alloying (MA) and spark plasma sintering (SPS) method was reported which can improve the wettability between the immiscible system, so these methods were employed to prepare TiC dispersion strengthened copper composites by different milling technological process, and the microstructure evolvement and the wear behavior the composites were discussed in this paper.

2. Experimental

Horizontal planetary ball mill was employed to the mechanical alloying with 10 mm diameter milling balls. The copper, titanium and graphite (purity 99.9%) are selected as starting element powders. The titanium and graphite powders with 4 : 1 weight ratio (atomic ratio of 1 : 1) were milled 10 h with 500 rpm speed and 40 : 1 ball to weight ratio, and then, copper powders were added to the milled titanium-carbon powders to from copper-titanium-carbon powders with 70 mass% copper by 1 h milling with 100 rpm speed, and the powders were recorded as powders A. The titanium, graphite and copper powders were mixed with weight ratio of 24 : 6 : 70 and milled 100h with 500 rpm speed and 40 : 1 ball to weight ratio as powders B. The powders A and B were sintered to prepare titanium carbide reinforcement copper matrix composites by spark plasma sintering (SPS) method. The powders were sintered at 800°C, 900°C and 1000°C for 3 min with 60°C/min heating rate and 30 MPa pressure. The dry sliding wear tests were conducted in air at room temperature with a pin-on-disc wear testing machine (MG2000, China), and GCr15 steel disc with a hardness of about 55 to 58 HRC was employed as counterpart. The applied loads were 20, 60, 100, 140 and 200N, and the sliding speed was 0.63 m/s. The specific wear rates and friction efficient were calculated by the following equation:

$$W_s = \frac{\Delta m}{\rho LF_N} \times 10^{-3}$$

Where $W_s$ is the specific wear rate (mm$^3$/N), $\Delta m$ is the mass loss of test samples during wear test (g), $\rho$ is the density of test materials (g/cm$^3$), $L$ is total sliding distance (m) and $F_N$ is the normal load on the pin (N).

$$\mu = \frac{F}{P} = \frac{M}{P \cdot r}$$

Where $\mu$ is friction coefficient, $M$ is measured friction torque (N-m) and $r$ is the radius of the corresponding disk (m).

3. Results and Discussion

3.1 Influence of mechanical alloying process on the phase composition of milled powders and composites

Curve A and B in Fig. 1 shows the X-Ray diffraction results of 10 h milled titanium and carbon powders and 100 h milled 70 mass% Cu-Ti-C powders respectively. It can be seen from the curve A that the specific diffraction peaks of titanium carbide are not observed, and titanium and carbon diffraction peaks become weaker and broader significantly, which indicate sharp decrease grain size of titanium and carbon, and increase of dislocations due to the heavy deformation during mechanical alloying. The grain size of copper and titanium was estimated from the integral width of peak broadening using the method described in previous work. It can be known from calculation results that the grain size of titanium decreased to 15 nm after milling process. Lu, L considered that cold welding and fracturing enable the powder particles to be always in contact with each other
with atomically clean surfaces and with minimized diffusion distance which can reduce the activation energy of diffusion and reaction significantly during the MA process.

The diffraction peaks in the curve B become broader and weaker too, moreover, the copper diffraction peaks move to lower angle after 100 h milling which due to the original titanium dissolved into the copper matrix, furthermore, Liu. X. R. 11) considered that the carbon may solid solution in copper at atomic level during milling. However, it is obvious that most of carbon atoms are located in graphite regions, namely, segregated in the interfaces and dislocations to form sub-solid solution. Furthermore it can be seen from the SEM micrograph of the powders B insert in the Fig. 1 that some of fine powder particles agglomerated, which due to the powders fragmentized and occurred cold welding. Therefore, the stored energy due to the increase of the dislocation and fresh interface ascribed to the fracture of the particles enhance the reactivity of the reactant constituents, and this effect plays an important role in Ti + C → TiC synthesis reaction during sintering.

Figure 2 shows the X-ray diffraction pattern of the composites A and B with different sintering temperature. It can be seen copper, titanium carbide and carbon diffraction peaks in the XRD pattern of the composites A. However, it can be seen copper, titanium carbide, carbon and Cu₃Ti₂ which isn’t observed in the composites A. In addition, the diffraction peak of copper matrix of the composites A and B insert in the Fig. 2(a) and (b) respectively, the copper peak (111) of both the composites A and B shift to lower diffraction angle at lower sintering temperature, and then the peak move to higher angle which approach to diffraction peak of pure copper following rising of sintering temperature. For the composites A, it’s due to titanium atoms dissolved into copper matrix by electric field diffusion effect as a result of DC pulse current, and then the titanium as solid solute in copper matrix precipitated and formed titanium carbide with carbon atoms continuously as rising of sintering temperature. Moreover, the intensity of copper matrix peaks of the composites A decrease constantly during rising of sintering temperature, but the peak become broader. The calculation results of the grain size of the composites A show that copper particulates melted as increasing sintering temperature and mixed with titanium carbide particles, and then molten copper rapidly solidified to form nanocrystalline. Instead, the intensity of the peak of the composites B increases following rising of sintering temperature, which due to the fine copper particles which were formed during milling growth up during sintering process.

3.2 Influence of mechanical alloying technological process on the microstructure of composites

Figure 3 shows SEM images of the composites A sintered with different temperature. It can be seen from Fig. 3(a) that...
copper are surrounded by fine titanium carbide particles which can be confirmed by X-ray and EDS analysis results when the composites were sintered with 800°C, which generated from milled titanium-carbon powders adsorbed to copper particles in the mixed process, and formed fine titanium carbide at the lower sintering temperature. Figure 3(b) displays the microstructure of the samples sintered at 900°C that the microstructure is composed of smooth area (such as point B) and coarse area (such as point A) around the smooth area. It can be observed from EDS analyses results that point A contains copper, titanium and carbon, but smooth areas, such as point B, is composed of almost pure copper. The copper particles melted continually with increasing sintering temperature and then molten copper mixed with titanium carbide and solidified to form coarse area. As increase sintering temperature to 1000°C, the modality of copper particles disappeared to form homogeneous microstructure as Fig. 3(c) shows, and EDS results shows that bright spots as indication by arrows are TiC. Furthermore, some of porosities were observed in the micrograph (c), as a result of more and more copper melted and was squeezed out through the gap between graphite dies at higher sintering temperature.

Figure 4 shows SEM images of the composites B sintered with different temperature. It can be seen from Fig. 4(a) that profiles of agglomerated particles as shown in Fig. 1 in the microstructure of composites B as sintered at 800°C. EDS analysis results show that component of the edge of agglomerated particles profiles is copper, which due to copper melted and permeated into porosity between particles. As rising of sintering temperature to 900°C, more and more molten copper caused contour line of agglomerated particles to broaden obviously such as image Fig. 4(b). As the sintering temperature rising, more and more copper melted and formed the homogeneous conformation such as Fig. 4(c) shows.

Akhtar F and D. Majcherczak studied ceramic metal interface of metal matrix composites which is a very important factor influencing the structure and properties of the composite. The TEM micrographs of composites A and B sintered at 900°C in Fig. 5 shown the different interface between the copper matrix and TiC in the composites A and B. For the composites A, the diffraction pattern inserted in Fig. 5(a) exhibits that the dark particle as an arrow was titanium carbide with size about 300 nm, moreover, the copper matrix shows a stress concentration region. However, Fig. 5(b) shows two types of titanium carbide microscopic geometry: larger particle which occurs between the copper matrix and ultrafine particles which distributed homogeneously throughout the copper matrix. The diffraction pattern insert in Fig. 5(b) indicates that the fine titanium carbide particles and copper matrix formed polycrystal. During the milling process, a part of titanium atoms dissolved into copper matrix, and then during sintering process, the titanium atoms joined together with carbon atoms formed the larger titanium carbide particles, others titanium atoms which dissolved into copper matrix formed fine titanium carbide particles in polycrystalline region as mentioned above.

3.3 Influence of mechanical alloying process on the average friction coefficients and specific wear rates

Figure 6 shows the variation of specific wear rates and average friction coefficients with different normal loads of composites A and B that were sintered with different temperatures. The average friction coefficients of the composites A increase gradually with rising of sintering temperature. As mentioned above, the decrease of content of the residual carbon which formed TiC with titanium such as Fig. 1 reduce the self-lubricating effect as rising of sintering temperature, which lead to increase of average friction coefficients. Instead the composites A sintered at 800°C
exhibit higher specific wear rates than the composites sintered at 900°C and 1000°C such as Fig. 6(b). However, the sintering temperature has not acted on specific wear rates and average fraction coefficients of the composites B.

Furthermore, it can be known from the Fig. 6 that the average friction coefficients and specific wear rates of the composites A show similar trend that decrease steeply as normal load increase from 20N to 60N (average friction coefficient from maximal 2.98 to 0.97, specific wear rates from maximal $18.75 \times 10^{-3}$ mm$^3$/Nm to $2.27 \times 10^{-5}$ mm$^3$/Nm), and then decrease linearly and mildly as rising of normal load from 60N to 200N. However, the average friction coefficients and specific wear rates of the composites B decrease linearly as rising of the normal load too without inflection point. The friction coefficients of the composites A and B sintered at 900°C with wear distance were recorded which show that obvious vibration with maximal instantaneous friction coefficient 4.36 and minimum approximately to 2 which lead steeply increase of the average friction efficient when normal load was 20N of the composites A. As rising of normal loads, the amplitudes and the averages of the curves decrease with more and more stable wear process. However, the composites B shown a steady-state wear at different normal loads during the test.

3.4 Different wear behavior and wear mechanisms of the composites

Figure 7 shows the worn surface composites A sintered at 900°C with different normal load as 20N, 60N, and 200N. Fine mechanical mixed layer as bright spots in the Fig. 5(a) which is projects from worn surface can be observed. The contact between two irregular surfaces induces wear particles corresponding to the granular third body which accumulates against geometric irregularities, and then the third body accumulation induces localized contact area with increasing pressure and temperature.

Such conditions modify the
density of the third body to form a plate. The local actual load of the samples increase steeply which is the result of rapid decrease of actual contact area which is reduced by accumulation of the mechanical mixed layer. In this study, when normal load was 20N, the formation of fine mechanical mixed layer leaded to rapid increase of local actual load, which leaded to rising of shear stress on the mechanical mixed layer. The higher shear stress induced falling of the mechanical mixed layer and sharp fluctuation in the wear test as mention above. As increase normal load, size of the mechanical mixed layer increase for resisting enhancement of local actual load such as Fig. 7(b) shows, and the friction and wear process became steady. J. H. Ouyang\textsuperscript{14} reported that the wear mechanism is not controlled by single mechanical wear in this test, and one of the dominant wear mechanisms in composites, were tribochemical wear as a result of higher loads and relatively higher temperatures. These tribochemical wear, which are stimulated by friction, can result in the formation of a mechanical mixed layer, which can reportedly lower the specific wear loss and gradually reduced friction coefficient as mention above. Farid Akhtar\textsuperscript{6} indicated that with loading conditions become higher, there is more and more fragmentation of the plate and hollows or valleys creation. In the test, continuously increase shear stress as increase of normal load to 200N led to serious fragmentation of the mechanical mixed layer such as Fig. 7(c).

Figure 8 shows micrographs of the worn surface with of composites B sintered at 900°C. Figure 8(a) demonstrates worn surface of the composites B which exhibited deformation layers and tracks along the direction of sliding. The lower normal load leads to slight localized plastic deforma-
tion on the worn surface. As rising of normal load to 100N, the consequent increased localized plastic deformation leads to the formation of subsurface cracks resulting in the delamination of surface layer which was shown in the Fig. 8(b). The micrograph in the Fig. 8(c) exhibits some dimples on the worn surface of the tracks caused by the cutting action of the abrasive particles generated from loose debris after wear test under 200N normal load.

Figure 9 shows SEM micrograph of the worn surface of the composites A and B sintered at 900°C with 60N normal load. Figure 9(a) indicates that the mechanical mixed layer can be observed on the worn surface of the composites A, moreover, it can be seen that mechanical mixed layer composed by light and dark regions. However, Fig. 9(b) represents distinct plastic deformations with shallowest grooves on the worn surface of the composites B with 60N load, and it is remarkable that the contours of conglomeration powder particles which were retained during sintering process are observed in the micrograph.

Table 1 shows the EDS analysis results of five points in the Fig. 9. The results show that the light areas in the mechanical mixed layer such as point A contains more iron and oxygen elements than dark regions such as B in Fig. 9(a), but less of titanium and carbon. The content of copper of the point D and E shows obvious difference that the content of copper of point E (75.46 at%) is much higher than point D.

![Fig. 8 Micrographs of worn surface of the composites B sintered at 900°C with different normal load. (a) 20N. (b) 100N. (c) 200N.](image1)

![Fig. 9 SEM micrographs of worn surface of the composites A and B sintered at 900°C with 60N normal load. (a) the composites A. (b) the composites B.](image2)

<table>
<thead>
<tr>
<th>Point</th>
<th>Cu</th>
<th>Ti</th>
<th>C</th>
<th>O</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>26.03</td>
<td>5.63</td>
<td>5.58</td>
<td>43.64</td>
<td>19.11</td>
</tr>
<tr>
<td>B</td>
<td>29.26</td>
<td>10.61</td>
<td>20.81</td>
<td>28.30</td>
<td>11.02</td>
</tr>
<tr>
<td>C</td>
<td>32.72</td>
<td>18.27</td>
<td>7.48</td>
<td>18.46</td>
<td>23.07</td>
</tr>
<tr>
<td>D</td>
<td>26.05</td>
<td>13.74</td>
<td>9.99</td>
<td>42.55</td>
<td>7.67</td>
</tr>
<tr>
<td>E</td>
<td>75.46</td>
<td>10.39</td>
<td>4.04</td>
<td>6.70</td>
<td>3.41</td>
</tr>
</tbody>
</table>

Fig. 9(a) indicates that the mechanical mixed layer can be observed on the worn surface of the composites A, moreover, it can be seen that mechanical mixed layer composed by light and dark regions. However, Fig. 9(b) represents distinct plastic deformations with shallowest grooves on the worn surface of the composites B with 60N load, and it is remarkable that the contours of conglomeration powder particles which were retained during sintering process are observed in the micrograph.
(26.05 at%), which due to the molten copper permeated formed contour line during sintering as mention above, and then the copper took place plastic deformation during wear test, however, extrusion of a mass of copper from coaggregation powder leaded the decrease of content of copper such as point D. It is notable that the contents of iron of points A, B and C are evidently higher than points D and E. As mentioned above, the wear mechanism of the composites A is the three-body abrasion, and the third body was formed by accumulation and compaction of the debris which come from the composites and corresponding disk, thus, the transfer of iron leaded enhancement of iron content on the worn surface of the composites A. However, the worn surface occur a plastic deformation by shear stress along the direction of sliding during wear test, which caused the much less transfer of iron to the worn surface of composites B.

4. Conclusions

(1) Titanium carbide reinforced copper matrix composites were fabricated by powder technology includes mechanical alloying and spark plasma sintering with different technological process. The composites show uniformly distributed titanium carbide, however, the composites with different technological process show different microstructure and phase composition.

(2) The wear resistance of the composites was studied against CG15 steel. The specific wear rates and fraction coefficients of composites A decrease during increase of normal load with obvious point of inflexion on the curves, however, The specific wear rates and fraction coefficients of composites B decreased gradually and linearly during increase of normal load.

(3) The composites A show third-body abrasion with mechanical mixed layer, but the composites B exhibits plastic deformation on worn surface.

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