Abstract:
Titanium boride (TiB) is characterized by good conductivity, high strength and high melting point. In this work, TiB was used to make Cu-TiB metal matrix composites (MMCs). Amounts of TiB added into Cu matrix were 2wt.%, 5wt.%, 10 wt.% and 15 wt.%. The samples were pressed at pressures of 500MPa, 600MPa, 700MPa and 800MPa and sintered at 820° and 920°, respectively. The properties of the sintered composites such as hardness and impact toughness were studied. Hardness and impact toughness of samples increased with increasing pressures and decreased with increasing contents of TiB. Composite with good mechanical properties and high conductivity was obtained from the sample containing 2wt.%TiB compacted at 800MPa and sintered at 920°. It was shown that 2wt.% TiB is a suitable content to make Cu-TiB MMCs with good mechanical properties and excellent conductivity.

Keywords: Titanium boride; Cu-TiB metal matrix composite; Powder metallurgy; Hardness; Conductivity.

1. Introduction

Electrical contacts made with Ag matrix usually have good conductivity [1, 2], but their production costs are very expensive. Cu is a potential material to substitute Ag to make MMCs for electrical contacts because of its low cost and relatively good conductivity [3][4][5]. However, hardness of Cu MMCs is not very high so the service lives of electrical contacts are decreased. In order to overcome this shortcoming, some hard additives such as Ti$_3$SiC$_2$ [6] and TiB$_2$ [7] were employed to enhance the strength of Cu MMCs. Ag electrical contacts made with CdO additive usually have good properties, but Cd is hazardous to circumstance [8]. New MMCs for applications of electrical contacts has been developed. Recently, relatively pure TiB powder was synthesized by Boronizing of Ti [9]. It was confirmed by X-ray and electron diffraction patterns that the fabricated TiB has face centred cubic structure with space group of Fm$ar{3}$m. The electrical resistivity of TiB was measured to be at level of $15 \times 10^{-7}$ Ω·m, indicating that TiB is a conductive ceramic. This TiB powder had been used as hardening materials for laser coating [10] and as electrodes for battery because of its high hardness and good electrical conductivity. In this study, we take TiB as additive to fabricate Cu-TiB MMCs through powder metallurgy method. The mechanical properties and electrical conductivity of such Cu-TiB MMCs are studied by varying compacting pressures, contents of TiB and sintering temperatures as well.

Corresponding author: hujd@jlu.edu.cn
2. Experimental materials and procedures

Starting materials used for making Cu-TiB composites are Cu powder and TiB powder. Their properties are listed in Tab. I and their microstructures are given in Fig.1.

<table>
<thead>
<tr>
<th>Tab. I</th>
<th>Properties of TiB and Cu powders.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TiB</td>
</tr>
<tr>
<td>density</td>
<td>4.51g/cm³</td>
</tr>
<tr>
<td>Melting point</td>
<td>&gt;2200 °</td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td>15×10⁻⁷ Ω·m</td>
</tr>
</tbody>
</table>

Fig. 1. SEM images showing morphology for (a) Cu powders and (b) TiB powders.

TiB powders were mixed with Cu powder for 2 hours. The contents of TiB powders added into Cu powders were selected to be 2wt.%, 5wt.%, 10wt.% and 15wt.%, respectively. These kinds of powders were put into an automatic mixer and it was rotated at a speed of 60 RPM. The mixed powders were pressed as samples under different pressures of 500MPa, 600MPa, 700MPa and 800MPa. The size of sample for impacting test is 55mm×10mm×10mm without any notch. Impacting tests were carried out on an impacting machine, model JB-150/300 J, made in China. Subsequently, the samples were sintered in a furnace protected with N₂ at a heating speed of 10°/min. Two sintering temperatures 820° and 920° were selected. Fig.2 presents this process of sintering.

A diffractometer model D/Max-2500PC (Japan) was used to check structure of sample, operated with CuKα, tube voltage 50kV and current 300mA. Scanning speed and step were 4°/min and 0.05°(2θ) in the 2θ range of 10°-90°.
Microstructural observations of sample were carried out at Scanning Electron Microscope (SEM, EVO18, Zeiss). The samples were etched in FeCl3(5g)+HCl(5ml)+H2O(100ml) solution for 10–20s before observation.

Density of sample was checked with Archimid’s formula. Hardness of the samples was measured using a Rockwell hardness tester. Mechanical property of the sample was checked by impacting test. Oxidation resistance of the sample was conducted by heating the sample in furnace at 200°C and then calculating the weight before and after heating.

The two-probe method as explained in Fig. 3 was employed to examine the electrical resistivity and the following formula is used to calculate the electrical resistivity:

$$\rho = \left(\frac{V}{I}\right)\left(\frac{A}{L}\right)$$

Where $\rho$ is electrical resistivity(cm·Ω); V is the measured voltage; I is the current of battery; A is area of cross section(cm²); L is length connecting meter (cm).

Fig. 3. Schematic two probe measurement.

3. Results and Discussion

3.1 Porosity

Fig. 4 shows the affect of compacting pressure on porosity for the samples with 2wt.% TiB, sintered at 920°C for 1.5h. As can be seen, porosity decreases with increasing pressure.

(a) 500MPa, (b) 600MPa, (c) 700MPa, (d) 800MPa, sintering temperature 920°C, 2wt.%TiB.

Fig. 4. Variation of porosity with different pressures
3.2 Distribution of TiB in Cu MMCs

Fig. 5 presents EDS mapping results for sample containing 2wt.% TiB, compacted at 800MPa and sintered at 920°. It can be seen that distribution of TiB in Cu matrix is homogeneous. Fig. 6 shows X-ray diffraction pattern for the sample with TiB 2wt.% sintered at 920° for 1.5h. Crystal structure of TiB in the sintered Cu/TiB composite remains the same before and after sintering. No any new phase was found based on XRD measurement results. This is because that the sintering temperatures were lower than temperature of melting point of TiB.

![Fig. 5. SEM image showing microstructure of sintered sample(a) and corresponding EDS mapping results of Ti(b) and Cu(c), compacting pressure 800MPa, sintering temperature 920°, 2 wt.%TiB.](image)

![Fig. 6. XRD pattern of sample, compacting pressure 800MPa, sintering temperature 920°, 2wt.%TiB.](image)

3.3 Effect of pressure on microstructure

Microstructures containing 2wt% TiB, sintered with different pressures 500MPa, 600MPa, 700MPa and 800MPa at 920° for 1.5h, are shown in Fig. 7. Effect of pressure on microstructure is obvious. Porosity of microstructure decreases with increasing pressure. Microstructure sintered at 500MPa contains a number of pores which are distributed as network, while Cu particles are closely contacted. However, situation is changed when pressure is up to 700MPa, microstructure is improved due to the decrease of pore. At the same time, grain boundaries were formed. Boundaries become clearer and power particles were well sintered, leading to dense microstructure when pressure is up to 800MPa. Fig.8 shows variation of density with compacting pressure measured from the samples added with 2wt.%
TiB and sintered at 920°. Densities increase with increasing pressures. Density at 500MPa has a value of 6.25GPa/cm³ but it is up to 8.0GPa/cm³ at 800MPa.

![SEM images showing microstructures for the samples compacted at different pressures, sintering temperature 920°, 2 wt.%TiB](a) 500MPa, (b) 600MPa, (c) 700MPa, (d) 800MPa.

**Fig. 7.** SEM images showing microstructures for the samples compacted at different pressures, sintering temperature 920°, 2 wt.%TiB

**Fig. 8.** Relationship of pressure and density.

### 3.4 Effect of TiB content on density

Fig. 9 presents relationship between densities and contents of TiB measured from samples sintered at 800MPa. The densities decrease with increasing TiB content. The density values decrease from 8.0g/cm³ to 5.5g/cm³ when the contents of TiB change from 2wt.% to 15wt.%. 

![Graph showing the relationship between pressure and density](Pressure vs Density Graph)
3.5. Effect of pressure and temperature on hardness

Hardness values increase with increasing pressures. Maximum value reaches to HRB 70 when pressure is at 800 MPa as shown in Fig. 10, it can be seen from Fig. 10, that samples sintered at high temperature 920 ° have relatively high hardness as compared with these sintered at 820 °.

3.6. Effect of TiB content on hardness

Variations of hardness values with content of TiB is presented in Fig. 11. The varying tendency is rather complex. The maximum hardness value was obtained at 2wt.%Ti. Subsequently, they dramatically decreases from HRB 70 to HRB 20 with increasing TiB content when contents changes from 2wt.% to 10wt.% . However, their difference becomes small between 10% and 15%. The reason for having this tendency is because TiB particles are not well contacted with Cu when TiB content is over 10%. The wettability between Cu and TiB particles is rather poor, leading to the expansion of samples after sintering. That is why the hardness decreased with increasing content of TiB.
3.7 Effect of TiB content on impact toughness

Fig. 12 presents relationship between impact toughness and content of TiB for the sample compacted at 800MPa and sintered at 920°C. Toughness values decrease with increasing content of TiB. The values of toughness are changed from 27 J to 0.2 J while content of TiB ranging from 2wt.% to 15wt.%. This varying tendency is the same as that between hardness and content of TiB as shown in Fig.11.

3.8 Effect of pressure and temperature on impact toughness with 2wt.% TiB

Values of impacting tests for the samples sintered at different temperatures and different pressures are plotted in Fig. 13. As can be seen, the values of impact toughness remain almost similar with changing pressures when the samples were sintered at 820°C. However, they become obvious with changing pressures when the samples were sintered at 920°C. A maximum value of 27J was obtained at pressure of 800MPa. The fractured surfaces of samples were observed with SEM (seen Fig. 14). The sample compacted at pressure 800MPa and sintered at 920°C appears to have much ductile feature with its fractured surface being characterized by a number of small dimples. In contrast, the sample compacted at 800MPa and sintered at 820°C appears as brittle fracture feature with its fracture surface being
characterized by a number of small cleavage facets, indicating that sintering temperature affects the toughness.

![Fig. 13. Impact energy relationship with sintering temperature and pressure.](image)

Fig. 13. Impact energy relationship with sintering temperature and pressure.

![Fig. 14. SEM fracture image at pressure 800MPa (a) 820°, (b) 920°](image)

Fig. 14. SEM fracture image at pressure 800MPa (a) 820°, (b) 920°

### 3.9. Effect of pressure on conductivity

Fig. 15 presents the relationship between conductivities (reciprocal of electrical resistivity) with compacting pressures. The conductivity increases with increasing pressure. Conductivity with content of 2wt.% TiB at 800MPa is three times as high as that at 500MPa, possessing a value of $2.94 \times 10^7$ Sm$^{-1}$. This is near the value given by Ref. 11. The reason for this is because that larger pressure could make TiB particle well connected with Cu so that dense composite was obtained.

![Fig. 15. Relationship of electrical conductivity and pressure.](image)

Fig. 15. Relationship of electrical conductivity and pressure.
3.10. Effect of TiB content on conductivity

Fig. 16 shows variation of conductivity with content of TiB for the samples compacted at 800MPa and sintered at 920°. Conductivity decreases with increasing content of TiB. In this curve, conductivity of pure Cu material (220×10^5 S m^{-1}) is given for comparison. As it can be seen, its conductivity is little bit higher than that composited with 2wt.% TiB(215×10^5 Sm^{-1}). From 2wt.% to10wt.%, conductivities dropped rapidly. Conductivities for 10% and 15% keep at the same level, 90 ×10^5 S m^{-1}.

![Fig. 16. Relationship of electrical conductivity and the content of TiB.](image)

4. Conclusion

(1) Processing parameters for making Cu-TiB MMCs with available properties were as follows: Compacting pressure was 800MP; sintering temperature was 920° and content of TiB was 2wt.%.

(2) Values of density and hardness increased with increasing compacting pressure; density 8.25g/cm³ and hardness 70.7HRB were obtained when samples with a content of 2wt.% TiB were compacted at pressure 800MPa and sintered at 920°.

(3) Values of impact toughness increased with increasing pressure. A value of 27J was obtained when the samples were compacted at 800 MPa and sintered at 920°.

(4) Values of conductivity increased with increasing pressure; a excellent value of 2.94×10^7 Sm^{-1} for the samples containing 2wt.%TiB was achieved when samples were compacted at 800MPa and sintered at 920°.

Acknowledgments

The authors thank National Natural Science Foundation of China for his financial support under the project No.51172088.

5. References


Садржај: Титанијум борид (TiB) се карактерише добром проводљивошћу, великом тврдоћом и високом температуром топљења. У овом раду, TiB је употребљен за прављење Cu-TiB металног композита (MMCs). Количине TiB додате у матрикс Cu су биле 2wt.%, 5wt.%, 10 wt.% и 15 wt.%. Узорци су пресовани под притиском од 500MPa, 600MPa, 700MPa и 800MPa и синтеровани на 820° и 920°, истим редоследом. Тврдоћа и жилавост су својства која су проучавана. Тврдоћа и жилавост узораца расту са порастом притиска пресовања и смањују се са повећањем удела TiB. Композит са добром механичким својствима и великом проводљивошћу је добијен за узорак са 2wt.%TiB компактиран на 800MPa и синтерован на 920°. Указано је и на то да је 2wt.% TiB довољна количина да се направи Cu-TiB MMCs са добром механичким својствима и извршном проводљивошћу.

Кључне речи: титанијум борид; Cu-TiB матални композит; металургија праха; тврдоћа; проводљивост