Effect of Cr Content on the Compression Properties and Abrasive Wear Behavior of the High-Volume Fraction (TiC–TiB₂)/Cu Composites

Feng Qiu · Yue Han · Ai Cheng · Jianbang Lu · Qichuan Jiang

Received: 18 April 2014 / Revised: 24 July 2014 / Published online: 9 October 2014
© The Chinese Society for Metals and Springer-Verlag Berlin Heidelberg 2014

Abstract The (TiC–TiB₂)/Cu composites with 50 vol% TiC–TiB₂ ceramic particles were successfully fabricated by the combustion synthesis and hot press consolidation in a Cu–Ti–B₄C–Cr system. The effects of the Cr content on the microstructures, hardness, compression properties, and abrasive wear behaviors of the composites were investigated. The final products consist of only Cu, TiC, and TiB₂ phases, and the ceramic particles are distributed uniformly in these composites. The size of the ceramic particles decreases with Cr addition. As the Cr content increases, the yield strength, ultimate compression strength, microhardness, and abrasive wear resistance of the composites increase, and the fracture strain decreases.

KEY WORDS: Metal matrix composites; Powder metallurgy; Combustion synthesis; Abrasive wear

1 Introduction

In recent years, the copper has been widely used in industrial applications due to its high electrical and thermal conductivities, low cost (compared with Ag and Au), and ease of fabrication. However, the relatively low hardness, low strength, and poor wear resistance limit its extensive applications [1–4]. These shortcomings could be avoided by the incorporation of ceramics into the copper matrix. Besides the SiC and Al₂O₃ ceramics, the TiC and TiB₂ ceramics are commonly used as reinforcements in the Cu matrix composites [5–8]. Moreover, the TiC and TiB₂ ceramic particles reinforced Cu matrix composites could be fabricated by the in situ method. While the composites with the monolithic ceramic particles exhibit relatively high

hardness, high wear resistance, and superior elevated temperature strength, the composites containing two-phase ceramic particles are believed to exhibit more superior properties [9, 10].

As known, the two-phase TiC–TiB₂ ceramic composite has higher wear resistance, mechanical and electrical properties compared with the monolithic TiC or TiB₂ [11–13]. In addition, minor additions should strongly influence the microstructures and mechanical properties of composites by combustion synthesis and hot press consolidation. However, few of systematic investigations of the effects of Cr addition on the combustion synthesis of (TiC–TiB₂)/Cu from a Cu–Ti–B₄C–Cr system have been carried out so far.

A number of fabrication methods have developed for the copper matrix composites, such as powder metallurgy technique [2, 3, 14–16], infrared infiltration technique [1], and pressureless infiltration [17]. Moreover, the combustion synthesis combined with hot press consolidation is another in situ method for producing the copper matrix composites with the advantages of the finer sizes and the more uniform dispersion of the synthesized ceramic particles, as well as the stronger interfacial bonding between the matrix and the reinforcements, which could lead to the

Available online at <http://link.springer.com/journal/40195>

F. Qiu · Y. Han · A. Cheng · J. Lu · Q. Jiang (✉)
Key Laboratory of Automobile Materials, Ministry of Education,
Department of Materials Science and Engineering, Jilin
University, Changchun 130025, China
e-mail: jqc@jlu.edu.cn

good mechanical properties and high wear resistance of the composites [18–21].

Therefore, in this study, the Cu matrix composites reinforced with 50 vol% TiC–TiB₂ ceramic particles were fabricated by the in situ method of the combustion synthesis combined with hot press consolidation in the Cu–Ti–B₄C–Cr system, and the effect of the Cr content on the microstructures, compression properties, and abrasive wear behavior of the composites was investigated in detail.

2 Experimental

The raw materials used were commercial copper powders (99.7% purity, ~47 μm in diameter), titanium powders (99.5% purity, ~25 μm in diameter), B₄C powders (98% purity, ~3.5 μm in diameter), and Cr powders (99% purity, ~47 μm in diameter). The theoretical molar ratio of TiC:TiB₂ in the composites was predetermined to be 1:2. Elemental powder blends corresponding to 50 vol% (TiC–TiB₂)/Cu with 0, 3, 5, and 7 wt% Cr addition were mixed sufficiently by ball milling for 8 h. After that, the mixtures were cold pressed into cylindrical samples 28 mm in diameter and 40 mm in height under a pressure of 42 MPa, and then the sample was put in a self-made vacuum thermal explosion furnace. The heating rate of the furnace was about 30 K/min and the temperature near the center of the compact was measured by K-type thermocouple. When the detected temperature rose suddenly, indicating that the sample had been ignited, then the sample was quickly pressed by employing a pressure of ~40 MPa for a 10 s duration, and then the sample was cooled down to room temperature.

The phase constituents of the products were investigated by X-ray diffraction (XRD, Moldel D/Max 2500PC Rigaku, Japan) with CuK α radiation. The microstructure was investigated by scanning electron microscopy (SEM, Moldel Evo18 Carl Zeiss, Germany). Cylindrical samples with a diameter of 3 mm and a height of 6 mm were used for the compression tests, and the parallel loading surfaces were polished. The uniaxial compression tests were carried out using the servo-hydraulic materials testing system (MTS, MTS 810, USA) at a strain rate of $1 \times 10^{-4} \text{ s}^{-1}$. Microhardness of the composites was measured by a Vickers hardness tester (Moldel 1600-5122VD, USA) using a static load of 2 N and a dwell time of 15 s.

Abrasive wear tests were carried out on a pin-on-disk-type apparatus at room temperature. The composites were machined into the block samples with the dimensions of 4 mm $\times$ 4 mm $\times$ 15 mm and the 4 mm $\times$ 4 mm faces were employed as the wear surfaces. The applied normal loads were 15, 25, and 35 N and the sliding distance was kept constant at 24.78 m. The worn Al₂O₃ abrasive paper was substituted for a new one for every sliding distance of

Fig. 1 XRD patterns of 50 vol% (TiC–TiB₂)/Cu composites with different Cr additions: **a** 0 wt%; **b** 3 wt%; **c** 5 wt%; **d** 7 wt%

8.26 m, making sure that the samples would contact with the fresh abrasive particles. The abrasive wear rate of the composites is defined as the volume loss suffered per unit sliding distance, and the volume loss is obtained from the ratio of weight loss to the density of the composites. The weight loss was measured before and after the wear test using an electronic balance with a resolution of 0.1 mg, and the density of the composites was measured by Archimedes' method. The worn surfaces of the samples were observed by SEM.

3 Results and Discussion

3.1 Phase Identification and Microstructures

Figure 1 shows XRD patterns for the 50 vol% (TiC–TiB₂)/Cu composites with 0, 3, 5, and 7 wt% Cr additions. It can be seen that all the products consist of Cu, TiC, and TiB₂ phases, without any intermediate phases, the phase constitutions of the composites are not changed with the addition of Cr. The inset in Fig. 1 shows that the peak position of the Cu (111) plane shifts to lower 2θ values, and the one of the TiC (200) plane shifts to higher 2θ values with the increase in the Cr content, implying the increases in the lattice constant of Cu, and the decreases in the lattice constant of TiC.

Fig. 2 SEM images of microstructures of 50 vol% (TiC–TiB₂)/Cu composites with different Cr contents: **a** 0 wt%; **b** 3 wt%; **c** 5 wt%; **d** 7 wt%

It is conjectured that Cr can occupy the positions of Cu in the Cu crystal lattice and the ones of Ti in the TiC crystal lattices. As a result, these lattices expand because the atomic radius of Cr (1.85 nm) is larger than that of Cu (1.57 nm) in the Cu matrix, and these lattices deflate because the atomic radius of Cr (1.85 nm) is smaller than that of Ti (2.0 nm) in TiC. Thus, it can be deduced that the severe lattice distortion in the Cu matrix and TiC occurred. Meanwhile, the full half width of the peaks of TiC (200) plane and TiB₂ (101) plane increases with increasing Cr addition. Hence, it is believed that the broad diffraction maxima (Fig. 1) can be attributed to the internal strain. As the Cr content increased, the internal strain increased and the sizes of the TiC and TiB₂ particles decreased.

Figure 2 shows the SEM images of the 50 vol% (TiC–TiB₂)/Cu composites with 0, 3, 5, and 7 wt% Cr additions. The composites fabricated by the in situ method are dense. The synthesized spherical TiC and hexagonal plates shaped TiB₂ particles are distributed uniformly in the copper matrix, and their sizes are nonuniform. The sizes of the TiC and TiB₂ particles decreased from ~2 μm to smaller than 1 μm as the Cr addition increased. It is in accord with increase in the full half width of the peaks of TiC (200) plane and TiB₂ (101) plane with increasing Cr addition in XRD.

The size decreases of the TiC and TiB₂ particles might be attributed to the decrease of the combustion temperature. As known, the growth of the ceramic particles is an exponential function of the combustion temperature [22], that is, the lower the combustion temperature is, the smaller the size of the ceramic particles is. Thus, the sizes of the ceramic particles decreased greatly with the Cr addition because only a portion of Cr participated in the reaction and more amount of heat was needed to melt increased Cr.

3.2 Compression Properties

Figure 3 shows the compression engineering stress–strain curves of the (TiC–TiB₂)/Cu composites with different Cr contents. The mechanical properties and microhardness of the composites are summarized in Table 1. The yielding strength (YS), ultimate compression strength (UCS), and microhardness of the composites increase from 1003 MPa, 1252 MPa, and 404 HV to 1315 MPa, 1827 MPa, and 543 HV, respectively, with increasing Cr content from 0 to 7 wt%, while the fracture strain (ϵ_f) decreases from 5.8% to 1.9%.

Fig. 3 Compression engineering stress–strain curves of 50 vol% (TiC–TiB₂)/Cu composites with different Cr contents

Table 1 Room-temperature compression properties and microhardness of 50 vol% (TiC–TiB₂)/Cu composites with different Cr contents

Cr content (wt%)	$\sigma_{0.2}$ (MPa)	σ_{UCS} (MPa)	ε_f (%)	Hardness (HV)
0	1003^{+33}_{-46}	1252^{+30}_{-54}	$5.8^{+0.3}_{-0.2}$	404 ± 8
3	1113^{+29}_{-43}	1161^{+35}_{-48}	$2.7^{+0.2}_{-0.3}$	436 ± 8
5	1315^{+46}_{-55}	1358^{+51}_{-45}	$2.3^{+0.2}_{-0.1}$	491 ± 10
7	–	1827^{+63}_{-52}	$1.9^{+0.1}_{-0.2}$	543 ± 10

The strength of the composites is determined by the strength of the reinforcement and matrix, and the interfacial bonding strength between the particles and the matrix. When the content of the Cr increases, the strength and hardness of the composites increase, which is due to the finer particles, the Cr solid solution in the Cu matrix and the TiC, and the improvement of the interfacial bonding strength between the ceramic particles and the copper matrix. The finer ceramic particles could be a factor for improving the compression strength and hardness of the composites with the Cr addition. It is well known that better reinforcing effect and higher hardness can be achieved in the composites with smaller ceramic particles. Another reason of composite strengthening is Cr solid solution in the TiC, which could result in the large lattice distortion and enhance strength and hardness of the TiC. Besides, the enhanced strength of the matrix is the other important factor. As known, the dissolution of Cr into the Cu matrix can increase its strength and hardness by solid solution strengthening. Lastly, the wettability between these ceramic particles and the Cu matrix is improved by the addition of Cr. It would enhance the interfacial bonding strength between the ceramic particles and the copper matrix.

Figure 4 shows the SEM images of the compression fracture surfaces of the (TiC–TiB₂)/Cu composites with different Cr contents. As indicated, all the ceramic particles

are well wrapped by the copper matrix, indicating that the bonding between the particles and the copper is quite satisfied. In this case, the compressive strength of the composites is mainly controlled by the finer ceramic particles, the Cr solid solution in the Cu matrix, and the improvement of bonding strength between these ceramics and the copper matrix. Thus, the increase of the Cr content will reduce the sizes of the TiC and TiB₂ particles in the composites, enhance solid solution strengthening in the Cu matrix and TiC, and enhance the bonding strength between the TiC/TiB₂ ceramics and the copper matrix. However, with too much solid solution of Cr in the composites, the composite matrix would be split due to the severe lattice distortion and then the ductility of the composites decreases with the Cr addition.

3.3 Abrasive Wear Properties

Figure 5 shows the variation of wear rate with the applied loads for the pure copper and the composites tested against the Al₂O₃ abrasive particles of 45 μm . It is apparent that the pure copper experiences an extremely high wear rate than the composites. This indicates that the Al₂O₃ abrasives can penetrate easily into the soft copper during sliding, resulting in excessive material removal from the surface, and the wear rate of the composites reduced as the Cr content increased. This can also be confirmed by the worn surfaces of the pure copper and the composites, as shown in Fig. 6. As it can be seen from Fig. 6a, the Al₂O₃ particles deeply penetrated into the pure copper, which could lead to the extensive deformation and fracture in the subsurface region of the pure copper.

The worn surfaces of the (TiC–TiB₂)/Cu composites with different Cr contents are shown in Fig. 6b–f, which are relatively smoother than that of the pure copper. Since the ceramic particles are much harder than the copper matrix, higher wear resistance can be obtained. Moreover, with the increase in the Cr content, the worn surfaces of the composites become smoother. The much harder and finer ceramic particles can act as barriers that can protect the copper matrix from the plastic deformation and removal, leading to the slighter micro-plowing and lower wear rate of the composites. Besides, the dissolution of Cr into the Cu matrix can increase its strength and hardness by solid solution strengthening. Therefore, the abrasive wear resistance of the composites is better than that of the pure copper. As the Cr content increases, the resistance to the penetration of the abrasive particles is increased, leading to the better abrasive wear resistance.

When the applied loads increase from 15 to 35 N, the worn surface of the 50 vol% (TiC–TiB₂)/Cu composite with 7 wt% Cr addition become rougher, as shown in

Fig. 4 SEM images of the compression fractured surfaces for 50 vol% (TiC-TiB₂)/Cu composites with different Cr contents: **a** 0 wt%; **b** 3 wt%; **c** 5 wt%; **d** 7 wt%

Fig. 5 Wear rate versus applied load under the counterface of 45 μ m Al₂O₃ abrasive particles for the pure copper and the (TiC-TiB₂)/Cu composites with different Cr contents

Fig. 6e, f. The Al₂O₃ abrasives will penetrate deeper as the applied load increases and subsequent sliding results in high wear rate in the composite. When the applied load is relatively large (35 N), these smaller TiC and TiB₂ ceramic particles are easily removed from the copper matrix, corresponding to the bigger depth of the furrow. The abrasive

particles of 45 μ m can easily penetrate into the composite and result in a serious wear of the composites. It is worth mentioning that the abrasive wear resistance of the 50 vol% (TiC-TiB₂)/Cu composite with 7 wt% Cr addition was improved by 138% and 39%, respectively, compared with pure copper and 50 vol% (TiC-TiB₂)/Cu composite when the applied load is 15 N.

As mentioned above, the abrasive wear of the (TiC-TiB₂)/Cu composites consists of two stages. First, the Al₂O₃ abrasive particles penetrate into the soft copper matrix and cut it, leading to excessive copper removal from the composites. Meanwhile, the Al₂O₃ abrasives also have an impact on the TiC and TiB₂ ceramic particles, resulting in the blunting of the Al₂O₃ abrasives. In the second stage, the TiC and TiB₂ ceramic particles are exposed from the copper matrix and they act as a barrier to the micro-cutting action of the abrasives, inducing the decrease in the cutting efficiency of the Al₂O₃ abrasives and the consequent wear rate of the composites. When the exposed TiC and TiB₂ ceramic particles are removed from the worn surface of the composites, the Al₂O₃ abrasives will impact the copper matrix and the TiC-TiB₂ ceramic particles simultaneously again.

Fig. 6 Worn surfaces of the pure copper **a**, 50 vol% (TiC–TiB₂)/Cu composites without Cr addition **b**, with 3 wt% Cr **c**, 5 wt% Cr **d**, 7 wt% Cr **e**, **f** additions. The applied load is 15 N for **a–e**, and the applied load is 35 N for **f**

4 Conclusions

- (1) 50 vol% (TiC–TiB₂)/Cu composites with different Cr additions were successfully fabricated by the combustion synthesis and hot press consolidation in a Cu–Ti–B₄C–Cr system. The ceramic particles are distributed uniformly in the composites and the ceramic particle sizes decrease from 2 μm to smaller than 1 μm with increasing the Cr content.
- (2) The yield strength, ultimate compression strength, hardness, and wear resistance of the composites increase as the Cr content increases. The composite with 7 wt% Cr possesses the highest hardness (543 HV) and the superior compression strength (1827 MPa), resulting in an overall increase by 35% and 45%, compared with those of the 50 vol% (TiC–TiB₂)/Cu composites without Cr addition, respectively.
- (3) The enhancement of the hardness, compression strength, and wear resistance of the composites with the increase of the Cr addition is mainly due to the refinement of the ceramics, and the solid solution of Cr in the Cu matrix and TiC.

Acknowledgments This work was financially supported by the National Natural Science Foundation of China (Nos. 51171071, 50971065 and No. 50531030), National Basic Research Program of China No. 2012CB619600, the Research Fund for the Doctoral Program of Higher Education of China (No. 20130061110037) and the Project 985–High Performance Materials of Jilin University.

References

- [1] P.K. Deshpande, R.Y. Lin, *Mater. Sci. Eng. A* **418**, 137 (2006)
- [2] S.C. Tjong, K.C. Lau, *Mater. Lett.* **43**, 274 (2000)
- [3] S.C. Tjong, K.C. Lau, *Mater. Sci. Eng. A* **282**, 183 (2000)
- [4] N. Zarrinfar, A.R. Kennedy, P.H. Shipway, *Scr. Mater.* **50**, 949 (2004)
- [5] D.W. Lee, G.H. Ha, B.K. Kim, *Scr. Mater.* **44**, 2137 (2001)
- [6] J.P. Tu, N.Y. Wang, Y.Z. Yang, W.X. Qi, F. Liu, X.B. Zhang, H.M. Lu, M.S. Liu, *Mater. Lett.* **52**, 448 (2002)
- [7] F. Shehata, A. Fathy, M. Abdelhameed, S.F. Moustafa, *Mater. Des.* **30**, 2756 (2009)
- [8] S.Y. Chang, S.J. Lin, *Scr. Mater.* **35**, 225 (1996)
- [9] W. Zhang, N. Travitzky, P. Greil, *J. Am. Ceram. Soc.* **91**, 3117 (2008)
- [10] F. Olevsky, P. Mogilevsky, E.Y. Gutmanas, I. Gotman, *Metall. Mater. Trans. A* **27**, 2071 (1996)
- [11] D. Vallauri, F.A. Deorsola, *Mater. Res. Bull.* **44**, 1528 (2009)
- [12] B.S. Du, S.R. Paital, N.B. Dahotre, *Scr. Mater.* **59**, 1147 (2008)
- [13] J.J. Liu, Z.D. Liu, *Mater. Lett.* **64**, 684 (2010)
- [14] F. Akhtara, S.J. Askaria, K.A. Shaha, X.L. Du, S.J. Guo, *Mater. Charact.* **60**, 327 (2009)
- [15] L. Xia, B.B. Jia, J. Zeng, J.C. Xu, *Mater. Charact.* **60**, 363 (2009)
- [16] S.R. Dong, J.P. Tu, X.B. Zhang, *Mater. Sci. Eng. A* **313**, 83 (2001)
- [17] L. Zhang, X.B. He, X.H. Qu, B.H. Duan, X. Lu, M.L. Qin, *Wear* **265**, 1848 (2008)
- [18] F. Akhtar, *J. Alloys Compd.* **459**, 491 (2008)
- [19] H.Y. Wang, L. Huang, Q.C. Jiang, *Mater. Sci. Eng. A* **407**, 98 (2005)
- [20] B.M. Chen, Q.L. Bi, J. Yang, Y.Q. Xia, J.C. Hao, *Mater. Sci. Eng. A* **491**, 315 (2008)
- [21] Y.H. Liang, H.Y. Wang, Y.F. Yang, R.Y. Zhao, Q.C. Jiang, *J. Alloys Compd.* **462**, 113 (2008)
- [22] Y. Choi, S.W. Rhee, *J. Mater. Sci.* **28**, 6669 (1993)