Tribological behavior of WC-4.32MgO-3.68B$_2$O$_3$ composite

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Abstract. WC-4.32MgO-3.68B$_2$O$_3$ composite material was prepared by spark plasma sintering technology, and then Si$_3$N$_4$ ball was used as the counter-grinding material to study the friction and wear behavior under different loading conditions by means of fretting friction. The research results show that: the distribution of the second phase has a significant effect on the wear behavior of the composites. During the fretting friction process, second phase particles peeled off from the structure, causing the abrasion of the matrix to increase. The research found that with gradually increase of the load, the friction coefficient of the material gradually decreases, but the degree of wear gradually increases. The number of furrows also increased significantly, which was related to the wear degree of convex on the surface of the materials. It can be observed from the wear scar that the main wear mechanisms of composite materials are abrasive wear and oxidative wear.

1. Introduction
WC-Co cemented carbide is widely used in mining, oil drilling and metal cutting for its high hardness, high toughness and high wear resistance. Due to the generation of friction heat[1], local temperature of cemented carbide will increase sharply and lead to the softening and oxidation of Co phase[2], thus, Co will be extruded in the process of friction and wear[3], which will cause the decrease of strength and wear resistance. In order to further improve the application range of cemented carbide under extreme working conditions, considerable number of researchers have carried out the preparation of WC based cemented carbide without metallic binder, and made progress in mechanical properties. However, there is little research on wear mechanism of WC based cemented carbide without metallic binder, and just a small amount of research on the friction and wear behavior of WC-Al$_2$O$_3$[4-6]. Therefore, it is necessary to conduct a comprehensive and in-depth study on the wear mechanism of WC based cemented carbide without metallic binder toughened by different second phases.

In previous, we have developed WC composites toughened by MgO-B$_2$O$_3$ and obtained good mechanical properties. In this study, WC-4.32MgO-3.68B$_2$O$_3$ (W8MB) with excellent comprehensive mechanical properties will be selected for fretting friction experiment to reveal the wear mechanism of W8MB composite, thus provide useful reference for improving the wear resistance of WC-MgO-B$_2$O$_3$ material system in the future.
2. methods and Material

2.1. Material preparation
The commercial powder of WC (0.8 μm, 99.9% purity), MgO (40 μm, 99.9% purity) and B₂O₃ (75 μm, 98.0% purity) were used as the starting powders. And the powders were mixed according to the proportion of WC-4.32MgO-3.68B₂O₃ (weight percentage). Then the mixed powder was milled on the planetary ball mill (QM3SP4) for 30 hours, and the composite powder (named W8MB) with the total added amount of MgO and B₂O₃ was obtained after drying.

The composite powder was then sintered via spark plasma sintering technology (Dr. Sinter model SPS-825) at 1400 ℃ for 5 min. After sintering, bulk material with dimensions of 30 mm × 9 mm, hardness of 18.16 ± 0.17 GPa, and fracture toughness of 9.45 ± 0.37 MPa·m¹/₂ was obtained, and the microstructure is shown in Fig.1. Then bulk material was processed into small specimens with dimensions of 8 mm × 8 mm × 8 mm.

![Figure 1 Microstructure of W8MB](image)

2.2. Experimental methods
The fretting friction tests were carried out using an Optimol SRV-IV (DIN51834) oscillating friction tester with the configuration of ball-on-flat, and Si₃N₄ ball with a diameter of 10 mm was chosen as the counter-grinding material for its high hardness and good wear resistance. The schematic of the tester is shown in Fig.2. As shown in the picture, the upper specimen is Si₃N₄ ball, and the lower specimen is W8MB material with a dimension of 8 mm × 8 mm × 8 mm. In the process of fretting friction, a certain load is applied from above, and Si₃N₄ ball is driven by the vibration motor to carry out reciprocating friction on the surface of the specimen. Specific parameters of fretting friction experiment are shown in Table 1. All the fretting tests were carried out under un-lubricated condition and at a temperature of 20 ℃ in air. In order to ensure that the fretting tests were conducted in the gross sliding regime, a relatively large displacement amplitude of 200 μm was employed. The friction coefficient is automatically recorded during the experiment. To measure the depth of the wear scar, a 3D surface profiler (RTEC UP) was used, and the surface topography was also characterized. Optical microscope (LEICA DM 2500M) was employed to observe the macro morphology of the wear scar. In order to investigate the wear mechanism, field emission scanning electron microscope (Nova Nano SEM 430) was used to characterize the worn surface, and the composition of local area on the worn surface was analyzed by Energy Dispersive Spectrometer (Bruker) in SEM.
3. Results and discussion

3.1. Friction coefficient

It can be seen from Fig.3(a) that the curve of friction coefficient under different loading conditions undergone a running-in process, of rapid increase and then decrease in the initial stage. In the initial stage of friction test, the interface contact of the friction pair is mainly surface convex, and produces a higher frictional resistance. Therefore, the friction coefficient is higher at first. It can also be seen from the curves of the friction coefficient in the stable stage, that with the increase of loads, the fluctuation of the friction coefficient curve gradually decreases. It is presumed that during the friction process, some hard particles peeled off from the microstructure of W8MB, which cause friction resistance increases, and lead to the fluctuation of the curve. However, in the case of high loading condition, the coarse particles will be crushed into fine particles, thus the friction resistance is lower, so the fluctuation of the friction coefficient curve is less intensely. As shown in Fig.3(b), with the increase of the loads, the average friction coefficient of the specimen gradually decreases. This is because under high loading condition, the surface of the specimens in contact with the Si₃N₄ ball is severely worn, and forming a smoother surface.

3.2. Wear scar profile

Wear scar profiles of W8MB specimens after friction for 150 min under different loading conditions are shown in Fig.4. It can be seen that as the loads gradually increase, the depth and width of the wear scar
gradually increase. Table 2 shows the parameters of the wear scar profile. When the load is increased from 10 N to 20 N, and then to 30 N, the depth of the wear scar correspondingly increased from 2.88 μm to 3.63 μm and then to 3.99 μm. This indicates that under the same friction time, the higher the load employed, the wear of the specimen is more serious.

| Load | Width (mm) | Depth (μm) |
|------|------------|------------|
| 10   | 0.76       | 2.88       |
| 20   | 0.82       | 3.63       |
| 30   | 0.85       | 3.99       |

Figure 4 Wear scar profiles of W8MB specimen after friction for 150 min under different loads.

3.3. Wear scar morphology

The 3D surface topographies (left) and optical micrographs (right) of the specimen’s wear scar after friction at different loading conditions are shown in Fig.5. It can be seen from the 3D surface topographies that there are a large number of furrows parallel to the friction direction in the wear scar, which indicates that there may be a large amount of two-body abrasive wear during the friction process[8]. And with the increase of the friction loads, the furrows are gradually increasing, indicating that friction loads have a great influence on the wear of the specimen’s surface. It can also be seen from the optical micrographs on the right that as loads increase, the size of the wear scars increase significantly, which consistent with the research results in wear scar profile. At the same time, as the loads increase, the material peeling off gradually appears in the middle of the wear scar.
Figure 5 The 3D surface topographies and optical micrographs of the wear scars on W8MB sample under different loads: (a), (b) 10 N; (c), (d) 20 N; (e), (f) 30 N.

A large number of furrows can also be observed in Fig.6 (a) and (b), indicating that the main wear mechanism of the material is abrasive wear. The formation of furrows is mainly due to the presence of micro-protrusions on the surface of the Si₃N₄ ball, which plows out the material on specimen surface during repeated friction, and form furrows. The formation of furrows is an important way of material loss during friction. As can be seen by comparing Fig.6 (a) and (b), when the normal load is 10 N, the width and depth of the furrow on the specimen surface are larger and deeper than those under the normal load of 30 N. It is well known that when the furrow is deeper, the material loss of specimen is more serious. However, the wear scar profile curve in Fig.4 shows that the specimen friction at 30 N wears more severely. The main reason for this contradiction is that the asperities on the surface of the Si₃N₄ ball at low loading condition have a lower degree of wear. Therefore, leave deeper furrows on the surface. And at high loading condition, the friction pair has been severely worn in the early stage, so the sharpness of the surface asperities is significantly reduced after a period of time, so that the depth and width of the furrow are lower.

The microscopic morphology of the furrow is shown in Fig.6 (c), and its further enlarged morphology is shown in Figure (d). Broken WC grains can be found in the furrow, which is presumed to be caused by being squeezed by Si₃N₄ ball during friction process. Under high loading condition, the contacting surface of Si₃N₄ ball and specimen has a large normal stress, lead to the crushed of WC grains during the friction. These broken grains will be peeled off after the long-term friction, which will cause the wear of the specimens. Further observation of the worn surface found that there are pits between the WC grains, indicating that the second phase particles peeled off from the matrix during the friction test. Due to the exfoliation of the grains, the contact stress between the Si₃N₄ ball and specimen increases,
resulting in the fragmentation of the WC grains. Such broken grains will cause the cracks to propagate further under the effect of long-term stress, and thus fracture and pull out[3]. This is another major factor of wear of W8MB material. According to the above analysis, there are wear phenomena such as micro-cutting, micro-cracks and grain flaking in W8MB.

Figure 6 The worn surface of W8MB sample after friction and wear under different conditions of (a) 10N, 50min; (b) 20N, 100min; (c) 30N, 50min; (d) 30N, 150min.

After 150 minutes of fretting friction under loads of 10 N, traces of wear and peeling of the second phase can be observed from Fig.7 (a). The composition of local area is shown in the table on the right. It can be seen that this area contains N and Si Element, indicating that the Si₃N₄ ball was worn during the friction process, and the generated abrasive particles remained in the second phase. In addition, the phase also contains more O elements, indicating that there was oxidation reaction occurred during the friction process. As shown in Fig.7 (b), after fretting friction for 150 minutes at the loads of 30 N, an adhered film was found on the wear scar of the specimen. Local composition of the film is shown in the table on the right. There is a large amount of O element in the film, indicating that oxidation occurred on the wear scar of specimen in the process of friction and wear, thus an oxide film was formed. The formation of oxide film may be caused by the rapid increased temperature in local area due to continuous accumulation of the frictional heat. According to related studies, the presence of oxide film can play a role in lubrication to a certain extent [2], thereby reducing friction resistance and friction coefficient, which is one of the reasons why specimen has lower friction coefficient under high loading condition.
4. conclusion

Through the fretting friction experiment, the friction coefficient, wear scar profile and wear scar morphology of W8MB were researched and analyzed, and the conclusions are drawn as follows:

(1) As the loads increase, the friction coefficient of the sample gradually decreases, and the size of the wear scar profile gradually increases;

(2) The main wear mechanism of W8MB is abrasive wear, and there is also a small amount of oxidative wear. The formation of oxide film on the surface is the main reason for the low friction coefficient under high loading condition.

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References

[1] J. Pirso, S. Letunovit, M. Viljus. “Friction and wear behaviour of cemented carbides”. Wear, vol. 257, pp. 257-265, August 2004.
[2] A. R. Boukantar, B. Djerdjare, F. Guiberteau, A. L. Ortizzb. “Spark plasma sinterability and dry sliding-wear resistance of WC densified with Co, Co+Ni, and Co+Ni+Cr”. Int. J. Refract. Met. Hard Mat., vol. 92, pp. 105280-105292. November 2020.
[3] X. Li, L. Chen, D. Yi, S. Zhao, Z. Zhang, X. Zheng. “Friction and wear performances of WC-11Co cemented carbides sliding against different rocks”. Mater. Sci. Eng. Powder Metall., vol. 3, pp. 398-405, July 2015.
[4] Q. Su, S. Zhu, H. Ding, Y. Bai, P. Di. “Effect of the additive VC on tribological properties of WC-Al2O3 composites”. Int. J. Refract. Met. Hard Mat., vol. 75, pp. 111-117, September 2018.
[5] Q. Su, S. Zhu, H. Ding, Y. Bai, P. Di. “Friction and wear behaviors of WC-Al2O3 composite paired with Si3N4 ceramics and YG6 cemented Carbide”. Mater. Mech. Eng., vol. 43, pp. 50-54, June 2019.
[6] Q. Su, S. Zhu, H. Ding, Y. Bai, P. Di. “Comparison of the wear behaviors of advanced and conventional cemented tungsten carbides”. Int. J. Refract. Met. Hard Mat., vol. 79, pp. 18-22, February 2019.
[7] Y. Duan, S. Qu, X. Li. “Effect of quench-tempering conditions prior to nitriding on microstructure and fretting wear mechanism of gas nitrided X210CrW12 steel”. Surf. Coat. Technol., vol. 360, pp. 247-258, February 2019.

[8] Y. Duan, S. Qu, S. Jia, X. Li. “Evolution of wear damage in gross sliding fretting of a nitrided high-carbon high-chromium steel”. Wear, vol. 464-465, pp. 203548-203560, January 2021.