Friction and Wear Properties of HfC-WC-Co Cemented Carbide

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Abstract. HfC-WC-Co composites were prepared by cold press forming and hot press sintering, and their relative density, hardness and flexural strength were tested. The friction and wear experiments were carried out with the MMW-1 vertical universal wear tester. The friction coefficient and wear amount of the material were tested. The microstructure and phase of the wear surface were observed and analyzed by SEM, ultra depth of field microscope and XRD. The results show that the particles extraction, furrow and exfoliation caused by annular microcracks are the main forms of WC-Co composite wear. And appropriate amount of HfC can effectively improve the relative density, hardness and fracture toughness of materials. At the same time, it can effectively improve the sintering quality, inhibit the microcrack initiation and expansion, reduce the phenomenon of particle extraction and furrowing, and improve the friction and wear characteristics.

1. Introduction
WC-Co cemented carbide has excellent properties such as high hardness, high strength, high modulus of elasticity, low coefficient of thermal expansion, strong wear resistance and corrosion resistance. Therefore, it is widely used in the wear-resistant fields such as cutting tools, nozzles and drilling [1,2,3,4]. However, due to its inherent brittleness [5,6], its application and development in the engineering field is greatly limited. Therefore, the development of wear-resistant WC-Co hard alloy with high toughness and high hardness has practical application significance. The researchers found that adding appropriate amount of TaC [7], Cr2C2 [8], VC [9], TiC [10] to WC-Co cemented carbide can effectively improve the friction and wear properties and enhance the wear resistance. Previous studies have found that HfC may also be an ideal particle reinforcement for WC cemented carbide. HfC with NaCl-type face-centered cubic lattice structure has the characteristics of high melting point, good thermal conductivity, small thermal expansion coefficient (6.6×10-6/℃), high hardness (26.1Gpa) and good impact performance [11,12], what’s more, It has strong phase stability, and has good compatibility with WC, which can change the state of Co binder, thereby improving the brittleness and wear resistance of WC-Co cemented carbide.

Therefore, in this paper, WC-Co-HfC cemented carbide is sintered by vertical vacuum hot-pressing sintering furnace, and then the relative density, hardness and fracture toughness of the material are tested. And friction and wear testing machine are used to test the friction coefficient and wear mass loss of the material. The super-depth three-dimensional microscope and scanning electron microscopy (FE-SEM) were used to observe the morphology after wear. The surface of the wear scar was detected.
and analyzed by XRD. The effect of HfC on the friction and wear characteristics of WC-Co cemented carbide was revealed.

2. Experiments

2.1. Material preparation
The base material of the experiment is WC, the binder is Co, and the grade is YG8. Adding HfC enhanced phase with mass fraction of 0%, 0.5%, 1.0%, 1.5%, 2%, 2.5% in the matrix. First, the matrix and additive materials were calculated according to the mass fraction ratio, weighed on an electronic analytical balance and placed in an agate tank of a planetary mill for ball milling. The ball mill tank is evacuated and then filled with argon. The argon concentration is 0.075 MPa, the ball milling time is 6 hours, the rotation speed is 360r/min, and the ball-to-material ratio is 5:1. Next, the above-mentioned ball-milled material is placed in a mold as shown in Figure.1 and cold-pressed at a cold pressure of 100 MPa, the pressure rate of 3 mm/min, and the pressure holding time of 120 s; Finally, the cold-formed sample is put into a graphite mold and sintered in a vacuum hot-pressing sintering furnace. The hot-pressing sintering process is shown in Figure 2. Samples cooled to room temperature were subjected to coarse grinding, fine grinding, fine grinding, polishing, ultrasonic cleaning, drying, and the like, and then subjected to relevant performance tests.

![Figure 1](image1.png)

**Figure 1.** Schematic diagram of cold forming for sample in the mould.

![Figure 2](image2.png)

**Figure 2.** Sintering process.

2.2. Experimental methods
The hardness of the samples was measured using a 1000 N-dimensional microhardness tester, and each set of samples was averaged ten times. Before the measurement, first grind and polish on the pre-grinding machine with 200, 800, 1200 mesh sandpaper. The fracture toughness test was carried out on a CMT 5105 micro-control servo universal testing machine with a span of 20 mm using a three-point bending method. The experimental loading rate was 0.6 mm/min, and 10 samples were tested in each group, and the arithmetic mean value was obtained. The relative density of the sintered samples was tested by the Archimedes test method, and each group was measured 10 times to obtain an average value. The friction and wear test was carried out using the MMW-1 vertical universal wear tester. The test conditions were normal temperature and no lubrication. The load required for the experiment was applied by the loading rod P=200 N, and the experimental time was t=240 min. At the same time, the test sample was rotated by the motor to make the tested sample rub against the dual surface. The friction force F was measured by the experimental machine. The friction coefficient was obtained according to the formula $\mu=F/P$, and the friction coefficient was taken as the average value of the experimental results. An electronic scale with an accuracy of 0.1 mg was selected to measure the mass of the sample before and after the experiment. The difference in mass before and after was the amount of wear during the experiment. The wear amount was taken as the average value of 10 measurements. The product of the wear scar surface was detected and analyzed by means of a Rigaku D/Max-2550PC.
type diffractometer (XRD) the microstructure of the sample was observed and analyzed by S-4800 scanning electron microscopy (FE-SEM).

3. Results and analysis

3.1. Relative density and mechanical properties of the sample

The relative density of the materials is shown in Table 1. From the table we can see that with the addition of HfC, the relative density of the samples begins to increase. When the mass fraction of HfC is 1.5%, the relative density reaches the maximum, and HfC continues to be added, and the relative density begins to decrease. This indicates that the addition of HfC can effectively improve the sintering quality of the sample, increase the density, and reduce the generation rate of the pores.

| HfC (wt%) | 0    | 0.5  | 1.0  | 1.5  | 2.0  | 2.5  |
|----------|------|------|------|------|------|------|
| Relative density (%) | 81.23 | 94.60 | 94.70 | 95.67 | 95.05 | 93.28 |
| Hardness (HV) | 763.43 | 844.13 | 930   | 973.87 | 844.2 | 654.8 |
| Fracture toughness (MPa·m$^{1/2}$) | 13.34 | 14.67 | 15.56 | 16.45 | 15.12 | 12.45 |

The hardness and fracture toughness of the material are shown in Table 1. It can be seen from the figure that the hardness and fracture toughness of the composite are significantly changed when HfC is added. When the HfC mass fraction is 1.5%, the hardness and fracture toughness of the composites are increased by 11.84% and 59.05%, respectively, compared to the samples without HfC. With the continued addition of HfC, the flexural strength and fracture toughness of the composites have a decreasing trend.

3.2. Friction and wear properties

Figures 3 and 4 show the changes in friction factor and wear amount of samples with different HfC contents. It can be seen from Fig. 3 that under the same rotational speed and load, the friction coefficient of the sample material increases first and then decreases with the increase of HfC content, and the friction factor is between 0.33 to 0.51. It can be seen from Figures 4 that under the same rotational speed and load, the wear amount begins to decrease with the increase of HfC. When the HfC mass fraction is 1.5%, the wear amount is minimized, and the wear amount is 0.038%. The amount of wear was reduced by 24% compared to the sample without HfC added. However, the addition of HfC continued, and the amount of wear did not decrease.

![Figure 3. Sample friction coefficient diagram.](image)

![Figure 4. Mass loss.](image)
improve the crack resistance of the sample under alternating load. As can be seen from Figure 5(a) and (b), the wear performance of Fig. 5(b) is significantly better than that of Figure 5(a).

![Figure 5. Topography of the sample after wear.](image)

Figure 6 is an XRD pattern of cemented carbide samples without HfC and 1.5% HfC added by Rigaku D/Max-2550PC diffractometer after abrasion. The surface of the sample to which HfC was not added (as Figure 6(a)) showed a strong WO₃ diffraction peak, while the peak of WC was weak, indicating that the hard phase WC in the composite had been decomposed by oxidation. The friction surface of the sample with 1.5% HfC added (as Figure 6(b)) also showed a strong WO₃ diffraction peak after abrasion, but the difference is that the peak of WC is stronger than the diffraction peak of WC in Figure 6(a), indicating that the hard phase WC in the sample to which 1.5% HfC is added is less decomposed. The diffraction peaks of CoO in Figure 6 (a) and (b) show that Co also undergoes an oxidation reaction during abrasion. During the friction process, the heat generated by the friction of the sample is much larger than the heat dissipated, so that the temperature of the sample rises and an oxidation reaction occurs, so that the surface is covered with an oxide film. During the friction process, the substrate is subjected to load, and the friction will be carried out on the oxide film. The elastic modulus and hardness of the WC oxidation products WO₃ and Co oxidation products CoO (or Co₃O₄) are lower than those of the matrix material. Therefore, the oxide film attached to the base material is easily broken. After the destruction, the new matrix exposed in the air acts on the surrounding environment to form a new oxide film. This repeated destruction and formation causes the surface wear of the sample to be intensified. The diffraction peak of HfO₂ does not appear in Figure 6(b), indicating that HfC does not undergo oxidation reaction, mainly because HfC has extremely strong phase stability from room temperature to melting point, and it is extremely difficult to react with oxygen. The elastic modulus of HfC and its hardness are also greater than that of the matrix oxide, and HfC replaces the matrix to wear, thereby improving the surface friction properties of the sample. And HfC can change the state of Co binder, making Co distribution more uniform in the matrix material, because the oxidation temperature of Co (350 °C) is much lower than the oxidation temperature of WC (500 °C). Therefore, the sample first generates an oxide of Co, and the oxide of Co in turn suppresses the formation of WO₃, thereby improving the friction properties of the samples.

Figure 7 shows the wear profile of the sample with 1.5% HfC added and no HfC added. As shown in Figure 7 (a) and (c), the sample to which 1.5% HfC was added had a good sintering quality. During the friction and wear process, the hard phase particles on the surface of the sample peel off from the friction surface under the action of the pressing force and the shearing force to form pits. At the same time, the peeled hard phase remains between the friction pairs to form abrasive grains, and the surface of the material forms a furrow during the relative sliding process. At the same time, the heat generated by the friction softens the binder phase of the sample, destroys the stability of the hard particles, and aggravates the abrasive wear. As shown in Figure 7(b) and 7(d), compared with Figure. 7(a) and 7(c), the sample to which no HfC was added was inferior in sintered quality, and a porous hole was formed on the surface. During the sliding contact with the stainless steel on the grinding head, the normal and
tangential stresses on the friction surface cause the hard particles to collide with each other, resulting in microcracks inside the grain boundaries or grains. Under the action of alternating loads, the microcracks continue to expand until they intersect each other, forming a ring-shaped crack, and finally pulling out. At the same time, in the process of microcrack expansion to form a ring-shaped crack, two processes including the extraction of the particles to form pits and the wear of the abrasive grains to form the furrow are also accompanied.

4. Conclusions
A study of the effect of HfC on Friction and Wear Properties of WC-Co Cemented Carbide have been conducted and the conclusions are listed as follows:

(1) Appropriate amount of HfC can effectively improve the friction coefficient and mass loss of WC-Co composites, both of which increase first and then decrease, and the friction factor is between 0.33 to 0.51. When the mass fraction of HfC is 1.5%, the friction coefficient and the mass loss of wear
are both at a minimum, and it has the advantages of high hardness and high fracture toughness. The furrow is shallow and the friction and wear performance is better.

(2) During the friction and wear process, the surface material of the sample is oxidized to form WO$_3$ and CoO oxide film, which aggravates the wear process, and the addition of HfC can inhibit the formation of WO$_3$, thereby improving the friction and wear properties.

(3) The wear of WC-Co composites is mainly achieved by particle extraction, furrows and exfoliation caused by annular microcracks. The addition of HfC can effectively improve the sintering quality, inhibit the microcrack initiation and expansion, reduce the phenomenon of particle extraction and furrowing, and improve the tribological properties.

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