Effect of Cobalt Content on Microstructures and Wear Resistance of Tungsten Carbide–Cobalt-Cemented Carbides Fabricated by Spark Plasma Sintering

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Abstract. We researched tungsten carbide–cobalt (WC–Co)-cemented carbides without binder and with little binder and sintered by spark plasma sintering with 0 wt. %, 0.2 wt. %, 0.5 wt. % and 0.8 wt. % Co at different temperatures. The microstructures, hardness, fracture toughness and wear resistance of the WC–Co-cemented carbides were investigated by scanning electron microscopy and mechanical property tests. The wear resistance of WC–Co-cemented carbides with little to no binder is acceptable and it decreases with increase in Co content. There is no significant difference in wear resistance at 0 wt. % and 0.2 wt. % Co content. By analysing the friction and wear mechanism, it can be concluded that because the Co phase was extruded first, the stability of the WC hard base was disrupted, the WC phase desquamated and abrasion occurred. WC-cemented carbide with 0.2 wt. % Co is the most suitable material. The best results were achieved at 1680°C with 2333 HV30 and 6.82 MPa.m1/2

1. Introduction

Tungsten carbide–cobalt (WC–Co)-cemented carbides are used widely for offshore oil exploitation engineering, in the mechanical industry and in aerospace engineering because of their high hardness, fine red hardness, suitable wear resistance and fracture toughness[1-3]. A significant improvement in mechanical properties can be achieved in cemented carbides with a finer grain size. Developments in the cemented carbide industry have led to nanomaterial additions to improve the mechanical properties of WC–Co-cemented carbides [4]. WC–Co-cemented carbides are composed mainly of a metallic ceramic and a cobalt binder and the Co content affects the hardness, fracture toughness and wear resistance of WC–Co-cemented carbides [5]. Therefore, WC-cemented carbides (Co content of less than 1wt. %) with no binder and little binder show a significant improvement in mechanical properties.

The optimum sintering method for WC–Co-cemented carbides is spark plasma sintering (SPS), which enables a powder compact to be sintered by Joule heat and high-pulsed electric current through the compact. In recent years, SPS has been used widely as a sintering method for different materials, including WC–Co-cemented carbides [6, 7]. WC-cemented carbides with little binder and as fabricated by SPS are compact and uniform; they have fine mechanical properties and an excellent wear resistance.
We have studied the microstructure, hardness, fracture toughness and wear resistance of WC-cemented carbides as sintered by SPS with 0 wt. %, 0.2 wt. %, 0.5 wt. % and 0.8 wt. % Co contents at different temperatures. Four specimens were investigated and compared to establish the optimum Co addition to the WC powder and the wear mechanism of the WC–Co-cemented carbides with little binder.

2. Experimental procedure

2.1. Materials
Table 1 lists the main characteristics of the WC powder (shown in Fig. 1a) and Co powder (shown in Fig. 1b) that were used as raw materials. Table 2 describes the nominal composition of the cemented carbides. The WC–Co composite powders were prepared using a wet ball-milled method in a high-energy planetary ball mill in which the milling ball was WC media of 5 mm and the liquid medium was ethanol. The ball-to-powder ratio was 5:1 and the rotational speed was 400 rpm. When milling was completed, the powder mixture was placed in a drying oven for 2 h at 70°C, after which the dried powder was sieved twice, using a 100-mesh (149-μm) sieve.

The sieved powders were poured into a graphite mold and placed in an SPS apparatus. Sintering was performed by applying a pulsed electric current to the SPS system. Table 3 shows the technological parameters used in the SPS process.

| Powder | Chemical composition (wt. %) | D50/μm (producers’ data) | Purity | Supplier |
|--------|-----------------------------|--------------------------|--------|----------|
| WC     | 6.11 Ct; 0.04 Cf; 0.30 VC; 0.5 Cr3C2; WC balance | 2.41 | 99.9% | Jinlu Tungsten Co. Ltd., China |
| Co     | -                           | 0.8                      | 99.9% | Nanjing Hanrui Co. Ltd., China |

Table 2. Nominal composition of alloys (mass %)

| Specimen Name | Co (Wt. %) | WC-Cr3C2-VC (Wt. %) | Theoretical density (g/cm³) |
|---------------|------------|----------------------|-----------------------------|
| WC-0Co        | 0          | 100                  | 15.556                      |
| WC-0.2Co      | 0.2        | 99.8                 | 15.543                      |
| WC-0.5Co      | 0.5        | 99.5                 | 15.523                      |
| WC-0.8Co      | 0.8        | 99.2                 | 15.503                      |

Table 3. Parameters used in SPS process

| Specimen Name | Temperature (°C) | Pressure (MPa) | Holding time (min) | Heating rate (°C/min) |
|---------------|------------------|----------------|--------------------|-----------------------|
| WC-0Co        | 1700             | 50             | 5                  | 200                   |
| WC-0.2Co      | 1680             | 50             | 5                  | 200                   |
| WC-0.5Co      | 1600             | 50             | 5                  | 200                   |
| WC-0.8Co      | 1500             | 50             | 5                  | 200                   |

2.2. Characterization of WC–Co-cemented carbides
The microscopic morphology of the WC–Co composite powders was characterized by scanning electron microscopy (SEM). Phase analysis was implemented by using PANalyticalX’Pert PRO X-ray diffraction (XRD) at 2θ angles from 20° to 80°. The WC–Co-cemented carbide morphology was
studied by using a JSM 7500F field emission SEM. The specimen density was measured by immersion in water using the Archimedes principle, to calculate the relative density of WC–Co-cemented carbides with different Co contents. The hardness and fracture toughness were measured using the Vickers hardness and fracture toughness tester or the Vickers indenter under a constant load of 5 kg. For accuracy, specimens were polished to a near-mirror finish and were checked for face parallelism before testing. All mechanical property tests were conducted three times and the arithmetic mean value from the three tests was calculated.

![Figure 1. SEM images of (a) WC powder, (b) Co powder.](image)

2.3. Friction and wear test

According to the ASTM G133-05 standard, reciprocating wear tests of WC–Co-cemented carbides were evaluated by using a Tripoli micro-tribemate in a ball-on-flat method. Four wear test specimens were ground to a finish of 1000#SiC abrasive papers, and were cut into specimens of (15 × 15 × 10 mm). Before and after each test, the surface was cleaned by ultrasound in acetone solution, and dried immediately with hot air. WC balls (diameter: 8.0 mm, hardness: 90.5 HRA) were used as counter bodies. Room-temperature dry tests (2 h) were performed under a normal load of 60 N, an amplitude of 5 mm and a frequency of 5 Hz.

After friction testing, the worn surfaces were studied by SEM and the wear track was analyzed by using white-light interferometry. The specific wear rate was studied as a measure of wear volume loss and total sliding distance, which was calculated as the ratio of wear volume loss over the normal load multiplied by the total sliding distance (mm³/Nm).

3. Results and discussion

3.1. Characterization and microstructures of WC–Co-cemented carbides

Figure 1 shows the morphological detail of the WC and Co powders. Both powders are uniform and fine, which yields a high surface energy for the solid WC particles and a fine sintering performance. XRD patterns of WC–Co-cemented carbides with different Co contents are shown in Fig. 2. WC phase peaks are clear, but Co phases are difficult to locate, possibly because very little Co was added, so they are relatively weak and therefore, are covered by the WC peak.

Figure 3 shows the SEM images of the WC-cemented carbides that contain 0 wt. %, 0.2 wt. %, 0.5 wt. % and 0.8 wt. % Co. At their respective temperatures and pressures, the four specimens exhibit good crystal structures, clear grain boundaries and a small and uniform grain size. The cohesive phases with different Co contents can sinter homogeneous and compact material specimens. As the Co content increases, the WC–Co-cemented carbide grain microstructure becomes more uniform and
compact; however, when the content exceeds 0.2 wt. %, the grain size variation decreases, and no change is apparent between the final two specimens, WC-0.5Co and WC-0.8Co. Therefore, further addition of Co to the system will not lead to any further improvement in performance of the cemented carbides.

Figure 2. XRD patterns of WC–Co-cemented carbides with Co content of (a) 0 wt. %, (b) 0.2 wt. %, (c) 0.5 wt. %, (d) 0.8 wt. %.

Figure 3. Microstructures of WC–Co-cemented carbides with Co content of (a) 0 wt. %, (b) 0.2 wt. %, (c) 0.5 wt. %, (d) 0.8 wt. %.
3.2. Mechanical properties
The variation in density and the porosity of the WC–Co-cemented carbides with different Co contents is shown in Fig. 4, as calculated using the Archimedes principle. According to the experimental results, the specimen density decreases with increasing Co content. The density of specimen WC-0Co is 15.498 g/cm³, whereas that of WC-0.8Co is lowest at 15.298 g/cm³. This occurs because the density of Co in the specimen is less than that of the WC. However, the actual density of each group differs little because the Co content in each cemented carbide is low. The porosity of the cemented carbides increases with increase in Co content, and the specimen compactness decreases accordingly. Porosity increases when the Co content increases to 0.50 wt. %, which may affect some mechanical properties adversely.

![Graph showing density and porosity vs. Co content](image1)

**Figure 4.** Dependence of density and porosity on Co content

![Graph showing Vickers hardness and fracture toughness vs. Co content](image2)

**Figure 5.** Dependence of Vickers hardness and fracture toughness on Co content

Hardness and fracture toughness are the two most important mechanical properties of cemented carbides. Figure 5 shows that with an increase in Co content, the specimen hardness decreased gradually, which shows that specimens with a greater Co content have a smaller Vickers hardness.
This occurs mainly because the Vickers hardness reflects the indentation-resistance ability of the WC–Co-cemented carbide, which is associated with the hard and binder phase contents and the WC solubility in the Co phase.

Conversely, the fracture toughness of the WC–Co-cemented carbides improves significantly with increasing Co content, which means that the fracture toughness of the four specimens increases with decreasing Vickers hardness. The fracture toughness of WC-0Co is lower than that of the other three specimens. The fracture toughness of WC-0Co is close to 3.98 MPa.m$^{1/2}$ and the fracture toughness’s of the other three specimens are similar in value. The main reason for this result is that the fracture toughness of the WC–Co-cemented carbides is affected by the WC grain size and the Co binding-phase content. When cracks propagate, the Co binding phase can still connect the cracks and apply a tensile stress to prevent crack expansion in the region near the crack tip. Therefore, Co addition can improve the fracture toughness of WC–Co-cemented carbides with little binder.

Therefore, WC-0.2Co exhibits a good microstructure and fine mechanical properties compared with the other three specimens, which affects the practical application of cemented carbide.

3.3. Wear properties and wear mechanism

During each test, the coefficient of friction was measured under the same conditions, and its variation was analysed after 4000 s of testing to remove the influence of the running-in period. Figure 6 shows the variation in friction coefficient of the WC–Co-cemented carbides with different Co contents. The friction coefficient of each specimens increases with increasing Co content. The average friction coefficient of the WC–Co-cemented carbides without Co is ~0.16, and a higher friction coefficient of approximately 0.21 was observed for WC–Co-cemented carbides with 0.8 wt. % Co. With increase in Co content, a higher specimen friction coefficient may result from the lower hardness. WC–Co-cemented carbides with 0.8 wt. % Co exhibited the smallest average grain size, which causes higher applied-stress propagating dislocations through the material and results in the highest friction coefficient.

![Figure 6. Relationship of frictional coefficient and time for each group of specimens](image)

The mean values of the volume wear rate of WC–Co-cemented carbides with different Co contents are shown in Fig. 7. The volume wear rate of WC–Co-cemented carbides without Co is $3.13 \times 10^{-8}$ mm$^3/(NM)$ and that of the other specimens was $3.43 \times 10^{-8}$ mm$^3/(NM)$, $5.21 \times 10^{-8}$ mm$^3/(NM)$ and $6.22 \times 10^{-8}$
mm$^3/(N\cdot M)$. When the Co content was 0 wt. % and 0.2 wt. %, there was no significant difference in wear resistance. The volume wear rate of the specimens increases with increasing Co content and this increase is distinct when the Co content exceeds 0.2 wt. %. Therefore, when the Co content exceeds 0.2wt%, the WC–Co-cemented carbide wear resistance decreases significantly.

![Figure 7. Volume wear rate for each specimen](image)

Figure 7. Volume wear rate for each specimen

Figure 8 shows the two-dimensional non-contact surface mapping of the wear tracks. The width and depth increase with increase in Co weight percentage. Excessive Co addition will reduce the material wear resistance. Figure 9 shows micrographs of the worn surface from a low to a high concentration. Some holes exist as caused by grain peeling in each worn surface. WC-0Co and WC-0.2Co have less exfoliation pits, whereas WC-0.5Co and WC-0.8Co show an obvious flaking on the surface. Peeling on the WC-0.8Co surface is serious with a large peeled area.

![Figure 8. Two-dimensional non-contact surface mapping of wear tracks with Co content of (a) 0 wt. %, (b) 0.2 wt. %, (c) 0.5 wt. %, (d) 0.8 wt. %](image)

Figure 8. Two-dimensional non-contact surface mapping of wear tracks with Co content of (a) 0 wt. %, (b) 0.2 wt. %, (c) 0.5 wt. %, (d) 0.8 wt. %.

WC–Co-cemented carbides are comprised mainly of a metallic ceramic and a cobalt binder. The WC phase, as the hard phase, possesses a high hardness and results in deformation, whereas the Co
phase is relatively soft and prefers to deformation plastically under a heavy load. Because the Co phase was extruded first, the WC hard base stability was reduced. When the contact stress exceeds its fracture toughness limit, WC grains are broken and peel off, which creates a peeling pit on the worn surface. The fine abrasive debris consists of pulverized detached WC particles that form a micro-cutting function in the sample surface. The peeling and micro-cutting phenomenon contribute to the material wear and tear. WC-0Co and WC-0.2Co specimens exhibit a lower volume wear rate and a stronger wear resistance. For WC-0.5Co and WC-0.8Co, the stability of the WC phase is affected by the increase in plastic deformation of the Co phase. Surface peeling is relatively obvious, and agrees with an increase in volume wear rate and the relatively weak wear resistance. Hence, for WC-0Co and WC-0.2Co, the wear mechanism is abrasive wear because of the low Co binder. For WC-0.5Co and WC-0.8Co, the main wear mechanism is adhesive wear by plastic deformation of the Co phase.

Figure 9. SEM micrographs of worn surface of WC–Co-cemented carbides with Co content of (a) 0 wt. %, (b) 0.2 wt. %, (c) 0.5 wt. %, (d) 0.8 wt. %.

4. Conclusion
WC–Co-cemented carbides are comprised mainly of a metallic ceramic and a cobalt binder, and the Co contents affect the hardness, fracture toughness and wear resistance of WC–Co-cemented carbides. The hardness and wear resistance of WC–Co-cemented carbides decrease as the Co content increases. However, the fracture toughness is improved as the Co content increases, which ensures a certain impact resistance of the WC–Co-cemented carbides. By analyzing the friction and wear mechanism, it can be concluded that because the Co phase was extruded first, the WC hard base stability was reduced, the WC phase desquamated and abrasion occurred.

Therefore, Co addition should be controlled within a certain range and a 0.2 wt. % Co sample possesses a high hardness, good fracture toughness and wear resistance. Sintering is by SPS at 50 MPa, a maximum of 1680°C and a holding time of 5 min. The Vickers hardness of the sintered carbide reached 2333 HV30, and the fracture toughness achieved 6.82 MPa·m^1/2.

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