Effect of Mo content on microstructure and mechanical properties of WCoB-TiC based cermets

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Abstract. The effect of Mo content on microstructure and mechanical properties of WCoB-TiC based cermets fabricated by boronizing sintering reaction was investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray analysis (EDX). Results showed that phase compositions of all the WCoB-TiC cermets with 0 to 20 wt% Mo addition were composed of W₂CoB₂, TiC, TiB₂, and the (211) diffraction peak of W₂CoB₂ phase was continuously shifted towards a high angle with Mo content, indicating that (W, Mo)₂CoB₂ solid solutions in cermets with 5-20 wt% were formed. Moreover, the cores of W₂CoB₂ grains were enriched in Mo, while rims of W₂CoB₂ grains had a relatively lower Mo content, resulting in the formation of a core/rim structure. As Mo content increased, the porosity gradually dropped, while the relative density continuously increased, due to the improved wettability of liquid phase in the hard phase. In addition, average grain sizes dropped initially and then rose gradually with Mo content. An increase in average grain sizes was due to the coalescence and growth of hard-phase particles. The WCoB-TiC cermet with an 10 wt% Mo addition showed excellent comprehensive mechanical properties with a transverse rupture strength of 815 MPa, a Rockwell hardness of 93.4 HRA, and a fracture toughness of 12.5 MPa·m⁰.⁵, respectively.

1. Introduction

WCoB-based cermets are a typical type of ternary boride material, showing great potential in engineering applications with high hardness, high melting point, extremely good oxidation resistance, and good chemical stability [1-3]. Owing to these outstanding properties, this kind of material can be applied as cutting and forming tools, injection models and wear-resistant coating [4-6]. However, it is hard to prepare WCoB based cermets due to the fact borides usually show poor sinterability, extreme brittleness, and strong reactivity with metals [7, 8]. Fabricating WCoB-TiC based cermets by the boronizing sintering reaction is an effective method to obtain high performance, which attracted much attention in recent years.

WC, TiB₂, and Co powders are usually used as raw material in the preparation of WCoB-TiC cermets by boronizing sintering reaction, and the content of each raw material plays a key role determining the microstructure and mechanical properties of WCoB-TiC cermets [9]. The effect of initial Co content on microstructure and mechanical properties of WCoB-TiC cermets was studied, and hardness of the material with a 18 wt% Co content reached the maximum value [10]. However, other mechanical properties including transverse rupture strength and fracture toughness were not
reported. Moreover, mechanical properties of TiB₂–WC–Co composite were improved by adding a 30 wt% TiC. Nevertheless, fracture toughness value of 6.5 MPa m⁰.⁵ was relatively low [11].

In addition, it has been reported that such additives as VC, Cr₂C₃, and Sm₂O₃ can refine the grain size and improve mechanical properties [8, 12]. With a Cr₂C₃ content increasing from 0 to 0.9wt%, mechanical properties of WCoB–TiC based cerments linearly increase [8]. WCoB-TiC based cerments doped with 0.3 wt% VC and 0.3 wt% Cr₂C₃ by hot-pressing at 1420 °C show the optimum mechanical properties and best dry sliding wear-resistance [12]. Moreover, grain size was refined and mechanical properties of WCoB-TiC cerments were improved by adding 0.3 wt% Sm₂O₃ [8]. Apart from these additives, Mo is an important alloy element additive and can reduce the wetting angle of liquid Co phase on TiC particles to zero, refining grain size and improving higher mechanical properties [13-15]. Therefore, it is considered that relative density, microstructure, and mechanical properties of WCoB-TiC based cerments may be improved by introducing a suitable content of Mo.

In this study, WCoB-TiC based cerments were fabricated by the boronizing sintering reaction using WC, TiB₂, Co, Mo powders as raw materials. The effect of Mo content on phase composition, microstructure, and mechanical properties was investigated.

2. Experimental

Commercial available WC, TiB₂, Co, Mo powders were used as raw materials. Characteristics of these powders are listed in table 1.

| Powders | WC   | TiB₂ | Co   | Mo   |
|---------|------|------|------|------|
| Particle size/µm | 4.45 | 6    | 1.46 | 2.99 |
| Oxygen content/wt.% | 0.042 | 0.44 | 0.45 | 0.10 |

In this study, the mole mass ratio of WC, TiB₂, and Co of all the cerments is designed as 1:2:2. Compositions of experimental samples with varying Mo content are presented in table 2. The powders were weighed and planetary milled in ethanol at 260 rpm for 24 h. After mixing, the slurries were dried and sieved. Subsequently, theses powders were compacted under 300 MPa. Finally, the compacts were sintered at 1400 °C for 1 h under vacuum. A vacuum of about 5.0 Pa was maintained during sintering.

| Cermets | WC   | TiB₂ | Co   | Mo   |
|---------|------|------|------|------|
| A       | 42.75| 30.98| 26.27| 0    |
| B       | 40.61| 29.43| 24.96| 5    |
| C       | 38.48| 27.88| 23.64| 10   |
| D       | 36.34| 26.33| 22.33| 15   |
| E       | 34.20| 24.78| 21.02| 20   |

Hardness was measured with a standard Rockwell hardness testing device according to ISO 3873. Transverse rupture strength (TRS) was determined using three-point bend test according to ISO 3327. Fracture toughness (KIC) was measured by indentation method using the expression derived by Shetty et al [16]. The above test values were obtained as the average of five measurements. Phase identification was conducted by XRD (Ultima IV, Rigaku, Japan) with Cu Kα radiation. Microstructure of polished samples was observed with SEM (S-3400N, Hitachi, Japan) in BSE mode. The distribution of the elements was determined by EDX (GENESIS2000) combined with SEM.

3. Results and discussion

3.1. Phase composition
Figure 1 shows XRD patterns of WCoB-TiC cermet with varying Mo content. As shown in Figure 1, the phase compositions of cermet A without Mo addition were composed of W_2CoB_2, TiC, TiB_2. The appearance of W_2CoB_2 and TiC phase was mainly due to reaction proposed in [17]:

\[
\begin{align*}
WC + xCo + TiB_2 \rightarrow WCoB + TiC + Co_{x-1}B \\
WCoB + WC \rightarrow Co_6WC_6 + W_2CoB_2 \\
WCoB \rightarrow W_2CoB_2 + Co \\
Co_6WC_6 + WCoB + Ti \rightarrow W_2CoB_2 + TiC
\end{align*}
\]

In addition, TiB_2 phase was also detected, indicating that TiB_2 could not react completely, which was owing to relatively low initial Co content [18]. Moreover, as Mo content increased, the phase compositions of cermets B-E were the same as that of cermet A, demonstrating that Mo addition did not change the phase composition of WCoB-TiC cermet.

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Figure 1. XRD patterns of WCoB-TiC cermet with various Mo content.

The (211) diffraction peak angles of W_2CoB_2 phase of WCoB-TiC cermet with different Mo content are listed in Table 3. As Mo content increased, (211) diffraction peak of W_2CoB_2 phase continuously shifted towards a high angle, implying that the lattice parameter of W_2CoB_2 phase decreased. Since atomic radius in cermet was W (0.1371 nm) > Mo (0.1363 nm) > Co (0.125 nm) > B (0.097 nm) [19], it could be concluded that Mo reacted with W_2CoB_2 to form (W, Mo)_2CoB_2 complex solid solutions.

Table 3. The (211) diffraction peak angles of W_2CoB_2 phase of cermet with different Mo content.

| Mo content (wt%) | 0  | 5.0 | 10.0 | 15.0 | 20.0 |
|------------------|----|-----|------|------|------|
| 2θ (Degree)      | 42.998 | 43.012 | 43.030 | 43.043 | 43.088 |

3.2. Microstructure

Figure 2 shows optical micrographs of WCoB-TiC cermet with varying Mo content. As shown in figure 2, the porosity of WCoB-TiC cermet decreased, while the relative density increased with the Mo content, which indicated that the addition of Mo improved the wettability of liquid phase to hard phase during sintering. It has been reported that Mo could reduce porosity and refine grain size in WC-TiC-Co cemented carbides, TiC-Co cermet, and Ti(C, N)-Co cermet [13-15]. In WC-TiC-Co cemented carbides, it was found that Mo could improve the wettability of liquid phase in TiC hard phase [13]. Similarly, in TiC-Co cermet and Ti(C, N)-Co cermet, Mo had been proven to reduce the wetting angle of liquid binder phase on carbonitride grains and result in finer grains and higher mechanical properties [15, 16]. Combined with the XRD results in figure 1, a certain amount of TiC was formed in all the cermet A-E after sintering at 1400 ℃, since the wettability of liquid Co binder phase to TiC hard phase was greatly improved by adding Mo, the porosity of cermet decreased, while the relative density increased with the Mo content.

Figure 3 shows SEM-BSE images of WCoB-TiC cermet with different Mo content. As shown in figure 3, microstructure of all the WCoB-TiC cermet was composed of bright W_2CoB_2, gray TiC, and black TiB_2 grains [18]. The volume fraction of gray TiC grains and black TiB_2 grains decreased when
Mo content increased, while that of bright $\text{W}_2\text{CoB}_2$ grains increased, as seen in figure 3. Moreover, as Mo content increased, the average grain size in cermet firstly decreased, followed by an increase. When Mo content was 5 wt%, the average grain sizes reached the minimum value. The decrease in average grain sizes was due to the improvement of wettability of liquid Co binder phase to TiC hard phase. When Mo content was equal or exceeded 10 wt%, grains aggregated and coalesced obviously, which resulted in the increase in average grain sizes. Overall, microstructure of cermet C with 10 wt% Mo content was most homogeneous.

Figure 2. Optical micrographs of $\text{WCoB}-\text{TiC}$ cerments with varying Mo content: cerments (a)-(e).

Figure 3. SEM-BSE images of $\text{WCoB}-\text{TiC}$ cerments with different Mo content: cerments (a)-(e).

Remarkably, the shape of $\text{W}_2\text{CoB}_2$ grain changed obviously with the Mo content. In cermet A without Mo addition, as shown in figure 3 (A), $\text{W}_2\text{CoB}_2$ grains were extremely irregular in shape and aggregated into abnormally large grains. When Mo content was 5 wt%, the shape of $\text{W}_2\text{CoB}_2$ grains changed into spherical, the amount of large grains with irregular shape decreased while the amount of small grains with irregular shape increased. When Mo content reached or exceeded 10 wt%, $\text{W}_2\text{CoB}_2$ grains obviously aggregated, resulting in coarse grains with irregular shape. Meanwhile, as shown in figure 3 (b)-(e), $\text{W}_2\text{CoB}_2$ grains in cerments with a 5-20 wt% Mo addition exhibited a core/rim structure, which was similar to Ti(C, N)-based cerments [20]. The cores appeared to be light gray while the rim was bright. Obviously, the volume fraction of light gray cores increased with the Mo content.

In order to elucidate the formation mechanism of the core/rim structure, cermet B with 5 wt% Mo addition was chosen to be further analyzed by EDX analysis. The Mo content in each phase of cermet B is listed in table 4. Both TiC and TiB$_2$ phases only contained a small amount of Mo and most of Mo was demonstrated to exist in $\text{W}_2\text{CoB}_2$ phase, indicating that Mo mainly dissolves into $\text{W}_2\text{CoB}_2$ phase. Moreover, the cores of $\text{W}_2\text{CoB}_2$ phase were proven to be enriched in Mo (19.45 wt%) and the rims of $\text{W}_2\text{CoB}_2$ phase had a relatively lower Mo content (3.34 wt%). While $\text{W}_2\text{CoB}_2$ phase was formed at relatively lower temperature [19], Mo would continuously dissolve in $\text{W}_2\text{CoB}_2$ phase, resulting in the formation of ($\text{W, Mo})_2\text{CoB}_2$ solid solution with a higher Mo content. As sintering proceeded, the
content of liquid Co binder phase decreased continuously [10], and thermodynamic equilibrium conditions were broken, \((W, Mo)_2CoB_2\) relatively poor in Mo precipitated around the early formed \((W, Mo)_2CoB_2\) solid solutions, leading to the formation of a core/rim structure. Based on different color contrast in SEM-BSE images, the \((W, Mo)_2CoB_2\) solid solution enriched in Mo corresponded to light-gray core, while the \((W, Mo)_2CoB_2\) solid solution with a relative lower Mo content corresponded to the white rim.

### Table 4. Mo content in each phase of cermet B.

| Phase          | W_{2}CoB_{2} | TiC | TiB_{2} |
|----------------|--------------|-----|---------|
| White rim      | 3.34         | 1.32| 0.45    |
| Light gray core| 19.45        | 0.29| 0.12    |

Element concentrations in \((W, Mo)_2CoB_2\) phase of WCoB-TiC cermets B-E are listed in Table 5. With an increase in Mo content in WCoB-TiC cermets, Mo content in the gray core increased gradually, while W content in the gray core decreased gradually, and the change of other elements was relatively small. This was due to the fact that the process of Mo replacing W was easier to carry out with an increase in Mo content, resulting in the formation of \((W, Mo)_2CoB_2\) solid solution with a higher Mo content.

### Table 5. Element concentrations in \((W, Mo)_2CoB_2\) phase of WCoB-TiC cermets B-E.

| Element | Cermet B | Cermet C | Cermet D | Cermet E |
|---------|----------|----------|----------|----------|
| B       | 30.51    | 40.00    | 41.18    | 39.83    |
| Mo      | 19.45    | 32.23    | 33.74    | 34.76    |
| Ti      | 01.33    | 01.04    | 00.86    | 01.01    |
| Co      | 12.86    | 12.95    | 12.99    | 15.86    |
| W       | 35.85    | 13.78    | 11.23    | 08.54    |

3.3. Mechanical properties

Figure 4 shows mechanical properties of WCoB-TiC cermets with different Mo contents.

![Figure 4](image)

**Figure 4.** Mechanical properties of WCoB-TiC cermets with different Mo contents.

As shown in figure 4 (a), with an increase in Mo content, the hardness of WCoB-TiC cermets increased gradually, followed by a decrease. When Mo content was 10 wt%, the hardness of WCoB-TiC cermet reached the maximum value of 93.4 HRA. Hardness was influenced by the relative density and average grain sizes, relative density of cermet gradually increased with Mo content increasing from 0 to 10 wt%, leading to an increase in hardness. However, when Mo content exceeded 10 wt%, average grain sizes increased, resulting in the hardness drop. Similarly, with an increase in Mo content, the transverse rupture strength (TRS) of WCoB-TiC cermets increased gradually,
followed by a decrease. When Mo content was 5 wt%, TRS of WCoB-TiC cermet reached the maximum value. According to the Hall-Petch equation, TRS increased with the decrease in grain size. When Mo content was 5 wt%, the grain size of WCoB-TiC cermet B reached the minimum value. Therefore, TRS of WCoB-TiC cermet reached the maximum value. When Mo content exceeded 5 wt%, large particles were formed due to coalescence and growth, resulting in a decrease of TRS. As shown in figure 4(b), the fracture toughness (K_{IC}) increased with Mo content rising from 0 to 10 wt%, which was due to an increase in the relative density. However, a continuous increase in Mo content to 20 wt% resulted in a decrease of K_{IC}. When Mo content exceeded 10 wt%, some particles coalesced and grew up, becoming the source of cracks and resulting in the fracture toughness drop.

4. Conclusions

1. Phase compositions of all the WCoB-TiC cerments with different Mo content were composed of W_{2}CoB_{2}, TiC, TiB_{2}. (211) diffraction peak of W_{2}CoB_{2} phase continuously shifted towards a high angle with an increase in Mo content.
2. As Mo content in WCoB-TiC cerments increased, the porosity gradually decreased, while the relative density continuously increased, due to the improved wettability of liquid phase in the hard phase.
3. Mo was mainly diffused in W_{2}CoB_{2} phase, cores of W_{2}CoB_{2} grains were enriched in Mo, while rims of W_{2}CoB_{2} grains had a relatively low Mo content, resulting in the formation of a core/rim structure.
4. WCoB-TiC cermet with a 10 wt% Mo addition showed excellent comprehensive mechanical properties with a transverse rupture strength of 815 MPa, a Rockwell hardness of 93.4 HRA, and a fracture toughness of 12.5 MPa·m^{1/2}, respectively.

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