Preparation of WC–WB–W₂B Composites from B₄C–W–WC Powders and their Mechanical Properties

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Sintered composites of WC–WB–W₂B were prepared from B₄C–W–WC powders using a reactive energization hot-pressing technique that initiated a solid state reaction between B₄C and W. Below a WC mole fraction of 0.769 in the starting powder, WB and WC were formed according to the reaction B₄C + 5W + xWC = WB + (1 + x)WC, while WB, W₂B, and WC were produced above a mole fraction of 0.854. Densely sintered bodies were not obtained for pure WC. Composites of WC–WB–W₂B obtained at WC mole fractions between 0.854 and 0.956 were fully consolidated, having high Young’s modulus and Vickers hardness values, and a fracture toughness which were comparable to those of WC.

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1. Introduction

Tungsten carbide (WC) is the base material of cemented carbide WC–Co, which is used for cutting tools and wear-resistant parts. Adding binder Co for liquid phase sintering increases strength and fracture toughness, but decreases hardness and Young’s modulus. In many WC–Co base cutting and machining tools, a very hard compound, e.g., TiC or Ti(C,N), is coated on the surface to improve cutting tool performance.¹,² Recently, reducing the amount of Co has also been tried in an attempt to increase hardness; however, it is difficult to manufacture Co-free WC dense bodies by pressureless sintering. For example, in the case of the conventional binder-less cemented carbide WC–3% TiC–2% TaC, hot isostatic pressing is performed as an additional densification treatment after pressureless sintering.³) Since hot isostatic pressing requires much time and energy, it is necessary to find new sintering techniques or binders that densify the binderless cemented carbide without decreasing its hardness.

Barsoum and Hounsg,⁵) and Brodkin et al.⁵,⁶) succeeded in preparing dense TiB₂–TiC composites at 1600°C using reactive hot-pressing, although TiB₂ and TiC are both poor sinterable, like WC. In their fabrication process, TiB₂–TiC composites were sintered from powder mixtures of B₄C and Ti by the solid-state reaction B₄C + 3Ti = 2TiB₂ + TiC. During this forming reaction a lower carbide TiC₀.₅ and a highly deficient TiC₁₋ₓ phase were formed as intermediate phases. Both phases are more plastic at high temperatures than either TiB₂ or TiC and their formation promoted the densification of TiB₂–TiC composites under applied pressure. We successfully applied essentially the same technique to prepare dense composites of TiB₂–TiC₁₋ₓ,⁷) TiB₂–TiN,⁸) and TiB₂–Ti(CN).⁹) The W–B¹⁰) and W–C¹¹) systems have W₂B and W₂C as lower boride and carbide phases, respectively. If WC powders containing B₄C and W are used as the starting powder and the solid-state reaction B₄C + 5W = 4WB + WC is allowed to proceed during hot pressing, Co-free WC-based ceramics are sintered easily at relatively low temperatures. This study investigated the possibility of applying this reactive hot-pressing technique to the preparation of dense, Co-free, WC-based ceramics. Powder mixtures of B₄C–5W–xWC (x = 0 to 130) which caused the reaction B₄C + 5W + xWC = 4WB + (1 + x)WC were sintered using an energization hot-pressing technique that involved directly heating a die and a sample, and their sinterability and the mechanical properties of the sintered bodies were examined.

2. Experimental

Powders of B₄C (Rare Metallic, purity 99 mass%, average particle diameter 1.5 µm), W (Rare Metallic, purity 99.9 mass%, average particle diameter 6.0 µm), and WC (Japan New Metals, average particle diameter 0.75 µm, chemical composition (mass%): total carbon 6.10, free carbon 0.01, Fe 0.01, Mo 0.02, W bal.) were used as starting materials. B₄C has a wide composition range,¹²) chemical analysis of the B₄C used in this study gave a composition of B₄₀C₁₀. These powders were weighed to produce a composition, shown in Table 1, to cause the reaction

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B₄C + 5W + xWC = 4WB + (1 + x)WC \quad (x = 0 \rightarrow 130)
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<table>
<thead>
<tr>
<th>Powder mixture</th>
<th>Mole fraction of WC</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₄C–5W</td>
<td>0</td>
</tr>
<tr>
<td>B₄C–5W–9WC</td>
<td>0.600</td>
</tr>
<tr>
<td>B₄C–5W–20WC</td>
<td>0.769</td>
</tr>
<tr>
<td>B₄C–5W–35WC</td>
<td>0.854</td>
</tr>
<tr>
<td>B₄C–5W–80WC</td>
<td>0.930</td>
</tr>
<tr>
<td>B₄C–5W–130WC</td>
<td>0.956</td>
</tr>
<tr>
<td>WC</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 1 Starting powder mixtures.
and were then mixed in a zirconia mortar. The mixture was packed in a 40-mm-high graphite die with a 50-mm outer diameter and a 20-mm inner diameter. The die was surrounded by a thick graphite felt sheet for heat insulation. An energization hot-pressing machine (Sumitomo Coal Mines, SPS-2080), also called a spark-plasma sintering machine, was used for sintering. In this device, the graphite die and the sample are heated directly by a pulsating current applied between upper and lower graphite punches. Every sample was sintered under the following conditions: applied pressure 50 MPa, heating rate 50°C/min, sintering temperature 1650°C, and sintering temperature holding time 20 min. Using an optical pyrometer, the temperature of the 10-mm inside from the surface of the die was measured through a small hole in the die.

The sintering temperature suitable for the B₄C + 5W + 80WC mixture was determined in preliminary experiments. The composite obtained at a sintering temperature of 1900°C had a bulk density of 15.56 Mg·m⁻³, and few pores were observed with an optical microscope. The composite sintered at 1650°C, had a similar bulk density (15.49 Mg·m⁻³) and few observable pores. In comparison, many pores were visible in composites sintered at below 1600°C. Since sintering at higher temperatures caused grain coarsening and a drop in hardness, a temperature of 1650°C was selected as a suitable sintering temperature that gave densely sintered bodies with small grains.

The sintered bodies obtained were analyzed with a powder X-ray diffractometer (Rigaku, RINT-2500VHF), and were examined metallographically with an electron probe microanalyzer (EPMA, JEOL, JXA-733). Density was measured by the Archimedean method. The mechanical properties evaluated were Vickers hardness, Young’s modulus, Poisson’s ratio, and fracture toughness. Young’s modulus and Poisson’s ratio were measured by the pulse-echo method with a high-temperature elastodynamic rate-measuring system (Toshiba Tungalooy, UMS-HL). Vickers hardness was measured under a 9.8 N load held for 15 s, and fracture toughness was estimated by the indentation method using Evans and Davis’s equation.²

3. Results and Discussion

3.1 Reaction products

Figure 1 shows typical X-ray diffraction (XRD) analysis results of the sintered bodies. Figure 2 shows the relative intensity of the sintered bodies, calculated from the intensities of the highest diffraction peaks for W₂B (211), WB (112), and WC (100), as a function of the WC mole fraction in the starting powder mixtures, given by \( x/(6 + x) \). As expected, the amount of WB produced decreased as the WC content increased. W₂B was formed between WC mole fractions of 0.854 and 0.956. The W₂B ratio increased with the WC content, and no WB was produced above 0.956. As shown in the W-C phase diagram,Ⅲ WC has nonstoichiometric composition. The chemical analysis of the WC used in this study gives a composition of WC₀.994, where it is assumed that the impurities Fe and Mo combine with carbon as Fe₃C and Mo₂C and that the free carbon will finally dissolve into WC phase. According to the W-C phase diagram,Ⅲ the content of W in the stable WC phase is lower than that of the WC used. Therefore, excessive W in the WC used produced W₂B.

3.2 Microstructure

Figure 3(a) shows the microstructure of the sintered body at a WC mole fraction of 0 in the starting powder. There are pores, small dark round grains with an average diameter of 1.0μm and slightly larger gray grains; there are fewer dark grains than gray ones. EPMA analysis showed that the dark grains contained C and the larger ones B. With considering the XRD results (Fig. 1), the dark and gray grains can be identified as WC and WB, respectively. Although the average particle diameter of W in the starting powder was 6μm, the products WB and WC have even smaller diameter than W.

Figure 3(b) shows the microstructure of the sintered body at a WC mole fraction of 0.930. Aggregates composed of white
grains are scattered in the photograph. Figure 4 shows the microstructure near some aggregates at the same WC mole fraction of 0.930; an aggregate consists of bright and light gray grains, as shown in Fig. 4(a). The bright and light gray grains both contain B and no C; the bright grains contain less B; the grains around the aggregates contain C and no B. Considering the XRD results (Fig. 1), the bright grains, the light gray grains and the grains around the aggregates are composed of $\text{W}_2\text{B}$, WB and WC, respectively. The light gray WB grains exist near the rims of the aggregate. When a W particle reacts with ambient smaller $\text{B}_4\text{C}$ particles, decomposed B and C will diffuse into the W particle, since they are much lighter and smaller elements than W. If B migrates in the product carbide WC and C migrates hardly in the product borides $\text{W}_2\text{B}$ and WB, this morphology will be formed after a solid-state reaction. As shown in Fig. 4(d), the surfaces of several $\text{W}_2\text{B}$ and WB grains are concave due to polishing. This suggests that there may be hardness differences between $\text{W}_2\text{B}$, WB
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Fig. 5 SEM micrograph (backscattered electron image) of the sintered body from the pure WC powder.

Fig. 6 Bulk density of the sintered bodies as a function of the WC mole fraction.

and WC depending on their crystallographic faces. The WC grains had an average diameter of 0.8 µm, almost the same as that of the starting WC powder. In this mole fraction, most of the WC grains result from the starting WC powder. Therefore, WC grains resulting from the starting WC powder grow little during sintering at 1650°C.

The sintered body of the pure WC (mole fraction = 1) has many pores as shown in Fig. 5. The bulk density of the sintered body for the pure WC is low, as shown in Fig. 6, and its relative density as calculated from a WC density of 15.664 Mg·m⁻³ is 90.5%. At a WC mole fraction of 0 the relative density is estimated to be 92.3% from a WB density of 15.744 Mg·m⁻³ and the WC density assuming that WC + 4WB were formed as calculated from eq. (1). The relative densities at 0.600 and 0.769 are 98.9 and 98.5%, respectively. The relative density in the range 0.854 to 0.956 could not be estimated, since the amounts of W₂B and WB could not be estimated. Both the number and size of pores in the sintered bodies in this range were almost the same as those at 0.600 and 0.769.

3.3 Mechanical properties

Figure 7 shows the Young’s modulus and Poisson’s ratio of the sintered bodies as a function of the WC mole fraction. Young’s modulus increased with the mole fraction of WC, had a maximum value of 690 GPa at 0.930 and 0.956, and then steeply decreased above 0.956. Young’s modulus of WC is reported as 696 GPa and 707 GPa. In this study, sintered WC has a modulus value of 541 GPa. The low relative density of WC resulted in this low value, since Young’s modulus decreases linearly with increasing porosity. If the sintered bodies were fully dense, the modulus should increase with the WC mole fraction. Poisson’s ratio was decreased slightly with the WC mole fraction.

Figure 8 shows the Vickers hardness of the sintered bodies as a function of the WC mole fraction. The hardness increased with the WC mole fraction, had a maximum value of 22.1 GPa at 0.930, and then decreased above a fraction of 0.956. This
tendency resembles that of Young’s modulus. The low hardness value for pure WC, as well as the Young’s modulus, is due to the low relative density. Samsonov reported hardness values of 23.7 and 36.8 GPa for W₂B and WB polycrystals, respectively. Okada et al. obtained hardness values of 25.3–26.7 GPa for the (001) plane of WB crystals. Crystals of WC show large hardness anisotropy: 22.0–24.6 GPa on the (0001) plane and 9.8–23.5 GPa on the (10\text{\bar{1}}0) plane. These data suggest that W₂B and WB are as hard as or harder than WC. For the dense sintered bodies obtained in this study, however, the hardness increased with the WC mole fraction.

The fracture toughness was obtained from the results of the Vickers indentation test using Evans and Davis’s equation, which is recommended as being valid for brittle materials, especially WC–Co hard metals. Figure 9 shows the fracture toughness as a function of the WC mole fraction. The fracture toughness increased with the WC mole fraction and had a value of 5.7 MPa m\textsuperscript{1/2} at a mole fraction of 0.930; Young’s modulus and hardness were both maximal at this value. This fracture toughness value is a little smaller than that reported for sintered WC.

4. Conclusions

Dense composites of WC–WB–W₂B were prepared by reaction sintering of B₄C–5W–xWC (x = 0 to 130) mixtures at 1650°C using the energization hot-pressing technique. The sintered bodies obtained were analyzed metallographically, and their mechanical properties were evaluated. Composites of WB–WC were formed in the WC mole fraction range of 0 to 0.769 in the starting powder mixtures according to the reaction B₄C + 5W + xWC = WB + (1 + x)WC. In addition to WB and WC, W₂B was produced at mole fractions above 0.854. Dense sintered bodies were obtained in the WC mole fraction range between 0.600 and 0.956. Young’s modulus, Vickers hardness, and fracture toughness increased with the WC mole fraction in the starting powder, while Poisson’s ratio was decreased. Good mechanical properties were obtained with mole fractions between 0.854 and 0.956.

REFERENCES