Microstructure and Mechanical Properties of W-C-B Ceramics Containing VC

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We prepared WC-based W-C-B ceramics by reactive resistance-heated hot pressing at 1600 to 1800°C from a B₄C-5W-80WC (molar ratio) powder mixture containing a small amount of VC, and examined the effect of VC on sinterability and the mechanical properties of the ceramics. The sintered bodies were composed mainly of WC and small quantities of W₂C, WB, W₃B and VC. Slight amounts of V were detected at the boundaries between WC grains. VC raised the sintering temperature necessary for obtaining dense bodies, and strongly suppressed the growth of WC grains. Young’s modulus for the dense bodies was slightly smaller than that without VC because of the low modulus value of VC. The suppressive effect of VC on the growth of WC grains avoided reducing hardness with increasing sintering temperature.

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1. Introduction

The cemented carbide WC-Co is a typical very hard material. Metallic binders like Co increase strength, but decrease hardness, Young’s modulus, and chemical stability. In uses requiring both a very high hardness and high chemical stability, e.g., abrasion-resistant parts used in corrosive aqueous solutions, it is effective to reduce the amount of the metallic phase. However, WC is so sintering-resistant that fully dense bodies are difficult to produce, even using pressure sintering. Consequently, binderless carbides were developed in which both TaC and TiC¹,² or Mo₂C³ were added and their starting materials contained no metallic binder. Subsequently, Engqvist et al.⁴ clearly showed that binderless carbides contained very thin Co layers between WC grains and between a WC grain and an additive carbide phase. They deduced that the Co phase was derived from the process used to manufacture the powder: milling with WC-Co balls. The added carbides might improve sinterability, but the Co phase acted as the most effective binder. These binderless carbides were less corrosion-resistant than metal-bonded cemented carbides,⁵ probably due to the Co phase in the binderless carbides. Consequently, no appropriate ceramic binder for sintering WC has been identified.

Recently, we found that reactive hot-pressing of WC, B₄C, and W powder mixtures was effective for producing dense metal-free WC-based W-C-B ceramics, in which the solid-state reaction B₄C + 5W + xWC → 4WB + (1 + x)WC (x ≤ 130) occurs during sintering.⁶ This reactive hot-pressing method was based on the technique developed by Barsoum and Houng,⁷ who synthesized a dense TiB₂-TiC composite. W-C-B ceramics with good mechanical properties were obtained at an x value of 80, in which the composition in the reaction equation was 95 mol% WC. This ceramic was still more sinterable than WC, and WC grains grew easily during sintering.⁸ However, the grain growth reduced hardness considerably. As a result, the appropriate sintering temperature range for obtaining a fine-grain body was very narrow. To widen the temperature range, the grain growth must be suppressed. A candidate grain-growth inhibitor for WC is VC, which suppresses the growth of WC grains in WC-Co cemented carbides in small amounts.⁹

Many studies⁹-¹⁶ have examined the mechanism of VC inhibition in WC-Co, and it is thought that the precipitation or adsorption of VC on WC/Co interfaces prevents the supply of W and C to the WC grains through the Co phase. In these investigations, thin VC layers were found at the WC/Co grain boundaries, or VC layers at the WC/WC grain boundaries contained Co. One exception is a report by Lay et al.¹⁶ suggesting that VC suppresses the grain growth of WC without Co.

Therefore, in the present study, we sintered a WC-based W-C-B ceramic with no metallic binder using reactive hot pressing of a B₄C + 5W + 80WC powder mixture containing VC and examined the effect of VC on the growth of WC grains and the mechanical properties of the ceramic.

2. Experimental

Powders of B₄C (average particle diameter 1.5 μm, purity 99 mass%, B/C molar ratio 4.0;Rare Metallic), W (average particle diameter 6.0 μm, purity 99.9 mass%; Rare Metallic), and WC containing VC (average particle diameter 0.66 μm, chemical composition [mass%]: total C 6.19, free C 0.11, Fe 0.05, Mo 0.02, V 0.43, W bal.; Japan New Metals) were used as the starting materials. The average particle diameter was determined for B₄C by laser diffraction spectrometry and for W and WC by the Fischer subsieve sizer method. The average particle diameter of the WC containing VC is similar to that of the WC powder (0.75 μm) used in the previous study.⁷ The powders were mixed stoichiometrically to cause the reaction,

\[ \text{B}_4\text{C} + 5\text{W} + 80\text{WC} \rightarrow 5\text{WB} + 81\text{WC}, \]

at high temperatures. The sintering procedure and characterization methods for sintered bodies were similar to those described previously.⁷ The powder mixtures were consolidated at 1600 to 1800°C using a resistance-heated hot pressing system (SPS-2080, the Spark-Plasma Sintering Machine; Sumitomo Coal Mining) at a heating rate of
50°C·min⁻¹, applied pressure of 50 MPa, and holding time at the sintering temperature of 20 min. The temperature was measured 10 mm inside the die surface through a small hole using an optical pyrometer. The sintered bodies were examined for reaction products using X-ray diffractometry (XRD) and metallographically with an electron microanalyzer (EPMA) and transmission electron micrography (TEM) with an energy-dispersive X-ray spectrometer (EDX), and the density, Vickers hardness, elastic modulus, and fracture toughness were determined. The Vickers hardness was measured under a 9.8 N load held for 15 s. The fracture toughness was estimated using the indentation method with Evans and Davis’s equation, which evaluates adequate values for WC-Co cemented carbides.

3. Results and Discussion

3.1 Reaction products and microstructure

The reaction \( B_4C + 5W + 80WC \rightarrow 5WB + 81WC \) should proceed during hot pressing. XRD analysis for sintered bodies showed that the compounds WC, WB, \( W_2C \), and \( W_2B \) were produced. No VC phase (chemical composition: \( V_8C_7 \)) was detected using XRD. The relative intensities, \( I_x/\Sigma I_i \), of the compounds, which were calculated from the highest peak intensity for each compound, are shown in Fig. 1. Most of the WC detected using XRD is from the starting material. Both \( W_2C \) and \( W_2B \) were also produced in the \( B_4C + 5W + 80WC \) powder mixture without VC, due to the slight W excess in the starting WC powder. In this study, assuming that the starting WC powder contains the impurities Fe, Mo, and V as the carbides \( Fe_3C \), \( Mo_2C \), and \( V_8C_7 \), respectively, the molar ratio W/C for C and W to combine is 1.003. The experimental results indicate that this value is slightly higher than that for the stable WC phase.

The density of the sintered bodies is shown in Fig. 2. The powder mixture was densely sintered above 1750°C. This temperature is 100°C higher than that used for a powder mixture without VC. Therefore, VC lowers the sinterability of the \( B_4C + 5W + 80WC \) powder mixture. The density of dense bodies was slightly lower than that without VC because of the low density of VC. The sintering of pure WC has already been attempted using the same hot-pressing method used here. Ohmori reported that pure WC powders could be consolidated at above 1900°C. In contrast, Cha and Hong showed that the fully sinterable temperature of WC decreased with the particle diameter of WC and that dense bodies were obtained above 1700°C for WC with particle diameters greater than 1.33 µm. In our preliminary experiments, pure WC with a density of 15.70 g·cm⁻³ was needed for sintering a WC powder with particle sizes similar to those used here at 1800°C.

The microstructure of the sintered body at 1800°C is shown in Fig. 3. The matrix is WC, and the white areas are aggregates of WB and \( W_2B \). The microstructure near an aggregate is shown in Fig. 4. The phase near the center of the aggregate is \( W_2B \), and the \( W_2B \) phase is surrounded by the WB phase. Small VC grains are scattered throughout or precipitated around the WB phase. According to the V-W-C phase diagram, WC and \( W_2C \) dissolve little VC, while VC dissolved considerable amounts of WC to form a \((V, W)C\) solid solution. In VC-added WC-Co cemented carbides, the precipitated phases at the WC/Co grain boundaries were
(V, W)C solid solution. Consequently, the VC grains shown in Fig. 4 were probably composed of (V, W)C solid solution. V diffused into the WB phase. Since the WB phase hardly contained C, it was probably (W, V)B solid solution. Without VC, WC grains had an average size of 0.8 μm at 1600 and 1650°C. The grain growth rate changed abruptly between 1650 and 1700°C, and at 1800°C WC grains grew up to 20 μm. With VC, the WC phase had a grain size of 0.6 μm even at 1800°C, showing that VC strongly suppresses the growth of WC grains.

To clarify the effect of VC on grain-growth suppression, the grain boundaries between WC were surveyed under a TEM. A TEM micrograph of the WC grain boundaries is shown in Fig. 5. The black areas between WC grains, which look like layers, are not boundary phases because the faces of the grain boundaries are not parallel to the observed direction. No boundary phases were apparently found between WC grains. However, small amounts of V were detected at WC/WC interfaces, as shown in Fig. 6, although the spectra of the WC grains indicated that there was no V or only a very slight amount. These results show that VC segregates at grain boundaries as an extremely thin layer, which restricts the coalescence of two grains into a larger grain.

Many studies on V segregation in VC-added WC-Co cemented carbides have suggested that VC precipitates or adsorbs on WC/Co interfaces from the liquid or solid Co phase containing V and C to prevent the supply of W and C to the WC grains through the liquid or solid Co phase. This is postulated based on the observation of thin VC layers at the WC/Co interfaces and thin Co-containing VC layers at WC/Co grain boundaries. Besides these layers, Lay et al. frequently observed a thin VC layer at random WC/WC grain boundaries. They deduced that the formation of WC...
skeletons in WC-Co was impeded by the presence of VC on the surface of WC grains. This is consistent with our results. Imasato et al. investigated the effect of Cr$_3$C$_2$ and VC on the mechanical properties of binderless carbides with 3.0 mass% TiC and 2.0 mass% TaC, and reported that Cr$_3$C$_2$ and VC suppressed the grain growth of WC. Since their binderless carbides must have contained small amounts of Co, as Engqvist et al. pointed out, it is not clear whether the additives impeded the grain growth of WC without Co.

3.2 Mechanical properties
Young’s modulus and Poisson’s ratio are shown in Fig. 7. Young’s modulus increased with the sintering temperature and became constant above 1750°C. The values for the dense bodies were slightly smaller than the value without VC at 1800°C (705 GPa), which was due to the small Young’s modulus value for VC (430 GPa). Poisson’s ratio did not change with the sintering temperature, and it averaged 0.21. This value is very similar to that without VC. The modulus is shown in Fig. 8 as a function of the bulk density. It increased linearly with the bulk density, as expected.

The Vickers hardness is shown in Fig. 9. Although the hardness decreased markedly with the sintering temperature above 1700°C for the powder without VC, it did not change with the sintering temperature. This is because grain growth did not occur at the temperature range examined. In WC-Co cemented carbides, as is widely known, a smaller WC grain results in harder cemented carbides. Gurland and Bardzil found a clear relationship between hardness and the mean free path, i.e., average thickness, of the Co phase between WC grains for WC-Co cemented carbides with different Co contents and WC grain sizes. A smaller mean free path of the Co phase between WC grains resulted in harder WC-Co cemented carbides with different Co contents and WC grain sizes. For the same Co content, decreasing WC grain size shortens the mean free path because the mean free path is defined by $f_{\text{Co}}/N_1$, where $f_{\text{Co}}$ is the volume fraction of the Co phase and $N_1$ is the number of noncontiguous WC grains intersected on a metallographic plane by a line of unit length. Consequently, fine-grain WC-Co cemented carbides are very hard. Our results show that small WC grains bring about the high hardness of a WC polycrystal directly. Therefore, the mechanism of hardening observed in this study is different from that in WC-Co.

The fracture toughness is shown in Fig. 10. The fracture toughness also did not change with the sintering temperature because the grain size did not change. The value was lower than the best value for the powder without VC.

4. Conclusions
Dense WC-based W-C-B ceramics were obtained at above 1750°C using reactive hot-pressing of a B$_4$C + 5W + 80WC powder containing VC. VC was barely soluble in WC, and precipitated in many places in the WC matrix or around the WB and W$_2$B product phases. Slight amounts of V were also detected at the boundaries between WC grains. This grain boundary segregation impeded the growth of WC grains. Young’s modulus for the dense bodies was slightly smaller
than that without VC because of the low modulus value of VC. The hardness did not decrease with sintering temperature because of the suppressed growth of WC grains. The fracture toughness was lower than the best value for the powder without VC.

REFERENCES