Microstructure and Mechanical Properties of WC-SiC Composites

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Tungsten carbide-silicon carbide (WC-SiC) composites were pressure-sintered with a resistance-heated hot-pressing machine at a sintering temperature of 1600°C. The dense sintered bodies were obtained by the SiC addition ranging from 2–10 mol%. Below 4.85 mol% SiC, WC grains grew abnormally, exhibiting high aspect ratios and intersecting one another. There were no preferential orientations for the abnormal WC grains, which had an irregular plate-like morphology with a thickness of about 3 μm and lengths ranging from 50–100 μm. The Vickers hardness decreased with increasing SiC up to 4.85 mol% and increased above this concentration. The Vickers hardness in the range of 2–4.85 mol% SiC was much lower than that of pure WC, 25.3 GPa, and had a constant value of 20.5 GPa above 7.5 mol% SiC. The fracture toughness increased with the addition of SiC, but large amounts of SiC decreased the fracture toughness. The fracture toughness of the WC-SiC composites was higher than that of the pure WC. [doi:10.2320/matertrans.M2011045]

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1. Introduction

Tungsten carbide (WC) has a very high melting point, Young’s modulus, and hardness as well as superior chemical stability. These properties are requisite for high-performance cutting tools, dies, and bits. Single-phase WC is difficult to sinter because of its refractory behavior in industrial applications. Therefore, WC-based cemented carbides are prepared by liquid-phase sintering in which metallic binders such as Co or Ni are added. The addition of Co significantly improves fracture toughness in WC-Co cemented carbides.¹ However, metallic binders deteriorate the Young’s modulus, hardness, and corrosion resistance. To prevent deterioration of these properties, the metallic binder must be ceramic. Silicon carbide (SiC) has a relatively high Young’s modulus of 440 GPa,² Its sintered bodies have been reported to have high hardness values over 20 GPa,³,⁴ and SiC film coatings also have high hardness values.⁵,⁶ Recently, we showed that the sintering temperature of WC was lowered by the addition of SiC whiskers.⁷ Preliminary experiments showed that SiC powder had the same effect on the sinterability of WC. SiC powder is an excellent candidate for improving the sinterability of WC because powder is easier to handle than whiskers, which are a controlled substance that is hazardous to human health.

In the present study, WC-SiC powder compacts were hot-pressed in the compositional range of 0–10 mol% SiC. The microstructure, particularly the morphology of WC grains, and mechanical properties of the sintered composites were examined, and the effect of the WC grain size on the hardness of the sintered composites is discussed.

2. Experimental Procedure

Powders of SiC (IBIDEN, average particle diameter 0.31 μm, chemical composition (mass%): free SiO₂ 0.39, free C 1.08, H₂O 0.20, total Al 0.0153, total Fe 0.0173, total Ca <0.0003, SiC balance) and WC (Japan New Metals, average particle diameter 0.75 μm, chemical composition (mass%): total C 6.15, free C 0.03, Fe max. 0.050, Mo max. 0.020, W balance) were used as starting materials. The starting powders were weighed to obtain compositions of WC-2, 4.85, 7.5, and 10 mol% SiC. The powders were mixed using an alumina mortar to prevent metallic contamination. Every mixture was pressed in a graphite die with an inner diameter of 20 mm at an applied pressure of 50 MPa. The obtained compacts were pressure-sintered with a resistance-heated hot-pressing machine (SPS-2080) at a heating rate of 50°C min⁻¹ and an applied pressure of 50 MPa at sintering temperatures of 1600°C and 1800°C. The temperature was measured 10 mm inside the outer die surface (5 mm outside the sample) through a small hole using an optical pyrometer. Both sides of each sintered body, with a diameter of 20 mm and a height of about 7 mm, were ground down by 0.75 mm. One ground surface was polished using a 1-μm diamond paste.

The density of the sintered bodies was measured using the Archimedean method. Young’s modulus was determined by a pulse-echo method with an elastodynamic rate-measuring system (Toshiba Tungaloy, UMS-HL). The phase constitution was analyzed with a high-power X-ray diffractometer (Rigaku, RINT-2500VHF). The microstructure of the sintered bodies was examined with an electron probe microanalyzer (EPMA, JEOL JXA-8200). The Vickers hardness was measured under a test force of 98 N at a holding time of 15 s. The fracture toughness was estimated by the indentation fracture method using Evans and Davis’s equation.⁸

3. Results and Discussion

3.1 Density

Figure 1 shows the change in the bulk and relative densities of WC-SiC ceramics. The X-ray densities of WC and SiC are 15.669 g·cm⁻³ and 3.216 g·cm⁻³, respectively.⁹,¹⁰ The theoretical density of the WC-SiC composites was
calculated using the X-ray densities of WC and SiC because they are immiscible in the solid state. Pure WC sintered at 1600°C had a relative density of 86%. No dense sintered body was obtained by solid-phase sintering at 1600°C without a binder. The densification of WC required a sintering temperature of 1800°C. The theoretical bulk density of WC-SiC composites decreased with increasing SiC content because WC is much denser than SiC. The measured bulk density of the sintered bodies also decreased with increasing SiC content. The relative density of the WC-SiC composites sintered at 1600°C was greater than 98%. The dense sintered bodies were obtained by the SiC addition ranging from 2–10 mol%.

3.2 Microstructure

Figure 2 shows the microstructures of the WC-SiC composites sintered at 1600°C. The rod-like and black regions correspond to WC phases and SiC phases (or a few pores), respectively. This black region corresponds to SiC phase because silicon and carbon were only detected by the EPMA analysis. Many high-aspect-ratio rod-like WC grains were observed at 2 and 4.85 mol% SiC. The rod-like WC grains decreased with increasing SiC content, and the WC-SiC composite changed to a granular structure at 10 mol% SiC. The abnormal growth of WC grains was significant at low SiC contents. Abnormal plate-like grains have been observed during liquid-phase sintering in SiC11–15) and Si3N416–18) ceramics containing sintering aids. The abnormal growth of WC grains was first observed in WC-SiC composites. In WC-Co hard materials, abnormal grain growth has frequently occurred during liquid-phase sintering.19–22) In these cases, the abnormal growth occurred in the presence of a liquid phase. The temperature difference between a graphite die and a WC sample was measured during resistance-heated hot pressing in the same conditions as this study.23) The sample temperature had a tendency to increase more than the sintering temperature. At a sintering temperature of 1600°C, the temperature of the sample is estimated to be about 1750°C.23) The appearance of a liquid phase was not expected in the composition range of the present study based on the phase diagram of W-Si-C systems, even at 1800°C.24) The melting point of the W5Si3 reaction product is 2320°C; thus, a liquid phase did not appear during sintering.25) Despite solid-state sintering, the WC grains grew abnormally. Interestingly, the WC rods appeared to intersect one another.

![Fig. 1 Bulk density and theoretical density of the WC-SiC composites sintered at 1600°C.](image1)

![Fig. 2 Microstructures of the WC-SiC composites sintered at 1600°C (backscattered electron images). SiC content: (a) 2 mol%, (b) 4.85 mol%, (c) 7.5 mol%, and (d) 10 mol%](image2)
The change in the constituent phase with SiC addition was examined using an X-ray diffractometer (Fig. 3). The reaction products WSi$_2$ and W$_5$Si$_3$ formed in small amounts below 4.85 mol% SiC, where the abnormal large WC grains formed in large quantity in the sintered bodies prepared at 1600°C. Hence, W$_5$Si$_3$ and WSi$_2$ phases relate probably to the appearance of abnormal plate-like grains. Above 7.5 mol% SiC, the reaction products disappeared, and only WC and SiC phases existed in the WC-SiC composites. Although SiC resulted in abnormal grain growth below 4.85 mol% SiC, large amounts of SiC inhibited WC grain growth.

The orientation of the WC grains in the sintered bodies was examined using X-ray diffraction because the fast-growing WC grains below 4.85 mol% SiC may have resulted from preferential orientation. The orientations were analyzed by comparing the WC peak intensity data from the Joint Committee on Powder Diffraction Standards (JCPDS) with those of the present study. If WC grains orient in a specific direction during pressure sintering, orientation will result from slip deformation of the WC crystalline plane. According to Schmid’s law, slip deformation tends to occur when the angle between the pressure direction and the direction normal to the slip plane is 45 degrees. Hence, a crystalline plane at an angle of 45 degrees to the slip plane will appear clearly on the pressed surface. The slip plane of a hexagonal WC crystal has been reported as {1100} by Takahashi and Freise. Figure 4 shows the interplanar angles between the prismatic planes and the X-ray diffracted planes versus the proportion of the measured X-ray relative intensities compared with those from JCPDS in the WC-SiC composites.

To examine the configuration of the WC grains, the microstructure of the WC-4.85 mol% SiC composite was observed from a surface, a cross section, and an oblique direction, as shown in Fig. 5. The coarse rod-like grains (50 μm long) were confirmed by SEM observations from both the surface (a) and the cross-sectional direction (b). If WC grains are rod-like, some cross sections of the rods can be observed on the surface or the cross-sectional surface. However, such cross sections were not confirmed by SEM observation in the present study. Observations from an oblique direction (c) show that some rod-like WC grains were connected at the edge. Consequently, the abnormal WC grains had a plate-like shape. Figure 6 shows a possible model for the intersection of plate-like WC grains grown during solid-state sintering. The irregular plate-shaped WC grains were interwoven during grain growth. Cutting along the dashed line (Fig. 6(b)) revealed that the plate-like grains appeared to cross the rod-shaped grains. Consequently, the abnormal WC grains had an irregular plate-like shape about 3 μm thick and 50–100 μm long.

3.3 Mechanical properties

Figure 7 shows Young’s moduli of the WC-SiC composites sintered at 1600°C. Young’s modulus for WC has been reported as 519–714 GPa. The dense WCs sintered with a resistance-heated hot-pressing machine at 1800°C had high Young’s modulus values of 702–714 GPa. Pure WC sintered at 1600°C, which was porous, had a Young’s modulus of 471 GPa, much lower than that of WC sintered at 1800°C. The low Young’s modulus was due to the low relative density of the WC composite. Young’s moduli of the WC-SiC composites changed very little with increasing SiC content. The values agreed with those of the WC-SiC whisker composites sintered at 1650°C.

Figure 8 shows the change in the Vickers hardness of the WC-SiC composites sintered at 1600°C. The hardness decreased with increasing SiC content up to 4.85 mol%. Above 7.5 mol% SiC, the hardness increased, reaching 20.5 GPa at 10 mol%. Since the sintered bodies had no preferential texture, the hardness values are regarded as those of isotropic materials. Polycrystalline ceramics with small
grain sizes have high hardness values according to a Hall-Petch-like relationship. The hardness values for pure WC with various grain sizes sintered at 1800°C have been reported as 18.1–26.2 GPa, and WC with small grain sizes have high hardness values. In this study, the hardness of the pure WC was 25.3 GPa due to its small grain size. The hardness decrease that occurred up to 4.85 mol% SiC was caused by increasing coarse plate-like WC grains, and the hardness increase above 4.85 mol% SiC was induced by disappearing those grains. The low hardness value for pure WC sintered at 1600°C was due to the low relative density caused by the low sintering temperature. The hardness in the SiC range of 2–4.85 mol% is much lower than pure WC.

Figure 9 shows the fracture toughness of the WC-SiC composites sintered at 1600°C. The addition of 2 mol% SiC significantly increased the fracture toughness of WC. The fracture toughness was greater than 7 MPa m$^{1/2}$ in the SiC range of 2–7.5 mol%. Above 7.5 mol% SiC, little decrease in the fracture toughness was observed. The low fracture toughness value for pure WC was due to its low relative density.
density. The fracture toughness of the WC-SiC composites was higher than that of the pure WC. In WC-Co cemented carbides, higher fracture toughness resulted from the presence of abnormal, large WC grains and higher density. In the present study, coarse plate-like WC grains also existed in the composites with high fracture toughness values: in the 2 and 4.85 mol% SiC composites in large quantity and in the 7.5 mol% SiC composite in small quantity as shown in Fig. 2. The 7.5 mol% SiC composite had high values for both hardness and fracture toughness.

4. Conclusions

WC-SiC composites obtained at a sintering temperature of 1600°C maintained a relative density greater than 98%. The dense sintered bodies were obtained by the addition of SiC ranging from 2–10 mol%. Despite solid-state sintering, WC grains grew abnormally in the concentration range of 2–4.85 mol% SiC. No preferential orientation was observed in the abnormal WC grains, as confirmed by a comparison between the measured and JCPDS X-ray relative intensities. Although each abnormal WC grain looked like a large rod in the observation of flat surfaces, they actually had an irregular plate-like shape with a thickness of about 3 μm and lengths ranging from 50–100 μm. The irregular plate-like WC grains became interwoven during solid-state sintering. The Vickers hardness ranging from 2–4.85 mol% SiC was lower than that of the pure WC due to abnormal large plate-like WC grains, and increased above 4.85 mol% SiC due to disappearing those grains. The fracture toughness of the WC-SiC composites was higher than that of the pure WC. The WC-7.5 mol% SiC composite had high values for both hardness and fracture toughness.

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