Paper

Preparation of (W, Mo)C–SiC Ceramics and their Mechanical Properties

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SYNOPSIS

Binderless cemented carbides consisting of a (W, Mo)C solid solution and SiC were synthesized and consolidated by resistance-heated hot pressing of WC–Mo₂C–C–SiC powder mixtures in the temperature range of 1600 to 1800 °C. The microstructures and reaction products of the ceramics were examined, and their density and mechanical properties were measured. The solid-state reaction for synthesizing (W, Mo)C solid solutions is $(1-x)\text{WC} + x/2\text{Mo}_2\text{C} + x/2\text{C} \rightarrow \text{W}_{1-x}\text{Mo}_x\text{C}$. Without the addition of SiC, Mo₂C remained after hot pressing. However, for (W, Mo)C–SiC ceramics obtained from the powder mixtures with SiC content $\geq 5\text{ mol\%}$ and $x \leq 0.2$, very little residual Mo₂C was observed. Each (W, Mo)C grain was composed of a W-rich core phase and a W-deficient phase on the core's periphery, suggesting a two-phase separation during cooling. The (W, Mo)C–SiC ceramics with $x \leq 0.2$ were densely sintered, and their Young's modulus changed with the SiC content according to the Voigt mixture rule. The (W, Mo)C–SiC ceramics sintered at 1600 °C had high hardness above 23 GPa and a fracture toughness of $\sim 5.8\text{ MPa m}^{1/2}$.

KEY WORDS

tungsten carbide, molybdenum monocarbide, silicon carbide, reactive hot pressing, mechanical properties

1 Introduction

Binderless (without metallic binders) cemented carbides, in which tungsten carbide (WC) is an essential material, have been used as glass-lens-forming dies and hard corrosion-resistant parts due to their excellent properties, including hardness, elasticity, thermal conductivity, and chemical stability. Kanemitsu *et al.*¹⁾ first developed a WC–TaC–TiC binderless cemented carbide. Since then, WC–SiC ceramics have been examined in detail for their sintering and mechanical properties^{2–4)}. However, the increasing demand and limited supply of tungsten have prompted the use of larger amounts of other carbides. We recently tried to manufacture dense ceramics composed of WC–MoC solid solutions ((W, Mo)C) using reactive resistance-heated hot pressing (spark-plasma sintering) of WC–Mo₂C–C powder mixtures to replace WC with MoC⁵⁾. Residual Mo₂C remained after hot pressing at 1700 °C. (W, Mo)C solid solutions ($< 20\text{ mol\% MoC}$) were produced by annealing the hot-pressed samples at 2000 °C. The SiC addition in WC enhanced the sintering reaction, resulting in significant WC grain growth^{2–4)}. This indicates that atomic migration in the bulk or at the interface of WC grains becomes more active due to SiC. Preliminary experiments

showed that the SiC addition in WC–Mo₂C–C powder mixtures accelerated the $\text{W}_{1-x}\text{Mo}_x\text{C}$ formation reaction and enabled the preparation of dense (W, Mo)C–SiC ceramics with only reactive hot pressing. Although (W, Mo)C ceramics have been synthesized for almost 30 years^{6,7)}, there has been little research done on their manufacturing method, microstructure, or mechanical properties for practical use.

The purpose of this study was to examine the amount of SiC required and the sintering conditions needed to prepare dense (W, Mo)C–SiC ceramics. The ceramics were synthesized and simultaneously consolidated by reactive resistance-heated hot-pressing of WC–Mo₂C–C–SiC powder mixtures. The reaction products, microstructures, density, and mechanical properties were examined.

2 Experimental

WC powders (Japan New Metals, average particle diameter $0.73\text{ }\mu\text{m}$, chemical composition (mass%): total carbon 6.13, free carbon 0.02, Fe 0.05, Mo 0.02), β -SiC (Yakushima Denko, average particle diameter $0.60\text{ }\mu\text{m}$, impurities (mass%): free carbon 0.85, Fe 0.015, Al 0.012, SiO₂ 0.30), Mo₂C (Japan New Metals, average particle diameter $1.57\text{ }\mu\text{m}$, chemical composition (mass%): total

carbon 5.95, free carbon 0.11, Co 0.08), and carbon black (Mitsubishi Chemical, Ketjenblack EC600JD) were used as the starting materials to produce $W_{1-x}Mo_xC$ by the solid-state reaction

during hot pressing. The experimental procedure was described in detail in a previous paper⁵⁾ and is briefly described here. Weighed powders for targeted chemical compositions of $W_{0.8}Mo_{0.2}C$ -SiC (0–30 mol% SiC) and $W_{1-x}Mo_xC$ -20 mol% SiC ($x=0$ –0.30) were mixed in ethanol with WC-8 mass% Co balls in a nylon pot for 24 h. Each powder mixture was sintered in the temperature range of 1600–1800 °C with a resistance-heated hot-pressing machine (Sumitomo Coal Mines, Spark-Plasma Sintering Machine SPS-2080). The density was measured by the Archimedeian method. The reaction products were analyzed with a powder X-ray diffractometer (XRD, Rigaku, RINT-2500VHF). The microstructure was evaluated with an electron microanalyzer (EPMA, JEOL, JXA-8230). Young's modulus was determined by the pulse-echo method with a high-temperature elastodynamic rate-measuring system (Toshiba Tungalloy, UMS-HL). Vickers hardness tests were carried out under a 9.8 N load. The fracture toughness was estimated by the indentation method using Evans and Davis's equation^{8,9)}.

3 Results and Discussion

3.1 Reaction products and microstructure

For targeted $W_{0.8}Mo_{0.2}C$ -SiC composition, residual Mo_2C always remained after hot pressing, without the addition of SiC. Above 5 mol% SiC, however, Mo_2C had almost disappeared entirely after hot pressing. Small amounts of the Mo_5Si_3C -type structure (Nowotny phase, JCPDS pattern No. 43-1199 of $Mo_{4.8}Si_3C_{0.6}$ ¹⁰⁾) were detected in ceramics containing SiC as a reaction product. EPMA analysis indicated that the compound contained W, in addition to Mo, Si, and C, verifying the Nowotny phase $(W,Mo)_5Si_3C$ ¹¹⁾. Figure 1 shows the relative intensity of Mo_2C and Nowotny-phase-type $(W,Mo)_5Si_3C$ in the ceramics. The relative intensity was calculated from the maximum peak intensities of $W_{1-x}Mo_xC$, Mo_2C , and/or $(W,Mo)_5Si_3C$ detected in the ceramics. The Mo_2C residue was attributed to incomplete development of the reaction given in Eq. (1). When unreacted Mo_2C remains in the ceramic, the reaction products must contain residual carbon. However, very small amounts of carbon (graphite) were detected by XRD only for $W_{0.7}Mo_{0.3}C$ -20 mol% SiC, which contained considerable amounts of Mo_2C and C in

the starting powder.

When fine WC powder was hot-pressed, small amounts of hemicarbide (W_2C) formed in the sintered ceramics^{2,12)}. Small amounts of W_5Si_3 were found after hot pressing fine powder mixtures containing WC and SiC^{2,4)}. These products are produced by surface oxidation of the starting fine WC powder: $7(5)WC + WO_3(WO_2) \rightarrow 4(3)W_2C + 6(2)CO$ for the W_2C formation and $3(7)WC + 3(8)SiC + 2WO_3(8WO_2) \rightarrow 1(3)W_5Si_3 + 6(16)CO$ for W_5Si_3 formation, where the values in parentheses correspond to the reaction for WO_2 . Consequently, the formation of small amounts of the low carbon compound $(W,Mo)_5Si_3C$ were attributed to the same cause.

When SiC was not added to the powdered mixture, unreacted Mo_2C remained after hot pressing. For SiC addition ≥ 5 mol%, small amounts of residual Mo_2C were evident. For $W_{0.7}Mo_{0.3}C$ -20 mol% SiC, with the addition of considerable amounts of Mo_2C and C, however, unreacted Mo_2C remained. Ceramics composed of (W,Mo)C-SiC were obtained for $x \leq 0.2$ and SiC content ≥ 5 mol%.

Figure 2 shows the microstructure of $W_{0.8}Mo_{0.2}C$ -20 mol% SiC and $W_{0.7}Mo_{0.3}C$ -20 mol% SiC. The $W_{0.8}Mo_{0.2}C$ -20 mol% SiC was composed of black, scattered SiC grains and a (W,Mo)C solid solution matrix. For $W_{0.7}Mo_{0.3}C$ -20 mol% SiC, dark Mo_2C grains were also found, consistent with the XRD results. Each (W,Mo)C grain was not compositionally homogeneous. Since no dissolution of SiC in the (W,Mo)C phase was detected by EPMA, the $W_{1-x}Mo_xC$ -SiC system is the same as the $W_{1-x}Mo_xC$ system for

Fig. 1 Relative intensity of Mo_2C and $(W,Mo)_5Si_3C$.

Fig. 2 Microstructures of the ceramics: (a) $W_{0.8}Mo_{0.2}C$ -20mol% SiC and (b) $W_{0.7}Mo_{0.3}C$ -20mol% SiC (backscattered electron images).

phase equilibrium in a (W,Mo)C grain. In the $W_{1-x}Mo_xC$ system examined in our previous study⁵⁾, every (W,Mo)C grain was composed of a W-rich core phase ($W_{0.92-0.98}Mo_{0.08-0.06}C$) and a peripheral W-deficient phase ($W_{0.52-0.56}Mo_{0.48-0.44}C$) and that the W-rich core phase was precipitated in the (W,Mo)C grain. Figure 3 shows the structural change in $W_{1-x}Mo_xC$ -20 mol% SiC with increasing x . The transmission electron microscope observation and analysis in the previous study⁵⁾ strongly indicated that the core structure was formed by a two-phase separation during cooling; such a region is not shown in the calculated WC-MoC phase diagram^{13,14)}. Considering the results of the previous study⁵⁾, a continuous W-rich phase (W,Mo)C was obtained for $x < 0.06$; the two-phase region composed of W-rich and W-deficient (W,Mo)C phases was obtained for $x = 0.06-0.48$.

3.2 Density

Dense ceramics were produced at SiC addition ≥ 5 mol%. Figure 4 shows the bulk density in the $W_{1-x}Mo_xC$ -20mol% SiC and $W_{0.8}Mo_{0.2}C$ -SiC systems. The calculated lines in the figure used the density values of $W_{1-x}Mo_xC$ determined from lattice parameters in our previous study⁵⁾ and β -SiC ($3.216 \times 10^3 \text{ kg m}^{-3}$)¹³⁾. Every measured value fell on the lines, except for $W_{0.7}Mo_{0.3}C$ -20mol% SiC. $W_{0.7}Mo_{0.3}C$ -20mol% SiC had residual Mo_2C and C. The low densities of the residual Mo_2C and C decreased the density of the resulting ceramic, which was lower compared with

Fig. 3 Change in the microstructure with x in the $W_{1-x}Mo_xC$ -20 mol% SiC ceramics: (a) $x = 0.05$, (b) $x = 0.1$, and (c) $x = 0.2$ (backscattered electron images).

ceramics composed only of the $W_{1-x}Mo_xC$ and SiC phases.

3.3 Mechanical properties

Figure 5 shows the Young's modulus in the $W_{0.8}Mo_{0.2}C$ -SiC and $W_{1-x}Mo_xC$ -20mol% SiC systems. The calculated line in Fig. 5 (a) was obtained using the Voigt mixture rule, $E = E_{W_{0.8}Mo_{0.2}C}V_{W_{0.8}Mo_{0.2}C} + E_{SiC}V_{SiC}$, where E , $E_{W_{0.8}Mo_{0.2}C}$, and E_{SiC} are the Young's modulus of the mixture, $W_{0.8}Mo_{0.2}C$ (this study 660 GPa), and β -SiC (hot-pressed β -SiC 440 GPa¹⁷⁾), respectively, and $V_{W_{0.8}Mo_{0.2}C}$ and V_{SiC} are the volume fraction of the $W_{0.8}Mo_{0.2}C$ and SiC phases, respectively. The volume fraction was calculated from the density of β -SiC and the measured density of $W_{0.8}Mo_{0.2}C$ shown in Fig. 4. As is widely known, the Voigt model is derived by assuming that the constituents exhibit the same strain under a constant applied stress. The measured Young's modulus in $W_{0.8}Mo_{0.2}C$ -SiC was very close to the calculated value.

The Young's modulus in the $W_{1-x}Mo_xC$ -20mol% SiC system decreased slightly with increasing x (for $x < 0.2$), and the reduction became larger for $x \geq 0.2$. $W_{0.7}Mo_{0.3}C$ -

Fig. 4 Bulk density of the ceramics: (a) $W_{0.8}Mo_{0.2}C-SiC$ and (b) $W_{1-x}Mo_xC-20\text{mol\% SiC}$.

Fig. 6 Vickers hardness of the ceramics: (a) $W_{0.8}Mo_{0.2}C-SiC$ and (b) $W_{1-x}Mo_xC-20\text{mol\% SiC}$.

Fig. 5 Young's modulus of the ceramics: (a) $W_{0.8}Mo_{0.2}C-SiC$ and (b) $W_{1-x}Mo_xC-20\text{mol\% SiC}$.

Fig. 7 Fracture toughness of the ceramics: (a) $W_{0.8}Mo_{0.2}C-SiC$ and (b) $W_{1-x}Mo_xC-20\text{mol\% SiC}$.

20mol% SiC had residual Mo_2C and C. The decrease in the Young's modulus suggests that this was due to the residual Mo_2C and C. The Young's modulus of a hot-pressed Mo_2C was reported to be 400 GPa¹⁸⁾, which is lower than that of the hot-pressed β -SiC (440 GPa)¹⁷⁾.

Figure 6 shows the Vickers hardness in the $W_{0.8}Mo_{0.2}C-SiC$ and $W_{1-x}Mo_xC-20\text{mol\% SiC}$ systems. The SiC addition

did not significantly decrease the hardness; there was little change in the hardness in the range of 5 to 30 mol%. Increasing the sintering temperature decreased the hardness; this was due to the growth of (W,Mo)C grains. The ceramics sintered at 1600°C showed high hardness values, ~23 GPa.

Figure 7 shows the fracture toughness in the $W_{0.8}Mo_{0.2}C-SiC$ and $W_{1-x}Mo_xC-20\text{mol\% SiC}$. The SiC addition and

the increase in x hardly influenced the fracture toughness. Raising the sintering temperature lowered the fracture toughness and hardness (Fig. 6). Consequently, the ceramics with higher hardness exhibited higher fracture toughness, contrary to the common inverse relation between hardness and fracture toughness (*i.e.*, the higher the hardness, the lower the fracture toughness). Similar results were obtained in (W,Mo)C ceramics reported in the previous paper⁵⁾. Hence, the (W,Mo)C phase undoubtedly caused this phenomenon; however, the reason was not clarified in this study.

4 Summary

Synthesis of (W,Mo)C-SiC ceramics from WC-Mo₂C-C-SiC powder mixtures, which lead to the solid-state reaction for synthesizing (W,Mo)C solid solutions, $(1-x)\text{WC} + x/2\text{Mo}_2\text{C} + x/2\text{C} \rightarrow \text{W}_{1-x}\text{Mo}_x\text{C}$, and their simultaneous consolidation were performed by reactive resistance-heated hot pressing in the sintering temperature range of 1600 to 1800 °C. Without the addition of SiC, unreacted Mo₂C remained after hot pressing. Above 5 mol% SiC for $x \leq 0.2$, only a very small amount of Mo₂C was evident. Each (W,Mo)C grain in the ceramics with $x \geq 0.1$ was composed of a W-rich core phase and a W-deficient phase on the core periphery; for $x \leq 0.05$, this core structure was hardly visible. Dense ceramics were obtained for SiC addition ≥ 5 mol% and $x \leq 0.2$, in good agreement with density calculations. The Young's modulus of the W_{0.8}Mo_{0.2}C-SiC ceramics obeyed the Voigt mixture rule. (W,Mo)C-SiC ceramics sintered at 1600 °C showed high hardness values above 23 GPa. The ceramics with higher hardness exhibited higher fracture toughness.

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