Spark plasma sintering of TiN-cubic BN composites

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In the present study, TiN–cBN composites were prepared from TiN and cBN powders by spark plasma sintering at temperatures from 1600 to 1800°C for 60 s under an uniaxial pressure of 100 MPa. The densification, phase transformation, microstructure and mechanical properties of the TiN–cBN composites were investigated. TiN–BN composites originally containing 10 to 30 vol% cBN without a phase transformation from cBN to hexagonal BN (hBN) were obtained at a sintering temperature of 1600°C. The densification of the TiN–cBN composites was retarded with increasing cBN content. The phase transformation from cBN to hBN in the TiN–BN composites started at 1650°C and was completed at 1800°C. The Vickers hardness and fracture toughness of TiN–BN composite, originally containing 10 vol% cBN, prepared at 1600°C were 17 GPa and 3.6 MPam1/2, respectively.

Key-words : Cubic boron nitride, Titanium nitride, Spark plasma sintering, Phase transformation, Mechanical properties

1. Introduction

Cubic boron nitride (cBN) has the second highest hardness and thermal conductivity next to diamond, and its thermal stability and low-reactivity with iron are superior to those of diamond. With these excellent features, cBN can be applied to cutting tools for high-speed machining of hardened steel and cast iron. However, it is difficult to obtain fully dense cBN material by conventional sintering due to the strong covalent bonding and low self-diffusion coefficients of B and N. In addition, cBN transforms to low-hardness hexagonal BN (hBN) with a graphite structure at high temperature and moderate pressure. Thus, cBN cutting tools are generally produced by sintering at a high temperature of 1000 to 1400°C under an ultra-high pressure of more than 5 GPa with various kinds of additives. For a wide range of applications of cBN to cutting tools, it would be economically useful if cBN-based materials could be densified at a moderate pressure of less than 100 MPa without using ultra-high pressure.

TiN is widely used in cutting tools because of its excellent hardness, wear resistance and corrosion resistance. Since TiN–Ni cermet tools in particular possess high fracture toughness, TiN–Ni material shows promise for use in cutting tools containing W. With these excellent features, cBN can be applied to cutting tools for high-speed machining of hardened steel and cast iron. However, it is difficult to obtain fully dense cBN material by conventional sintering due to the strong covalent bonding and low self-diffusion coefficients of B and N. In addition, cBN transforms to low-hardness hexagonal BN (hBN) with a graphite structure at high temperature and moderate pressure. Thus, cBN cutting tools are generally produced by sintering at a high temperature of 1000 to 1400°C under an ultra-high pressure of more than 5 GPa with various kinds of additives. For a wide range of applications of cBN to cutting tools, it would be economically useful if cBN-based materials could be densified at a moderate pressure of less than 100 MPa without using ultra-high pressure.

In the present study, TiN–cBN composites were prepared from TiN and cBN powders by spark plasma sintering at temperatures from 1600 to 1800°C and the effects of cBN content and sintering temperature on the densification, phase transformation, microstructure and mechanical properties of these composites were studied.

2. Experimental procedure

TiN (Wako Pure Chemical Industries, Ltd., average particle size: 60 nm, total oxygen content: 2.58 mass%) and cBN (SBN–F, Showa Denko K. K., average particle size: 2.8 μm, total oxygen content: 0.19 mass%) powders were used in the present work. cBN powder was added to TiN in compositions of 0 to 50 vol% cBN. The powders were mixed by ball-milling in a plastic bottle with plastic balls with a small amount of ethanol for 48 h. The mixed powders were dried and passed through a sieve with a pore-opening size of 150 μm. A graphite die 10 mm in inner diameter was filled with the powder mixtures, which were then sintered at a sintering temperature of 1600 to 1900°C for 600 s in a vacuum under a uniaxial pressure of 100 MPa at a heating rate of 1.7°C/s using an SPS apparatus (SPS–210LX, SPS Syntex Inc.). Pulsed direct current (pulses of 60 ms on/10 ms off) was applied. The temperature of the surface of the graphite die was measured by an optical pyrometer. The linear shrinkage of the specimens during the SPS process was continuously monitored by displacement of the punch rod. The specimens after sintering were about 3 mm in thickness. The bulk densities of the specimens were measured by the Archimedes method, and then the relative densities were calculated from the theoretical densities of TiN (5.39 g/cm3), cBN (3.49 g/cm3) and hBN (2.34 g/cm3).

The phase transformation of cBN and the phase compositions of the cBN-based materials could be densified at a moderate pressure of less than 100 MPa without using ultra-high pressure. Therefore, the grain growth should be inhibited at high temperatures so as to accelerate the densification and maintain the finer grains. Low-sinterability materials such as cBN may be densified at a moderate temperature and many nitrides and carbides have been fully densified by SPS. Moreover, the phase transformation from cBN to hBN would be suppressed because of the short sintering time by SPS.

In the present study, TiN–cBN composites were prepared from TiN and cBN powders by spark plasma sintering at temperatures from 1600 to 1800°C and the effects of cBN content and sintering temperature on the densification, phase transformation, microstructure and mechanical properties of these composites were studied.

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Rigaku Co.) with Cu Kα radiation. The fractured surfaces of the specimens were observed by scanning electron microscopy (SEM; S–3100H, Hitachi, Ltd.). The surfaces of the specimens were ground with a diamond wheel and then finally polished with 1-μm diamond slurry. The Vickers hardness (HV) and fracture toughness (KIC) of the polished surfaces of the specimens were measured using a micro-hardness tester (HM–221, Mitutoyo Corp.) at loads (P) of 0.98 and 9.8 N, respectively. The hardness was calculated from the following formula:

\[ H_V = \frac{P}{d^2} \]

(1)

where \( P \) is the applied load and \( d \) is the average value of two diagonal lengths for Vickers indentation.

The fracture toughness was calculated by eq. (2) using the half length of the crack (c) formed around the corners of indentations: \(^{20}\)

\[ K_{IC} = 0.073 \times (P/c)^{1.5} \]

(2)

3. Results and discussion

The densification of specimens during the SPS process was evaluated based on the displacement of the punch rod by the shrinkage of the powder compacts. Figure 1 shows the shrinkage of the monolithic TiN body and the TiN–BN composites originally containing 10 to 50 vol% cBN with increasing temperature up to 1600°C. The isothermal shrinkage at 1600°C for up to 600 s is also shown in Fig. 1. The shrinkage of the monolithic TiN started at 1200°C and was completed at 1600°C. In contrast, the temperature at which shrinkage commence for the TiN–BN composites originally containing 10 to 50 vol% cBN became higher than that for the monolithic TiN, and increased with increasing cBN content. No further shrinkage of the TiN–BN composites originally containing 10 to 20 vol% cBN was observed when the temperature was maintained at 1600°C. TiN–BN composites originally containing 30 to 50 vol% cBN continued to shrink slightly when the temperature was maintained at 1600°C. In our previous study on Al₂O₃–cBN composites, \(^{13}\) the starting and finishing temperatures of shrinkage for Al₂O₃–BN composites were similarly elevated with increasing cBN content.

Figure 2 shows the XRD patterns of a TiN–BN composite originally containing 20 vol% cBN prepared at 1600 to 1800°C for 600 s. The peak of hBN was detected at 1650°C, indicating slight phase transformation from cBN to hBN. At 1800°C, the strongest peak of (111) cBN disappeared. In Al₂O₃–cBN composites, the phase transformation from cBN to hBN was observed at 1400°C. \(^{13}\) Thus, the transformation temperature of the cBN phase in TiN–BN composites into the hBN phase was higher than that in Al₂O₃–BN composites. The transformation temperature from the cBN phase to the hBN phase in the monolithic cBN body was 1650°C. \(^{14}\) Therefore, the starting temperature of the cBN phase transformation in TiN–BN composites was almost the same as that in monolithic cBN body. The TiB₂ phase was identified in all the TiN–BN composites sintered at 1600 to 1800°C. Other researchers have also reported that TiN and TiC reacted with cBN to form Ti₇B; at 1600°C, \(^{21,22}\) Benko et al. \(^{23}\) have shown that TiN reacted with BN to form titanium borides such as TiB and TiB₂ in a wide range of temperature and pressure. Since the bonding strength between TiN and BN would be decreased by the formation of brittle TiB₂, the sintering temperature should be lowered below the formation temperature of TiB₂.

Figure 3 illustrates the effect of cBN content on the relative density of TiN–BN composites prepared at 1600 and 1800°C for 600 s. The relative density of the composites was calculated by assuming that most of the specimens consisted of two phases of TiN and BN because of a tiny amount of TiB₂ at 1600 to 1800°C, as shown in Fig. 2. At the sintering temperature of 1600°C, the relative density of the monolithic TiN body was 93%. The TiN–BN composites originally containing 10 to 30 vol% cBN had a density of 92 to 93%, which was almost the same as the density of the monolithic TiN body. When 50 vol% cBN was added, the density of the TiN–BN composite decreased to 82%. At the sintering temperature of 1800°C, the density of the TiN–BN composites decreased with increasing cBN content. With sinter-
ing at 1800°C, the density of TiN–BN composites originally containing 10 to 30 vol% cBN was lower than that with sintering at 1600°C. In a previous study on Al₂O₃–cBN composites, 13) the relative density of monolithic Al₂O₃ body sintered at 1200°C was more than 99%, whereas that of Al₂O₃–cBN composite decreased to about 85% at 10 vol% cBN. Martínez and Echeberria 9) have studied the sintering behavior of WC–Co–cBN composites with the addition of up to 50 vol% cBN. They reported that the addition of cBN significantly retarded the densification of WC–Co. Martín et al. 23) have also reported that the densification of cBN–Cu–Ti composites decreased with increasing cBN content.

Figure 4 shows SEM micrographs of the fractured surface of the TiN–BN composite originally containing 20 vol% cBN, which was sintered at 1600 to 1800°C for 600 s. The dark phase (arrow in Fig. 4(a)) was BN grains. Angular edges of BN grains remained in the TiN matrix sintered at 1600°C. At 1800°C, TiN grains significantly grew and the angular BN grains changed to a flake texture similar to that of graphite (arrow in Fig. 4(d)). As we have previously reported in Al₂O₃–cBN and β-SiAlON–cBN composites, the flake texture was characteristic of hBN transformed from cBN. 13),14),24) The cBN phase in the TiN–BN composites transformed into hBN at 1650 to 1700°C, as indicated in Fig. 2.

Figure 5 shows the effect of sintering temperature, 1600 to 1800°C for 600 s, on the Vickers hardness of monolithic TiN bodies and TiN–BN composites originally containing 10 to 30 vol% cBN. With sintering at 1600°C, the hardness of the TiN–BN composite originally containing 10 vol% cBN without the transformation of cBN phase was 17 GPa. This value was higher than the hardness of the monolithic TiN bodies. The increase in the hardness of the TiN–cBN composites would be due to the dispersion of high-hardness cBN grains in the TiN matrix (Fig. 4) and due to almost the same density as monolithic TiN bodies (Fig. 3). With sintering at 1600°C, the hardness of the TiN–BN composites originally containing 20 to 30 vol% cBN was lower than that of the monolithic TiN bodies, although the larger amounts of cBN grains existed in the TiN matrix. This may have been caused by a decrease in the density of the TiN–BN composites with increasing content of low-sinterable cBN. The monolithic TiN body sintered at 1600°C had a hardness of 16 GPa that slightly decreased with increasing sintering temperature. With increasing sintering temperature from 1600 to 1800°C, the hardness of the TiN–BN composites decreased. This would be due to the phase transformation of cBN (Hᵥ = 45 GPa) 25) to low-hardness hBN (Hᵥ = 0.1–0.2 GPa) 25) in the TiN–BN composites from sintering temperature of 1650°C. Moreover, the growth of the TiN grains in the TiN–BN composites with increasing sintering temperature might affect the decrease in the hardness of the TiN–BN composites (Fig. 4).

In our previous study, 13),14) the Vickers hardness of fully dense Al₂O₃–cBN composites originally containing 10 to 20 vol% cBN without the transformation of cBN phase was 26 GPa. This value was about 4 GPa higher than that of monolithic Al₂O₃ bodies. The hardness of the Al₂O₃–BN and β-SiAlON–cBN composites also decreased with increasing sintering temperature. The hardness of WC–Co–cBN composites prepared by hot isostatic pressing reached 25 GPa. 19) Furthermore, in WC–Co–cBN composites prepared by SPS, the hardness increased from 19 to 21 GPa by the addition of cBN. 26) In cBN–TiN–Al composites, the hardness increased with increasing cBN content and the hardness of the composite containing 75 vol% cBN was 30 GPa. 8)

Figure 6 shows the effect of sintering temperature, 1600 to 1800°C for 600 s, on the fracture toughness of monolithic TiN bodies and TiN–BN composites originally containing 10 to 30 vol% cBN sintered for 600 s.
of cBN to TiN. The toughness of the monolithic TiN bodies sintered at 1600 to 1800 °C was 3.0 to 3.2 MPa-m$^{1/2}$ and decreased with increasing sintering temperature. On the other hand, with sintering at 1600 °C, the toughness of the TiN–BN composites originally containing 10 to 20 vol% cBN reached 3.4 to 3.6 MPa-m$^{1/2}$. When sintering temperature increased, the toughness of the TiN–BN composites decreased from around 3.5 to 2.8 MPa-m$^{1/2}$. The TiN–BN composites had almost the same toughness, irrespective of cBN content. The fracture toughness in TiN–BN composites indicated a similar tendency to that in Al$_2$O$_3$–BN composites. In Al$_2$O$_3$–BN composites, the toughness increased from 2.1–2.7 to 4.1 MPa-m$^{1/2}$ by the addition of cBN to Al$_2$O$_3$. In addition, the toughness decreased with increasing sintering temperature. Crack deflection was confirmed around the cBN grains in the Al$_2$O$_3$–BN composites. The cracks propagated straight through BN grains with the phase transformation to hBN in the Al$_2$O$_3$–BN composites.

4. Conclusions

TiN–cBN composites were prepared using SPS at sintering temperatures of 1600 to 1800 °C for 600 s under a moderate pressure of 100 MPa. The addition of cBN to TiN increased the temperature at which shrinkage started and finished and decreased the relative density. The phase transformation from cBN to hBN in the TiN–BN composites started at 1650 °C and was completed at 1800 °C. TiN–BN composites originally containing 10 to 30 vol% cBN with a relative density of 92 to 93% without the phase transformation were obtained at a sintering temperature of 1600 °C. The Vickers hardness and fracture toughness of TiN–BN composite originally containing 10 vol% cBN sintered at 1600 °C reached 17 GPa and 3.6 MPa-m$^{1/2}$, respectively.

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References