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Densification and mechanical properties of cBN–TiN–TiB_2 composites prepared by spark plasma sintering of SiO_2-coated cBN powder

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Abstract

cBN–TiN–TiB_2 composites were fabricated by spark plasma sintering at 1773–1973 K using cubic boron nitride (cBN) and SiO_2-coated cBN (cBN(SiO_2)) powders. The effect of SiO_2 coating, cBN content and sintering temperature on the phase composition, densification and mechanical properties of the composites was investigated. SiO_2 coating on cBN powder retarded the phase transformation of cBN in the composites up to 1873 K and facilitated viscous sintering that promoted the densification of the composites. Sintering at 1873 K, without the SiO_2 coating, caused the relative density and Vickers hardness of the composite to linearly decrease from 96.2% to 79.8% and from 25.3 to 4.4 GPa, respectively, whereas the cBN(SiO_2)–TiN–TiB_2 composites maintained high relative density (91.0–96.2%) and Vickers hardness (17.9–21.0 GPa) up to 50 vol% cBN. The cBN(SiO_2)–TiN–TiB_2 composites had high thermal conductivity (60 $W\,m^{-1}\,K^{-1}$ at room temperature) comparable to the TiN–TiB_2 binary composite.

Keywords: Spark plasma sintering; Titanium nitride; Titanium diboride; Cubic boron nitride

1. Introduction

Cubic boron nitride (cBN) is the second hardest material after diamond and shows low-reactivity with ferrous materials.[1–3] Therefore, cBN is used as a cutting tool in high-speed machining of hard steel and cast iron.[1,2] However, it cannot be densified by conventional hot pressing because of the strong covalent bonding[1] and volume change from cBN to hexagonal boron nitride (hBN) at high temperatures.[4–6] Thus, bulk cBN has generally been manufactured at pressures greater than 5 GPa,[7–12] which is not cost-effective for industrial scale applications.

The sintering of cBN composites with various kinds of metal and ceramic binders at moderate pressures has been intensively investigated. Binders and composites affect the phase transformation of cBN to hBN.[13–19] The phase transformation temperature of monolithic cBN is approximately 1923 K at ambient pressure.[16,17] The phase transformation of cBN in cBN-metal composites, such as WC–Co and Ni, takes place at approximately 1573 K,[13–15] whereas in cBN-ceramic composites containing Si-based materials, *e.g.* cBN–SiAlON,[16,17] cBN–mullite[18] and cBN–SiO_2,[19] phase transformation occurs at 1923–1973 K. Therefore, SiO_2 coating on cBN powder effectively retards the phase transformation of cBN.

TiN and TiB_2 possess high hardness and wear resistance as well as good oxidation resistance at high temperatures; therefore, they are often used in cutting tools.[20–22] TiN and TiB_2 are thermodynamically compatible with BN at high temperatures,[23] thus cBN–TiN–TiB_2 composites are promising materials for cutting tools. TiN–TiB_2 composites represent a binary eutectic system[24] in which the eutectic composites are more easily sintered than monolithic materials.[25] The TiN–TiB_2 composite (30:70 in vol%), which is near the eutectic composition, showed the highest densification and optimum mechanical properties when sintered just below the eutectic temperature.[26] Therefore, TiN–TiB_2 (30:70 in vol%) is a candidate matrix for cBN-based composites.

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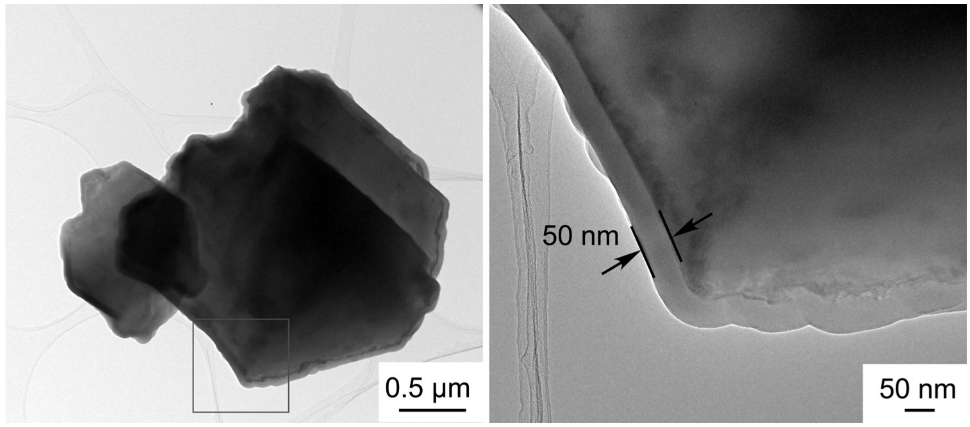

Fig. 1. TEM images of SiO_2-coated cBN powder prepared by RCVD.

In the present study, cBN–TiN–TiB_2 composites using SiO_2-coated cBN were prepared by spark plasma sintering (SPS). Subsequently, we investigated the effect of cBN content and sintering temperature on the phase composition, densification, microstructure and mechanical properties.

2. Experimental procedure

TiN (particle size 1.2–1.8 μm; Wako Pure Chemical, Osaka, Japan), TiB_2 (particle size 2–3 μm; Kojundo Chemical Laboratory, Sakado, Japan) and cBN (particle size 2–4 μm; Showa Denko, Tokyo, Japan) powders were used as starting materials. The cBN powder surface was coated with a SiO_2 layer by rotary chemical vapour deposition (RCVD).[27] The SiO_2 layer thickness was approximately 50 nm (Fig. 1). Hereafter, the SiO_2-coated cBN powder is denoted as cBN(SiO_2) without noting the amount of SiO_2 for simplicity. The cBN and cBN(SiO_2) content varied from 0 to 80 vol%, whereas the TiN–TiB_2 volume ratio was fixed at 30:70 in the remaining fraction. cBN and cBN(SiO_2) powders were manually mixed with TiN and TiB_2 powders in an agate mortar and then passed through a 200-mesh sieve. The powder mixture filled a graphite die (inner diameter of 10 mm) and sintered in an SPS apparatus (SPS-210LX, Fuji Electronic Industrial, Kawasaki, Japan) in vacuum. A uniaxial pressure of 100 MPa was applied during sintering. The sintering temperature increased to 1773–2073 K at a heating rate of 1.67 K s^{-1} and was maintained for 300 s. The sintering temperature was measured using a pyrometer (Chino, Tokyo, Japan) through a small hole on the die surface. The shrinkage of the specimens during sintering was monitored by the displacement of a punch rod. Density was measured with the Archimedes method and relative density was calculated from the theoretical density of TiN (5.4 Mg m^{-3}), TiB_2 (4.5 Mg m^{-3}), cBN (3.5 Mg m^{-3}) and SiO_2 (2.2 Mg m^{-3}).

Phase compositions were examined by using X-ray diffraction (XRD; RAD-2C, Rigaku, Tokyo, Japan) with CuKα radiation. The microstructures were observed using a scanning electron microscope (SEM; S-3400, Hitachi, Tokyo, Japan) and a transmission electron microscope (TEM; EM-002B, TOPCON, Tokyo, Japan). The Vickers hardness was measured using a microhardness tester (HM-221, Mitutoyo, Tokyo, Japan) on

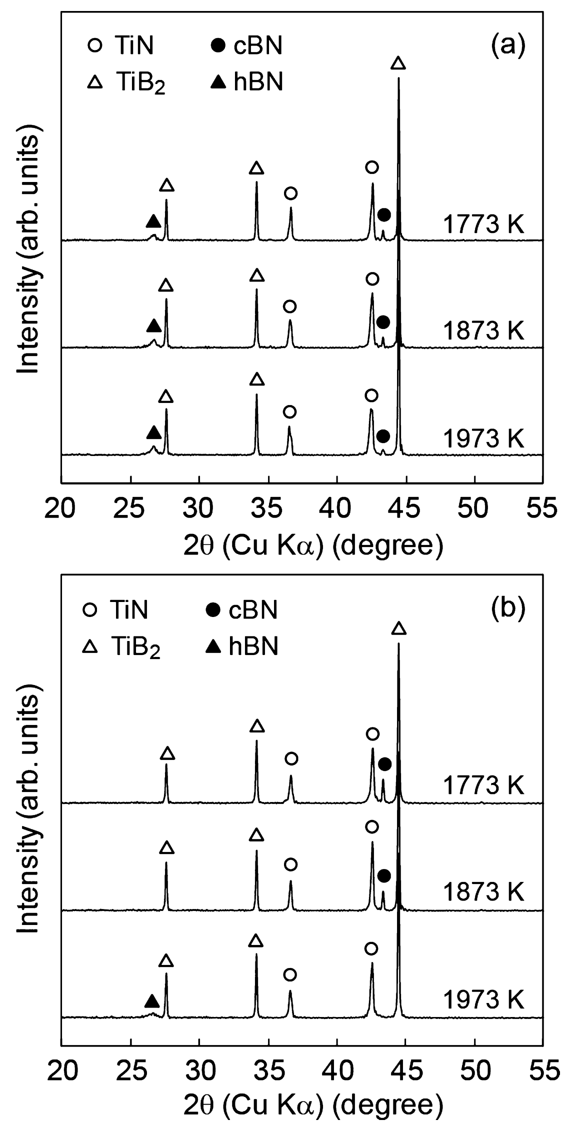

Fig. 2. XRD patterns of cBN–TiN–TiB_2 (a) and cBN(SiO_2)–TiN–TiB_2 (b) composites (30 vol% cBN) sintered at 1773–1973 K.