Densification of hBN with the as-coated SiO2 nanolayer by rotary chemical vapor deposition

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In the present study, SiO2 nanolayer was coated on hBN by RCVD at 700°C using tetraethyloxysilicate (TEOS) as a precursor. The morphology of SiO2 nanolayer and the related coating mechanism was characterized and discussed. Then the effects of SiO2 content and sintering temperature were investigated on the relative density, microstructure and hardness of hBN.

1. Introduction

With excellent lubrication, high volume resistivity and good chemical inertness, hexagonal boron nitride (hBN) can be used for various applications, such as a lubricant, an electric insulator, a crucible and an evaporating boat.1,2 However, hBN is resistant to sintering due to its strong covalent bonding nature and anisotropic plate-like structure,3 and the development of effective densification techniques and effective sintering aids has attracted much attention. Hagio et al. reported pressureless anisotropic plate-like structure,3) and the development of effective coating of hBN on the surface of the reactor. Full exposure of the surface of hBN powders to TEOS, argon and oxygen gases by relative density to a maximum value of 96.2%

hBN has not been reported yet. Therefore, other sintering aids, such as SiO2 or mullite have been tried by many researchers to assist the densification of hBN using mechano-chemical treated powders,4,5) at 1900°C. Four blades were attached to the inner surface of the reactor to keep the hBN powder floating using rotation, and the fluctuation duration of the powder was controlled by changing the rotation rate of the reactor. The total pressure of the RCVD apparatus was 800 Pa. SiO2 content (C_{SiO2}, mass %) were calculated from the mass difference of the hBN after and before the RCVD process, which represents the weight gain of SiO2.

After the RCVD process, the as-obtained hBN-SiO2 powder ground slightly, filled into the graphite die of 10 mm in inner diameter, and then consolidated using SPS (SPS-210LX, SPS Syntex Inc.) at 1600–1900°C for 600 s. The heating rate was 1.67°C·s<sup>−1</sup>. The load pressure was 80 MPa. The temperature was measured using an optical pyrometer, which was focused on a hole (φ 2 × 5 mm) in a graphite die. In order to optimize possible measurement errors in the SPS process, all other conditions, including heating rate, consolidation time, cooling rate and infrared temperature measurement position, were exactly fixed, except for the sintering temperature.

The phase composition of the as-obtained hBN (hereafter hBN-SiO2) powder and consolidated specimens was examined using X-ray diffraction (XRD; Geigerflex, Rigaku Corp., Tokyo, Japan (XRD, RAD-2C, Rigaku, Japan) with Cu Kα radiation. The

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microstructures of the hBN-SiO2 powders were observed using scanning electron microscopy (SEM; Hitachi: S-3400, Hitach, Japan) and transmission electron microscopy (TEM; EM-002B, Topcon, Japan). The densities of the specimens were measured using the Archimedes method and the relative densities were calculated using the theoretical densities of hBN (2.28 g·cm⁻³) and SiO2 (2.20 g·cm⁻³). The Vickers hardness (HV) at room temperature was measured using a Vickers micro-hardness tester (HM-221, Mitutoyo, Japan) and each reported value was averaged from ten points.

3. Results and discussion

Figure 1 shows the dependence of the SiO2 content (C_{SiO2}) on the TEOS precursor supply rate (R_s), which could be distinguished into three regions from I to III. In these regions, C_{SiO2} increased slowly in I and III, but sharply in II, indicating that the conversion rate from the TEOS precursor to the SiO2 final product was the highest in region II. Figure 2 shows the TEM images of hBN-SiO2 powders prepared at R_s = (a, b) 0.28 × 10⁻⁶, (c, d) 0.56 × 10⁻⁶, (e, f) 0.84 × 10⁻⁶ and (g, h) 1.67 × 10⁻⁶ kg·s⁻¹. The hBN powder used in the present study was in flake shape with a diameter <10μm and 100–200nm in thickness. The SiO2 nanoparticle 11 nm in thickness was uniformly coated on hBN powder surface at R_s = (b) 0.28 × 10⁻⁶ kg·s⁻¹. With increasing R_s to 0.56, 0.84 and 1.67, the thickness of SiO2 nanoparticle increased correspondingly to 19, 34–39, and 39–49 nm, respectively. Figure 3 shows the FESEM images of hBN (a, b) and hBN-SiO2 powders prepared at R_s = (c, d) 0.56 × 10⁻⁶ kg·s⁻¹ and (e, f) 1.67 × 10⁻⁶ kg·s⁻¹. When a small amount of SiO2 was coated at R_s = (c, d) 0.56 × 10⁻⁶ kg·s⁻¹, the outer surface of hBN powders was almost the same with that of hBN except some slightly uneven protrusions of SiO2. With increasing R_s = (e, f) 1.67 × 10⁻⁶ kg·s⁻¹, the distinctly uneven protrusions and blocks of SiO2 were observed on the hBN powder substrate.

Many literatures dealt with the decomposition of TEOS to form SiO2 nanoparticle or nanolayer. The coating procedure of SiO2 nanolayer on hBN was proposed in Fig. 4. Due to the rotation movement of the reactor in the present study, the hBN powders were kept in a “floating” state by falling down continuously. Thus the full surface of the powder could be exposed to the reaction gas and the SiO2 nucleus was adhered tightly and uniformly on the surface of hBN. With the stable proceeding of the reaction, more SiO2 nuclei were covered on the surface of hBN to contact each other and thus SiO2 nanolayer formed. However, if the precursor supply rate was too high, the SiO2 could not form tightly and thus blocks occurred, which could be used to explain the presence of SiO2 blocks and protrusions as shown in Fig. 4.

Figure 5 shows the XRD patterns of hBN-SiO2 sintered at T_{SPS} = 1400–1900°C. No patterns of SiO2 were detected at the full temperature range, indicating that SiO2 was still kept amorphous even at a temperature high as 1900°C. Figure 6 shows the effect of C_{SiO2} on the relative density of hBN-SiO2 composites by SPS at 1600, 1800 and 1900°C, respectively. SiO2 content (C_{SiO2}, mass %) were calculated from the mass gain after the RCVD process. At 1600°C, the relative density of hBN-SiO2 composites increased from 87 to 91% with increasing C_{SiO2} from 0 to 31 wt%. At 1800 and 1900°C, however, the highest relative density was 95.6 and 96.2% at C_{SiO2} = 17 wt%, respectively. With increasing the C_{SiO2} to 30.8 wt%, the relative density decreased slightly to 94.0 and 94.5%, respectively. Figure 7 shows the comparison of the shrinkage curves of hBN-SiO2 (C_{SiO2} = 24 wt %) and hBN from 800 to 1600°C and the isothermal shrinkage at 1600°C for 0.3 ks. The shrinkage of hBN was almost not observed up to 1500°C and only a little from 1500 to 1600°C, indicating that hBN was almost not densified.

**Fig. 1.** The effect of TEOS supply rate on the SiO2 content (C_{SiO2}) in the as-treated hBN powder.

**Fig. 2.** TEM images of hBN-SiO2 powders prepared at R_s = (a, b) 0.28 × 10⁻⁶, (c, d) 0.56 × 10⁻⁶, (e, f) 0.84 × 10⁻⁶ and (g, h) 1.11 × 10⁻⁶ kg·s⁻¹.
The curve of hBN-SiO2 was lower compared to that of hBN, indicating that SiO2 nanolayer assisted the densification of hBN apparently.

Although the detailed mechanism was not clear and thus much more future work is still necessary, the uniform distribution of SiO2 as a continuous nanolayer as shown in Fig. 4 is proposed here as a key factor for the beneficial effects of SiO2 on the densification of hBN. Duan et al. fabricated hBN ceramics with mullite (3Al2O3·2SiO2) as a sintering additive at 1900°C for 60 min in 1 atm N2 atmosphere. Since mullite has a melting point...
of 1810°C, it would melt at the sintering temperature of 1900°C, the densification of hBN was thus assisted by filling in the pores and accelerating the atom-diffusion of hBN, as verified from Figs. 6 and 7. On the other hand, SiO2 has been proved to assist the densification of other ceramics such as SiC whiskers (SiCW) and Al2O3 powder by viscous flow.21-23 The densification of the SiO2 coated Al2O3 could be divided into two stages of the transient viscous flow the amorphous silica layer below 1350°C and the Mullitization of composite coating particles at 1500°C. In the present study, however, the SiO2 was still kept in amorphous state even at the high temperature of 1600–1900°C as shown in Fig. 6. The melting point of SiO2 is about 1650°C, which is located in the region of 1600–1900°C. Therefore, the beneficial effects of SiO2 on the densification of hBN could be divided into two stages of transient viscous flow at 1600°C and the liquid sintering at 1800 and 1900°C. Figure 7 shows that the expansion of hBN stared up to 1600°C and then the shrinkage started. However, the shrinkage curve of hBN kept almost flat, indicating that the densification was still not finished from 1600 to 1900°C. On the other hand, the shrinkage of hBN-SiO2 accelerated, especially between 1800–1900°C, indicating that liquid SiO2 enhanced the densification of hBN effectively. As the content of SiO2 was higher than a critical value, the SiO2 nanoparticles agglomerated, bulky grains formed and were detached from the hBN powder substrate, for which the relative density decreased slightly (as shown in Fig. 5).

Figure 8 shows the effects of C_{SiO2} on the Vickers’ hardness (Hv) of hBN-SiO2. The hardness of hBN sintered at 2173 K was 0.15 GPa. The incorporation of SiO2 increased the hardness of hBN apparently. At 1600°C, the hardness increased to about 0.38 GPa and then kept about the same with increasing C_{SiO2} to 31 wt%, indicating that the slight increase of relative density from 90 to 91% with increasing C_{SiO2} from 17 to 31 wt% did not contribute to the increase of Hv. At 1800°C, the hardness increased sharply from 0.11 to 0.54 GPa with increasing C_{SiO2} from 0 to 17 wt%, and the trend became flat with increasing the C_{SiO2} further to 31 wt% and the hardness reached 0.61 GPa. At 1900°C, the hardness curves look similar and the hardness at C_{SiO2} = 31 wt% was 0.62 GPa, the same with that at 1800°C. Chen et al. fabricated hBN-SiO2 composites by the combustion reaction method with high pressure gaseous nitrogen,41 and found that the incorporation of 10 wt % SiO2 only increased the hardness from 0.1 to 0.2 GPa. In the present study, however, the hardness of the hBN-9 wt%SiO2 reached about 0.37 GPa after sintering at 1900°C, almost twice that of Chen et al.’s result, suggesting that the uniform distribution of SiO2 nanolayers by the rotary CVD technique and the rapid spark plasma sintering are promising to get high-dense and high-performance hBN ceramics.

4. Conclusions

SiO2 nanolayer was coated on the surface of hBN plate powders by rotary CVD technique using tetraethylorthosilicate (TEOS) as a precursor at 700°C. With increasing R5, to 0.56, 0.84 and 1.12, the thickness of SiO2 nanolayer increased correspondingly to 19–21, 34–39 and 39–49 nm, respectively. Due to the kept “floating” state of the hBN powders and the stable proceeding of the reaction of TEOS with oxygen at an appropriate ratio, the SiO2 nanolayer was coated uniformly on hBN. The viscous flow or liquid sintering of the uniformly distributed SiO2 nanolayer sintering aids contributed to the elevated relative density and Vickers hardness of hBN.

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