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Preparation and pressureless sintering of chemical vapour deposited SiC–B composite powder

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SiC–B composite powder was prepared by chemical vapour deposition (CVD) using $(CH_3)_2SiCl_2 + B_2H_6 + H_2$ as source gases at 1673 K. The powder was β-type polycrystalline silicon carbide containing several per cents of boron and carbon. The boron content increased from 0 to 7.7 mass% as the B_2H_6 gas concentration increased from 0 to 0.7 mol%. Boron and carbon in amorphous form dispersed homogeneously in the β-SiC polycrystalline particles. The particles were spherical, non-agglomerated and uniform in size with an average particle size of about 50 nm. Sintering tests were performed with the resulting composite powder without applying pressure. Powder containing 1 mass% boron and 2 mass% carbon was sintered to a density of 3.16×10^3 kg m^{-3} at 2273 K, and the Vickers hardness of the sintered body was 30 GPa. When the sintering temperature was higher than 2323 K, significant grain growth due to the phase transformation from β to α form occurred, which decreased bulk density and Vickers hardness.

1. Introduction

Silicon carbide (SiC) is a promising material for engineering and electronic applications due to its large energy band gap, high mechanical strength, excellent thermal shock resistance and superior chemical inertness at high temperatures. SiC body can be sintered without applying pressure by adding appropriate sintering aids, e.g. boron and carbon. However, the sintering temperature should be 2400 to 2500 K to obtain a fully dense body (density > 3.1×10^3 kg m^{-3}) [1–4]. At such high temperatures, a rapid grain growth, which is often described as abnormal grain growth, will occur particularly when β-SiC powders are used due to the phase transformation from β to α form at more than 2273 K [5–7]. This abnormal grain growth causes heterogeneous microstructure and mechanical degradation [5, 8]. In order to obtain a high strength SiC body, microstructure should be dense, fine grained and homogeneous. If fine powders in nanometer size are used, the full densification could be achieved at a low temperature without the abnormal grain growth [9, 10].

We synthesized β-SiC powders by chemical vapour deposition (CVD) using $(CH_3)_2$ $SiCl_2$ + H_2 and SiH_4 + CH_4 + H_2 systems and reported their microstructures and properties [11, 12]. When the $(CH_3)_2$ $SiCl_2$ + H_2 gas system was used, spherical polycrystalline β-SiC particles about 50 nm in diameter were obtained [11]. These fine particles might be suitable as starting materials. So far, several attempts [13, 14] have been made to sinter CVD fine powders by a pressureless process; however, sintering aids were necessary and the sintering temperature was almost the same as those required for conventional powders. If the sintering aids (i.e. boron and carbon) are co-deposited in β-SiC particles, the resulting particles are expected to be sinterable at lower temperatures. In this work, β-SiC powder containing boron and carbon (i.e. SiC–B composite powder) was prepared by CVD, and SiC bodies were fabricated using the composite powder by pressureless sintering.

2. Experimental procedure

2.1. Preparation and characterization of composite powder

CVD reaction was carried out in a tube reactor at a total gas pressure (P_{tot}) of 0.1 MPa. CVD apparatus and the experimental details were reported elsewhere [11]. A mixture of 2 mol% B_2H_6 (99.999%) + 98 mol% H_2 was used as the boron source. Liquid $(CH_3)_2SiCl_2$ (99.9%) was carried with H_2 gas (99.999%) into the reactor. Reaction temperature and total gas flow rate were 1673 K and 2.0×10^{-5} m^3 s^{-1}, respectively. The $(CH_3)_2$ $SiCl_2$ concentration was kept at 7.0 mol%, and the B_2H_6 concentration was changed from 0 to 0.7 mol% (B/Si molar ratio ranged from 0 to 0.2).

The shape and structure of particles were observed by transmission electron microscopy (TEM) (Jeol: JEM-2000EX). The crystal phases were identified using X-ray diffractometry (Rigaku: RAD-C, nickel filtered, CuK_α). The contents of silicon, carbon, hydrogen and oxygen in the powder were determined by chemical analyses. The boron content was determined by inductively coupled plasma (ICP) spectroscopy (Seiko: SPS1200A).

2.2. Pressureless sintering

CVD SiC–B composite powder containing 1 mass % boron and 2 mass % carbon was used as starting powder. Disc-shaped pellets 15 mm in diameter and 3 mm thick were prepared by cold isostatic pressing at 200 MPa. The green density of the powder compacts was about 1.54×10^3 kg m^{-3}. The pellets were sintered in a graphite furnace in an argon atmosphere at 2073–2423 K for 1 h. The temperatures were raised at a heating rate of 5 K min^{-1}. A commercial β-SiC powder (Ibiden: 0.28 μm in diameter) was also sintered with the addition of 1 mass % boron (Starck: amorphous boron particle) and 2 mass % carbon black. After sintering, shrinkage and bulk density were measured. Hardness was measured using a Vickers indenter (Akashi: MVK-E) at 0.5 kg load. The microstructures were observed by optical microscopy for polished surfaces after etching by Murakami's reagent (10 g NaOH + 10g $K_3Fe(CN)_6$ + 100 ml H_2O).

3. Results and discussions

3.1. Powder characterization

In the $(CH_3)_2SiCl_2 + H_2$ CVD system, the composition of the powders varied significantly with reaction temperature. Single-phase β-SiC powder was obtained at 1673 K, but those obtained below 1623 K were the composites of β-SiC and silicon [11]. In this work, the CVD temperature was fixed at 1673 K to avoid the formation of free silicon. Boron was co-deposited in various content by changing B_2H_6 gas concentration. Fig. 1 shows the relationship between boron content in the powder and B/Si molar ratio in the source gas. The boron content increased from 0 to 7.7 mass % as the B/Si molar ratio increased from 0 to 0.2. The chemical analyses showed that the as-prepared powders contain about 1 mass % oxygen, 0.1 mass % hydrogen and several mass % of free carbon. The amounts of oxygen and hydrogen were independent of reaction condition, however, the content of free carbon increased with increasing B/Si molar ratio. Thermodynamic calculations [15] explained that the addition of B_2H_6 to the $(CH_3)_2SiCl_2 + H_2$ system promotes the decomposition of CH_4 (one of the products of $(CH_3)_2SiCl_2$ decomposition) into free carbon.

Fig. 2 shows the electron micrograph and electron diffraction pattern of the SiC–B composite particles containing 1 mass % boron and 2 mass % carbon. The average particle size was about 50 nm, and the β-SiC crystalline size was several nanometres. Particles were spherical, non-agglomerated and uniform in size. The electron diffraction pattern shows that the particles are a single phase of polycrystalline β-SiC. Detailed studies [15, 16] on the state of boron and carbon have been performed by X-ray diffraction, X-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (EELS). Both boron and carbon are amorphous. Boron is present inside SiC particles up to 2 mass %, and also present on the surface of SiC particles when the total boron content is > 2 mass %. The free carbon could exist at the grain boundary of the β-SiC crystallites [11, 17].

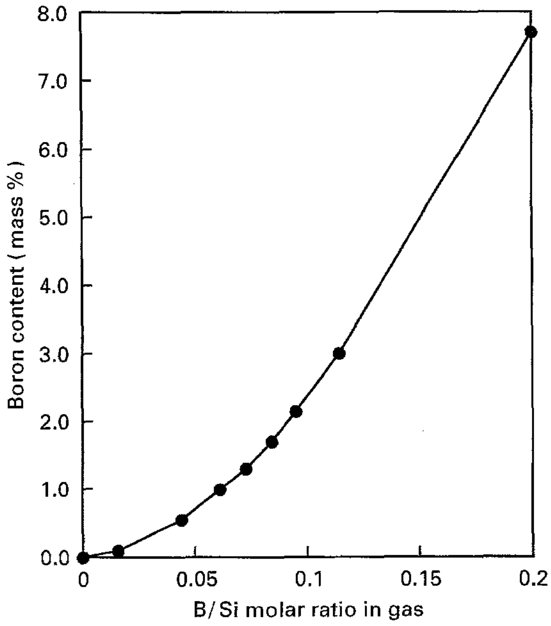


Figure 1 Relationship between boron content in powder and B/Si molar ratio in inlet gas.

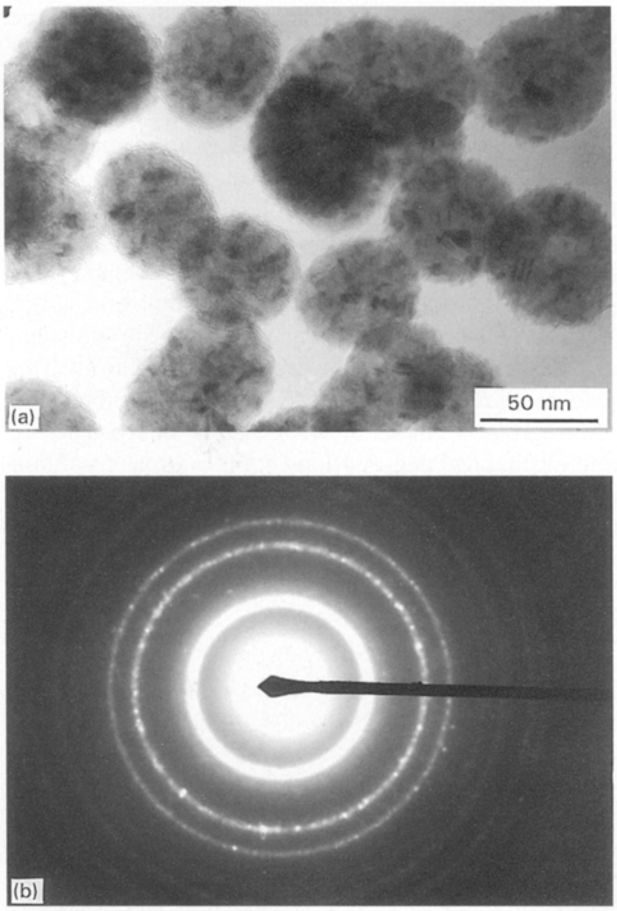


Figure 2 Electron micrograph (a) and electron diffraction pattern (b) of CVD SiC–B composite powder.

3.2. Pressureless sintering

SiC–B composite powder containing 1 mass % boron and 2 mass % carbon was sintered without applying pressure. Fig. 3 shows the effect of sintering temperature on density. The results of commercial β-SiC powder were compared in the same figure. In the case of the commercial β-SiC powder, densification began at 2073 K and the bulk density reached the maximum value of 3.15×10^3 kg m^{-3} (98.0% of theoretical density) at 2373 K, which agreed with those reported in the past [1–5]. On the other hand, in the case of CVD SiC–B composite powder the densification proceeded at a lower temperature and the density reached the maximum value of 3.16×10^3 kg m^{-3} at 2273 K. After reaching the maximum point, the density decreased with sintering temperature.

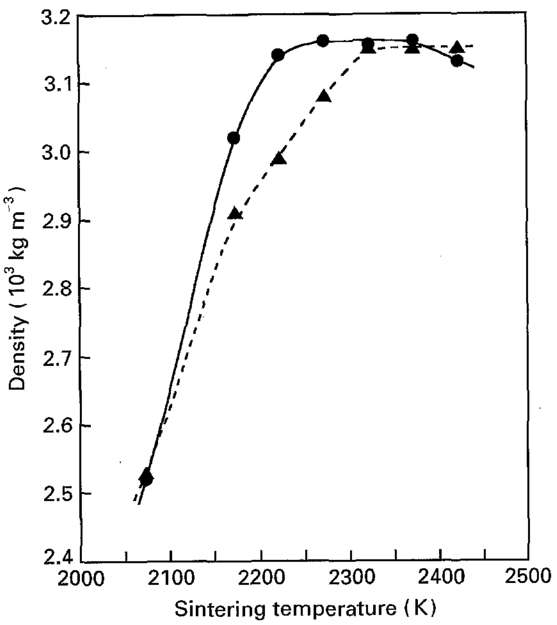
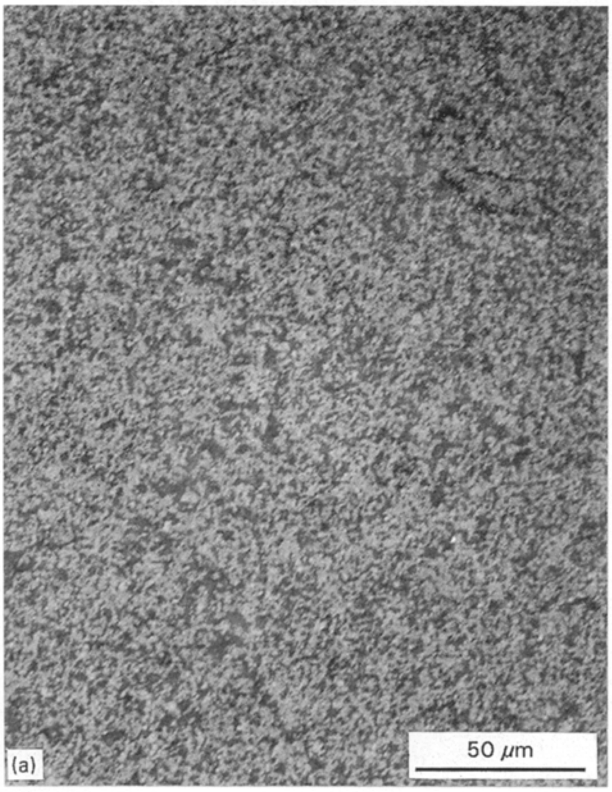


Figure 3 Relationship between sintered density and sintering temperature. (●) CVD SiC–B composite powder; (▲) commercial β-SiC powder (with additives: 1 mass % boron and 2 mass % carbon).



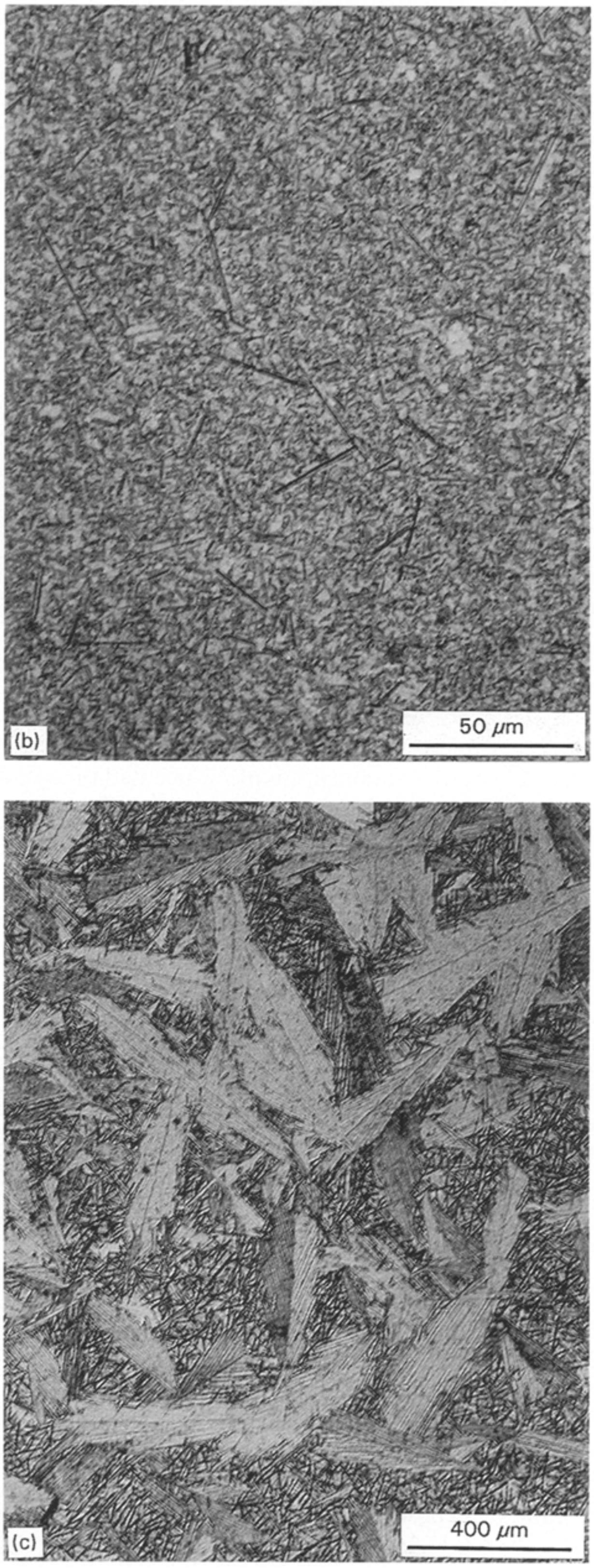


Figure 4 Optical micrographs of the etched surface of sintered SiC. Sintering temperature: (a) 2223 K, (b) 2273 K and (c) 2323 K.

Fig. 4 shows the optical micrographs of sintered SiC body. Fig. 5 depicts the average grain size calculated from the optical micrographs. The sample sintered at 2223 K had equiaxed grains of about 1 μm in diameter

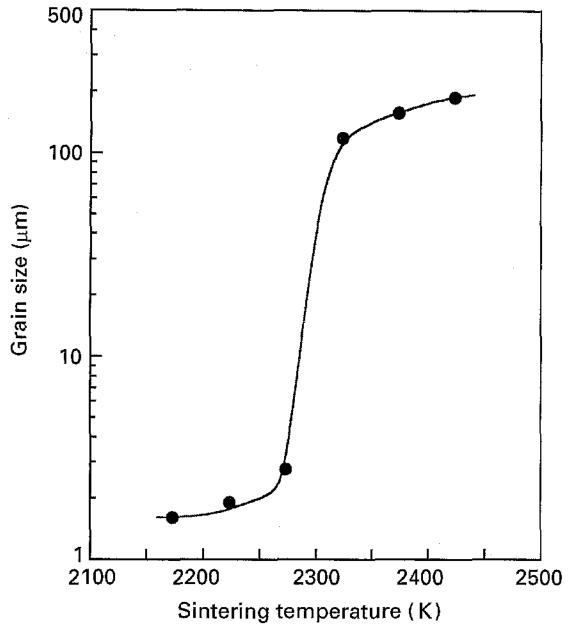


Figure 5 Relationship between grain size and sintering temperature.

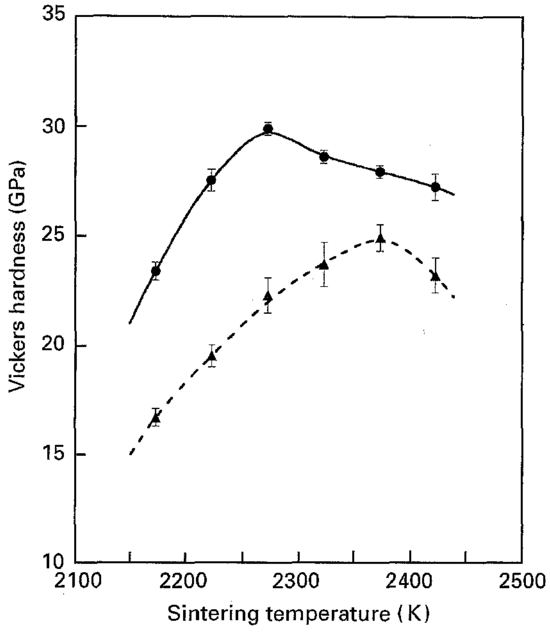


Figure 6 Relationship between Vickers hardness and sintering temperature. (●) CVD SiC–B composite powder; (▲) commercial β-SiC powder.

and some micropores. When the sintering temperature was 2273 K, the obtained sample, which had the maximum density, had a dense microstructure consisting of equiaxed fine grains with a small amount of platelet grains which might be α-SiC [5, 6, 18, 19]. Additionally no micropores were observed. When the sintering temperature was higher than 2323 K, coarse feather-shaped α-SiC grains larger than 100 μm were observed. The phase transformation from β to α form began at about 2273 K, and significant grain growth of α-SiC was observed when the sintering temperature was higher than 2323 K. This result agreed with past reports [5–7]. In order to prevent the abnormal grain growth, the sintering temperature should not be higher than 2273 K.

Fig. 6 shows the effect of sintering temperature on Vickers hardness. The hardness increased with sintering temperature up to 2273 K, and had the maximum value of 30 GPa which is the highest level for SiC reported so far [20, 21]. After reaching the maximum point, the hardness decreased with sintering temperature, which coincided with the temperature dependency of the bulk density. These might have resulted from grain coarsening as shown in Figs 4 and 5. The hardness of a SiC body prepared by commercial powder was lower than that prepared by CVD SiC–B composite powder as shown in Fig. 6.

Okabe *et al.* [14] prepared SiC–B composite powder by CVD using a $(CH_3)_4Si + BCl_3 + H_2$ system and sintered the composite powder. They obtained 94% theoretical density at 2173 K. Baumgartner and Rossing [19] and Suyama *et al.* [22] synthesized SiC–B composite powders, by plasma CVD using a $SiH_4 + CH_4 + B_2H_6 + H_2$ system. Baumgartner and Rossing [19] reported that the composite powder needed a sintering temperature higher than 2373 K (100 to 200 K higher than the present work) to obtain more than 95% theoretical density. The microstructure had a large proportion of coarse feather-shaped α-SiC grains [19]. That composite powder prepared by plasma CVD had an average particle size of about 300 nm with a wide size distribution ranging from 100 to 500 nm. However, the CVD SiC–B composite powder prepared in the present work had a much smaller particle size of about 50 nm and a narrower size distribution.

4. Conclusions

SiC–B composite powder was prepared by chemical vapour deposition of $(CH_3)_2SiCl_2 + B_2H_6 + H_2$ system at 1673 K. The powder was polycrystalline β-SiC containing several mass % of boron and carbon in amorphous form. The boron content changed from 0 to 7.7 mass % with increasing B/Si molar ratio in the source gas. Amorphous boron and carbon dispersed homogeneously in the particles. The composite particles were spherical and non-agglomerated. The average particle size was about 50 nm.

Composite powder containing 1 mass % boron and 2 mass % carbon was sintered up to a density of 3.16×10^3 kg m^{-3} at 2273 K. The sintered body had a dense and fine microstructure, and Vickers hardness was 30 GPa. When the sintering temperature was higher than 2323 K, the abnormal grain growth due to the α to β phase transformation occurred.

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References

1. S. PROCHAZKA, in "Special Ceramics 6", edited by P. Popper (British Ceramic Research Association, Stoke-on-Trent, 1975) p. 171.
2. S. PROCHAZKA and R. M. SCANLAN, *J. Amer. Ceram. Soc.* **58** (1975) 72.
3. Y. MURATA and R. H. SMOAK, in Proceedings of the International Symposium Factors in Densification and Sintering of Oxide and Non-oxide Ceramics, Hakone, Japan, 1978, edited by S. Somiya and S. Saito (Gakujustu Bunken Fukyu-Kai, Tokyo, 1979) p. 382.
4. H. TANAKA and Y. INOMATA, *J. Mater. Sci. Lett.* **4** (1985) 315.
5. H. TANAKA, Y. INOMATA, H. TSUKUDA and A. HAGIMURA, *Yogyo-Kyokai-Shi* **92** (1984) 461.
6. A. H. HEUER, G. A. FRYBURG, L. U. OGBUJI and T. E. MITCHELL, *J. Amer. Ceram. Soc.* **61** (1978) 406.
7. L. U. OGBUJI, T. E. MITCHELL and A. H. HEUER, *ibid.* **64** (1981) 91.
8. S. PROCHAZKA and R. J. CHARLES, *Amer. Ceram. Soc. Bull.* **52** (1973) 885.
9. H. K. BOWEN, *Mater. Sci. Eng.* **44** (1980) 1.
10. C. GRESKOVICH and J. H. ROSOLOWSKI, *J. Amer. Ceram. Soc.* **59** (1976) 336.
11. L. CHEN, T. GOTO and T. HIRAI, *J. Mater. Sci.* **25** (1990) 4614.
12. *Idem, ibid.* **24** (1989) 3824.
13. K. MIYACHI, Y. OKABE, J. HOJO and A. KATO, *J. Chem. Soc. Jpn.* **1** (1983) 28.
14. Y. OKABE, K. MIYACHI, J. HOJO and A. KATO, *ibid.* **9** (1981) 1363.
15. L. CHEN, Thesis, Tohoku University, 1990.
16. L. CHEN, T. GOTO and T. HIRAI, *J. Mater. Sci. Lett.* **9** (1990) 997.
17. M. ENDO, T. SANO, K. MORI, N. URASATO and N. SHIRAISHI, *Yogyo-Kyokai-Shi* **95** (1987) 114.
18. R. H. J. HANNINK, Y. BANDO, H. TANAKA and Y. INOMATA, *J. Mater. Sci.* **23** (1988) 2093.
19. H. R. BAUMGARTNER and B. R. ROSSING, in "Ceramic Transactions, Vol. 2: Silicon Carbide '87", edited by J. D. Cawley, C. E. Semler (American Ceramic Society, Westerville, 1989) p. 3.
20. T. SAKAIDA and M. YAMAMOTO, in "Tankakeiso Seramikkusu (SiC Ceramics)", edited by S. Somiya and Y. Inomata (Uchida Pokakuho, Japan, 1988) p. 373.
21. I. J. MCCOLM, in "Ceramic Hardness" (Plenum Press, New York and London, 1990) p. 217.
22. Y. SUYAMA, R. M. MARRA, J. S. HAGGERTY and H. K. BOWEN, *Amer. Ceram. Soc. Bull.* **64** (1985) 1356.

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