JOURNAL OF MATERIALS SCIENCE **39** (2004) 3801 – 3803 LETTERS

Effect of processing on densification of nanostructured SiC ceramics fabricated by two-step sintering

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In recent years there has been increased interest in nanostructured ceramics because their properties (e.g., sinterability, mechanical properties, or superplastic behavior) are often significantly different and considerably improved compared with conventional ceramics with coarser grain structures [1–4]. Several attempts to provide nanostructured ceramics (<100 nm in grain size) have been reported: (1) the use of a two-step sintering that separates grain-boundary diffusion from grain growth [3], (e.g., a pure Y_2O_3 specimen was first heated to 1310 °C and then heat-treated at 1150 °C for 20 hr, resulting in a grain size of 60 nm); (2) the addition of second- or third-phase particles to a single- or two-phase ceramics [5]; (3) the application of ultra-high pressure, such as ~1 GPa [6, 7]. Compared with the latter two methods, the two-step sintering is believed to be quite cost effective for production of nanostructured ceramics. Recently, feasibility of densification without appreciable grain growth by two-step sintering was tested in liquid-phase sintered SiC ceramics and a fully dense nanostructured SiC ceramic with a grain size of ~40 nm has been obtained [8].

In this study, the effect of processing parameters on densification behavior of nanostructured SiC ceramics was investigated in the two-step sintering process. The processing window for fabricating nanostructured SiC ceramics through two-step sintering is suggested.

Ultrafine β-SiC powders (Sumitomo-Osaka Cement Co., Japan) were oxidized at 600 °C for 2 hr in air to eliminate free carbon and then treated with HF to remove SiO_2. A combination of SiC powder mixed with 7 wt% Al_2O_3, 2 wt% Y_2O_3 and 1 wt% CaO was milled for 6 hr in a vibratory mill. Through observation by TEM, the average particle size after the milling was determined to be ~20 nm. The powder compacts were heated to a temperature (designated as a peak temperature, T1) ranging from 1550 to 1750 °C to achieve an intermediate density, then immediately cooled down and held at a lower temperature (designated as a sintering temperature, T2) ranging from 1500 to 1600 °C to achieve full density. The specimens were sintered at T2 for up to 8 hr under an applied pressure of 20 MPa in argon atmosphere. The heating rate was 20 °C/min, and the cooling rate from the sintering temperature to 1200 °C was 40 °C/min. The heating schedules are shown in Table I.

The relative densities of the sintered specimens were determined by the Archimedes method. The sintered specimens were cut and polished, then etched by a CF_4 plasma containing 7.8% O_2. The microstructures were

TABLE I Sintering schedules adopted in this experiment

Sample designation	Peak temperature (T1, °C)	Sintering temperature (T2, °C)	Holding time at T2 (hr)
SC1	1750	1550	0
SC2	1750	1550	1
SC3	1750	1550	4
SC4	1750	1550	8
SC5	1700	1500	8
SC6	1700	1550	8
SC7	1700	1600	8
SC8	1650	1500	8
SC9	1650	1550	8
SC10	1650	1600	8
SC11	1600	1550	8
SC12	1550	1550	8

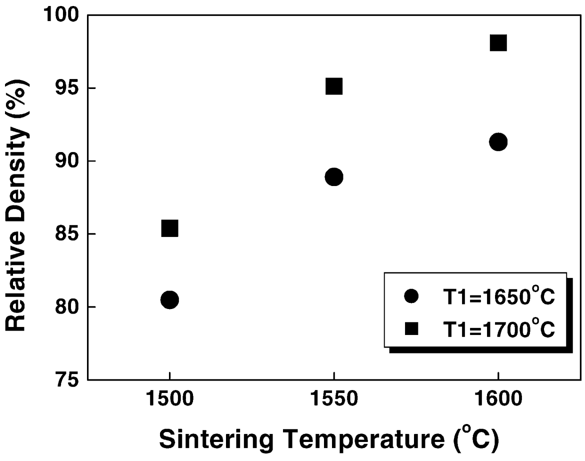

Figure 1 Relative density of nanostructured SiC ceramics as a function of sintering temperature. The peak temperature (T1) was fixed as 1650 °C or 1700 °C.

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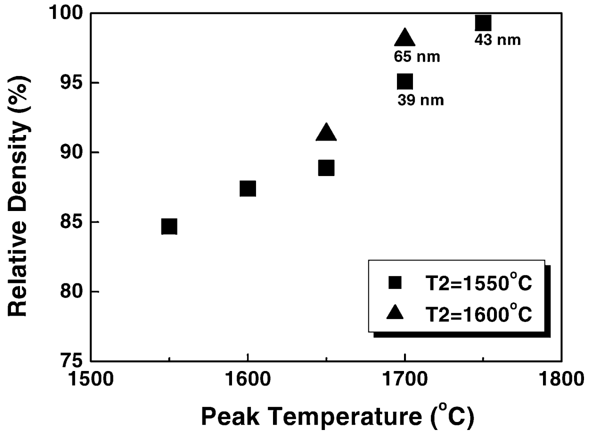

Figure 2 Relative density of nanostructured SiC ceramics as a function of peak temperature. The sintering temperature (T2) was fixed as 1550 °C or 1600 °C. The grain sizes of dense specimens with sintered densities greater than 95% were shown.

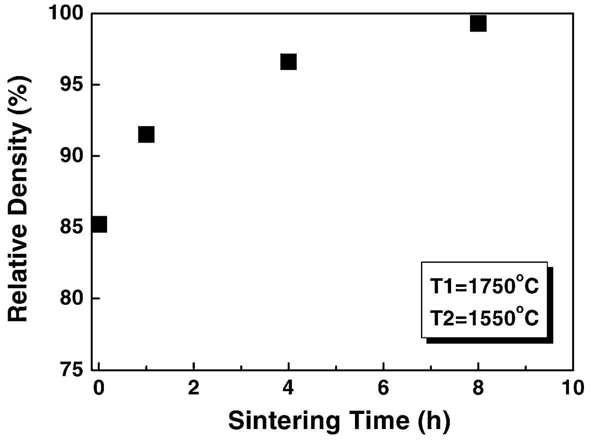

Figure 3 Relative density of nanostructured SiC ceramics as a function of sintering time. The peak temperature (T1) and the sintering temperature (T2) were 1750 and 1550 °C, respectively.

observed by scanning electron microscopy (SEM). The average grain size (the 50% value of the cumulative area curve) was determined by using an image analyzer (Image-Pro Plus, Media Cybernetics, Maryland, USA).

Fig. 1 shows the effect of sintering temperature (T2) on densification of nanostructured SiC ceramics when T1 = 1650 °C or 1700 °C. Relative density increased with increasing the sintering temperature. The highest density (98.1% of TD) was obtained for a specimen (SC7) heated to 1700 °C and sintered at 1600 °C for 8 hr. When the peak temperature was 1700 °C, the nanostructured SiC ceramics with densities greater than 95% could be obtained at sintering temperatures ranging from 1550 to 1600 °C.

When T2 = 1550 °C or 1600 °C, the effect of peak temperature on sintered density of nanostructured SiC ceramics is shown in Fig. 2. Relative density increased with increasing the peak temperature. The maximum density (99.3% of TD) was obtained for a specimen (SC4) heated to 1750 °C and then cooled down and held at 1550 °C for 8 hr. The final grain size of SC4 was 43 nm. When T2 = 1550 °C, the nanostructured SiC ceramics with densities greater than 95% could be obtained at peak temperatures ranging from 1700 to 1750 °C.

Fig. 3 shows the effect of sintering time on sintered density of nanostructured SiC ceramics heated to 1750 °C and then, cooled down and held at 1550 °C for up to 8 hr. The relative density of specimens fabricated by two-step sintering increased continuously with the sintering time. It has been observed that the longer the sintering time the higher sintered density. Almost full density was obtained after 8 hr sintering.

The microstructures of two-step sintered specimens are shown in Fig. 4. The grain sizes of SC6 and SC7 were 39 and 65 nm, respectively. The grain size distributions of both specimens were uniform throughout the specimens. It is well known that SiC containing Al_2O_3-Y_2O_3-CaO as sintering additives was densified through liquid-phase sintering mechanism [9, 10]. During the liquid-phase sintering, the final stage of densification is known to occur mainly by the elimination of isolated pores through the liquid flow into them. It has been determined that the smaller the pore size the faster the elimination process. In this regard, the density and pore size obtained after the first step would be a critical factor

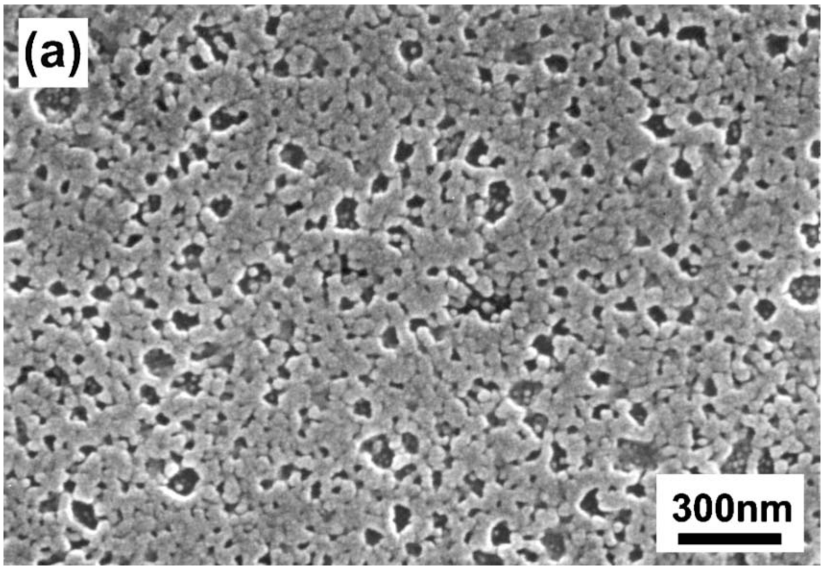

Figure 4 Microstructures of nanostructured SiC ceramics: (a) SC6 and (b) SC7 (refer to Table I). (*Continued*)

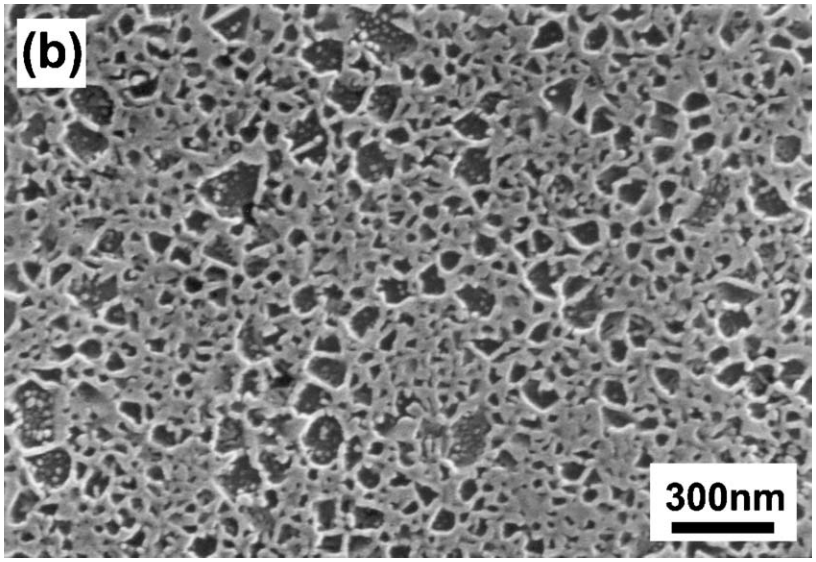

Figure 4 (Continued)

for achieving a full density in subsequent second-step sintering. A previous study [8] has shown that the grain size of a zero-time sintered specimen after sintering at 1750 °C for 0 hr was 38 nm and it showed 85% of TD. For SC4-specimen, therefore, the densification from 85 to 99% of TD has occurred during the second step at 1550 °C without any notable grain growth. For the fabrication of nanostructured SiC ceramics with densities greater than 98% of TD, densities higher than 85% of TD were required after the first step.

Present results suggest that nanostructured SiC ceramics can be obtained via two-step sintering when the specimen was first heated to temperatures ranging from 1700 to 1750 °C and then cooled immediately for long treatment (8 hr) at lower temperatures ranging from 1550 to 1600 °C.

The finest grain size of fully dense liquid-phase sintered SiC ceramics examined so far lies around ∼40 nm (see Fig. 4a), and is about two times the starting powder size. This increase was entirely due to the grain growth during heating up to the peak temperature. We believe that there should be a processing window for nanostructured microstructures, i.e., "quasi-frozen region" that separates densification from grain growth during liquid-phase sintering in other liquid-phase sintered systems. We consider that the simplicity of this method makes it useful for fabricating dense nanostructured materials that will give us improvements in grain-size-dependent properties such as hardness, strength, and wear resistance [11].

Acknowledgments

One of authors (Y.-W. Kim) gratefully acknowledges useful discussion with Prof. D.-Y. Kim at Seoul National University. This work was supported by the Korea Science and Engineering Foundation (KOSEF) under Grant No. R01-2001-00255.

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Received 2 December 2003
and accepted 11 February 2004