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Fabrication of Si_3N_4/SiC nanocomposites by spark plasma sintering of amorphous SiCN powders derived from a polymeric precursor

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Si_3N_4/SiC nanocomposites were fabricated by spark plasma sintering (SPS) of amorphous SiCN ceramic powders derived from a polymeric precursor with 3 wt% yttria as an additive. It was found that the SPS parameters, such as sintering temperature, dwell time, pressure and heating rate, remarkably affected the density and grain size of the nanocomposites obtained. This provided a new method to fabricate Si_3N_4/SiC nanocomposites without applying the high pressure and high sintering temperature used by the conventional process.

Key words: Si_3N_4/SiC nanocomposites, Spark plasma sintering, Polymeric precursor.

Introduction

Nanocrystalline materials have attracted extensive interest during the past decade, with the expectation that their properties could be different from and superior to those of materials with coarser grains [1]. However, fabrication of bulk nanocrystalline materials is not straight forward and often limited by the grain coarsening during sintering. This is particularly true for silicon-based ceramics (e.g. SiC and Si_3N_4) since the high temperature and long dwell time required to densify the materials can lead to significant grain growth and result in a grain size of at least 200-300 nm even when starting with nano-sized powders [2, 3]. Up to date, several unusual methods have been developed to produce Si_3N_4/SiC nanocomposites. Pootenman and co-workers [4] fabricated Si_3N_4/SiC nanocomposites by nitridation of silicon carbide. The materials they obtained were composed of sub-micronmetre-sized silicon nitride and silicon carbide particles, along with nano-sized SiC particles embedded in silicon nitride grains. Wan et al. [5] have fabricated Si_3N_4/SiC nano-nano composites with ~30 nm grain size by crystallization of bulk amorphous SiCN. However, these porosity of the synthesized nanocomposites was relatively high. Si-based ceramic nanocomposites can also be obtained using a high-pressure sintering technique [6-10]. More recently, Wan et al. [11] reported the fabrication of Si_3N_4/SiC nanocomposites using spark plasma sintering (SPS) of SiCN amorphous powders. By varying the amount of sintering aids, nano/nano-composites with a mean grain size of ~40 nm and fairly high density were obtained.

In this paper, Si_3N_4/SiC nanocomposites were fabricated using spark plasma sintering of amorphous SiCN powders derived from a polymeric precursor. Compared to the previous study [11] that reported the effect of additive content on the sintering behavior of the amorphous SiCN powders, the present study focuses on the effect of SPS parameters, such as sintering temperature, dwell time, pressure and heating rate.

Experimental Procedure

Polyureasilazane (Ceraset, Kion Corporation, Huntingdon Valley, PA) was used as the starting precursor. The as-received Ceraset, which is liquid at room temperature, was first solidified by heat-treatment at 260 °C for 0.5 hours in nitrogen. The solidified precursor was then crushed and ball-milled into powder. The powder was then placed in a high purity alumina crucible and heat-treated at 1000 °C for 2 h in flowing nitrogen in a conventional tube furnace to convert it into SiCN ceramic powder [12]. The ceramic powder obtained was then crushed into fine powder by high-energy ball milling for 24 h with 3 wt% Y_2O_3 as additive. Three grams of the SiCN powders were packed into a graphite die 19 mm in diameter and sintered using an SPS system (Dr. Sinter 1050, Sumitomo, Japan) in a vacuum. The sintering schedule was: after applying the given pressure, samples were heated to 600 °C in 2 minutes and then ramped to the sintering

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Table 1. Sintering conditions for different composites

Mater.	Sintering Temp. (°C)	Dwell Time (minutes.)	Pressure (MPa)	Heating Rate (K/minute)
M1	1600	5	80	100
M2	1600	10	80	100
M3	1600	15	80	100
M4	1600	10	40	100
M5	1600	10	60	100
M6	1600	10	80	50
M7	1600	10	80	200
M8	1600	10	80	300
M9	1550	10	80	100
M10	1650	10	80	100
M11	1700	10	80	100

temperatures at the given heating rates. The samples were held at the sintering temperatures for varied times before turning off the power. To study the effect of SPS parameters on the densification and grain growth behavior, the sintering temperature, dwell time, pressure and heating rate were varied systematically, as illustrated in Table 1.

The sintered products were characterized using X-ray diffraction (XRD, Automated D/Max-RB, Rigaku, Tokyo, Japan) and scanning electron microscopy (SEM, JSM-6301F, JEOL, Tokyo, Japan).

Results and Discussion

The composites obtained were first characterized using XRD to identify their phase compositions. Figure 1 shows the typical XRD patterns, which are similar for all the samples obtained at different conditions, revealing that the composites consist of β-SiC (JCPDS Card No. 29-1129) as the major phase, α-Si_3N_4 (JCPDS Card No. 41-0360) and β-Si_3N_4 (JCPDS Card No. 33-1160) phases, along with a small amount of α-$Y_2Si_2O_7$ (JCPDS Card No. 38-0223). This result is quite different from that reported previously [11] where a composite obtained under the similar conditions consisted of only β-SiC and β-Si_3N_4 phases, along with a small amount of Si_2N_2O phase; no α-Si_3N_4 and α-$Y_2Si_2O_7$ phases were observed. The major crystalline phase which is SiC can be understood since at the present sintering conditions (1600 °C and a low N_2 partial pressure), SiC is more stable than Si_3N_4 [13-15]. Co-existence of α-Si_3N_4 and β-Si_3N_4 is due to a relatively small amount of liquid phase and a shorter dwell time that limited the complete conversion of Si_3N_4 to SiC and transformation of α-Si_3N_4 to β-Si_3N_4.

Figure 2 shows SEM images of the fracture surfaces of the nanocomposites obtained at different conditions.

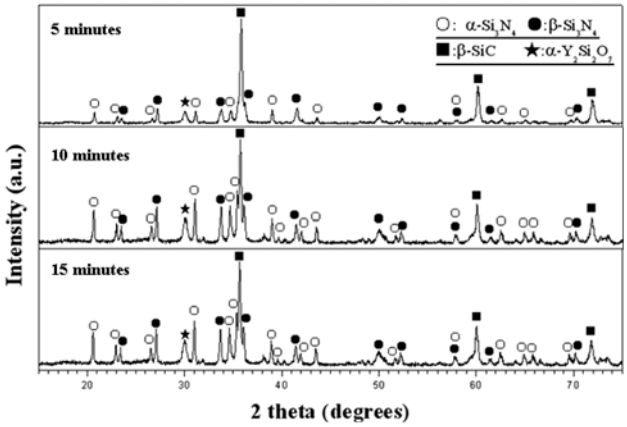

Fig. 1. XRD patterns of Si_3N_4/SiC nanocomposites synthesized at 1600 °C and 80 MPa with different dwell times as indicted. The heating rate was 100 K/minute.

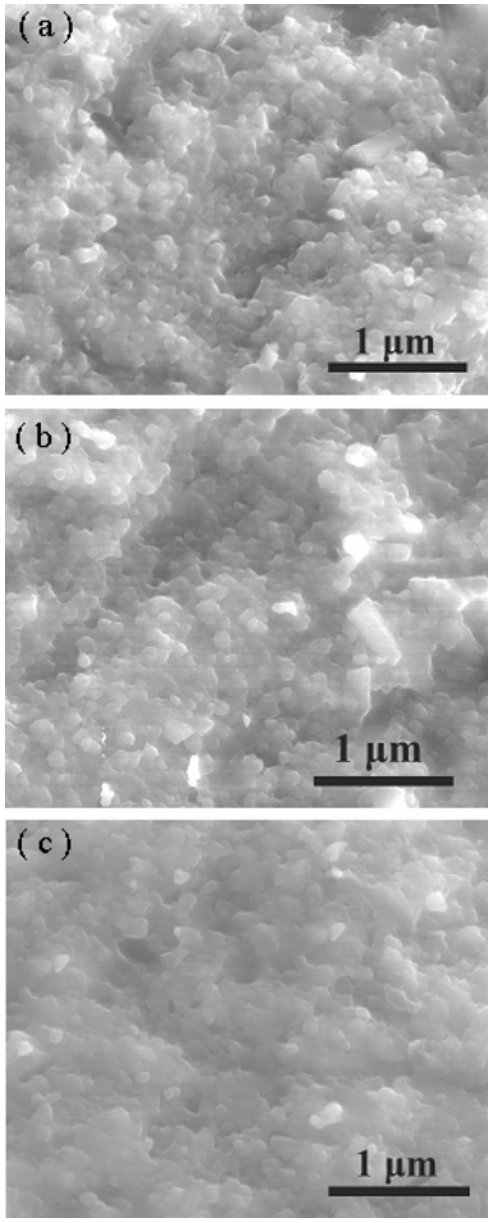

Fig. 2. SEM micrographs showing the fracture surfaces of Si_3N_4/SiC nanocomposites synthesized at 1600 °C and 80 MPa for dwell times of (a) 5 minutes, (b) 10 minutes and (c) 15 minutes. The heating rate was 100 K/minute.

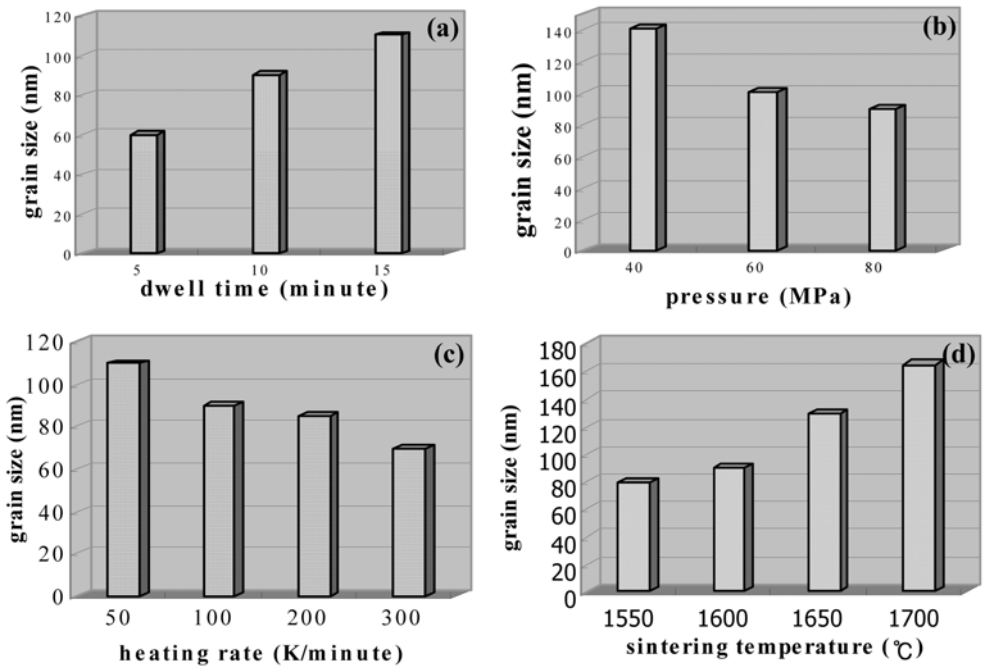

Fig. 3. Grain sizes as a function of SPS conditions: the data points were measured from samples (a) M1, M2 and M3; (b) M2, M4 and M5; (c) M2, M6, M7 and M8; (d) M2, M9, M10 and M11 (for the M codes, see table 1).

Besides a few large elongated silicon nitride grains, the composites consist of a homogenous mixture of silicon nitride and silicon carbide with equiaxed grains. No obvious pores can be observed from the micrographs, suggesting that the samples have a relatively high density and sintering is uniform (no "giant" pores due to local densification).

The grain size was measured from the SEM images for all the composites. The mean grain size (averaged from at least 200 grains) is plotted as a function of sintering conditions (Fig. 3). As expected, the grain size increases with dwell time and sintering temper-

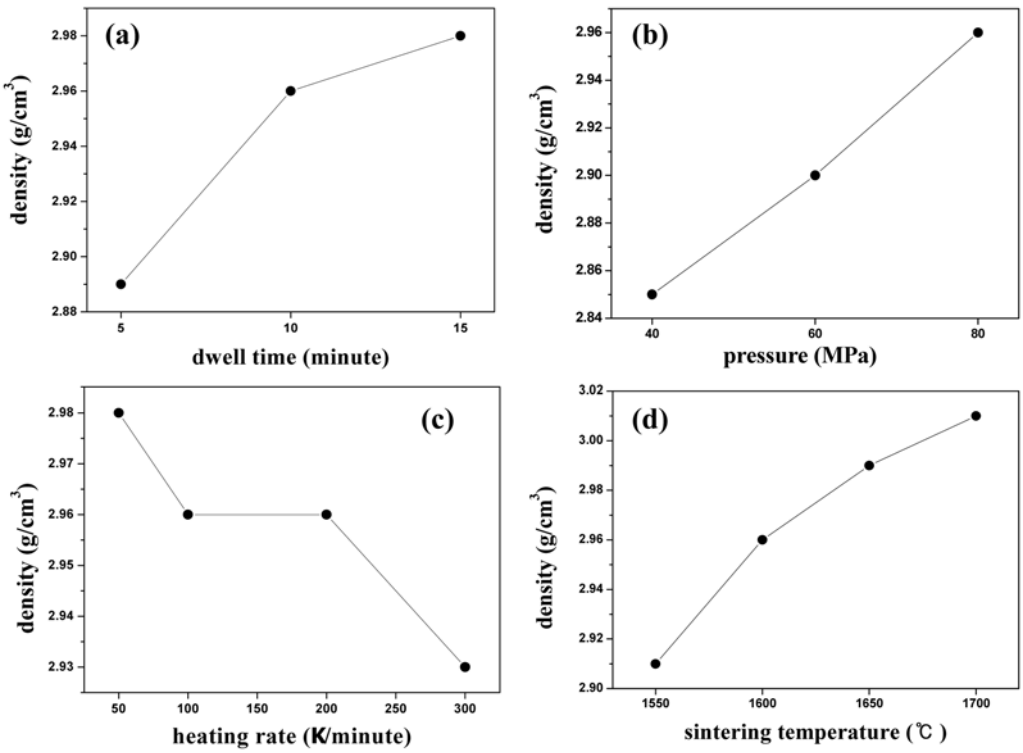

Fig. 4. Densities as a function of SPS conditions: the data points were measured from samples (a) M1, M2 and M3; (b) M2, M4 and M5; (c) M2, M6, M7 and M8; (d) M2, M9, M10 and M11.

ature (Fig. 3a and d), with the temperature has the most effect. The grain size decreases with pressure (Fig. 3b), suggesting pressure can suppress grain growth. The grain size also decreases with heating rate (Fig. 3c), indicating that the grain growth already started at temperatures lower than the sintering temperature (1600 ^{o}C).

The densities of the composites synthesized at different conditions were measured by the Archimedes' immersion method and are presented in Fig. 4. It can be seen that the density increases with dwell time, sintering temperature and pressure. The density slightly decreases with heating rate, which is consistent with a previous study [11] that revealed that a small amount of densification occurred at temperatures lower than 1600 ^{o}C.

The above results suggest that while dwell time and sintering temperature can help to achieve a higher density, both of them also significantly enhance the grain growth. Therefore, nanocomposites (grain size < 100 nm) with a high density cannot be obtained by increasing either the dwell time or sintering temperatures. Pressure can significantly increase the density and meanwhile suppress the grain growth, thus high pressure is desired to obtain dense nanocomposites. While it can lead to a slight decrease in density (2.98 g/cm^3 at 50 K/minute to 2.93 g/cm^3 at 300 K/minute), increasing the heating rate can remarkably decrease the grain size (110 nm at 50 K/minute to 70 nm at 300 K/minute). Therefore, a high heating rate is required to obtain nanocomposites with a high density.

Conclusions

In this study, the densification and grain growth during synthesis of Si_3N_4/SiC nanocomposites by spark plasma sintering of amorphous SiCN powder were studied as a function of sintering temperature, dwell time, pressure and heating rate. It was found that all these SPS processing parameters have a noticeable effect on the grain size and density of obtained composites. This would provide a new method to fabricate Si_3N_4/SiC nanocomposites without applying high pressure and high sintering temperature used by the conventional process.

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