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Effect of Milling on the Densification of SiC-Based Composites from Polysilazane

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Abstract

High density SiC-based composites from polysilazane were fabricated by high energy milling and hot pressing. After cross-linking at 200 °C, the polysilazane was pyrolysed at 1000 °C in N₂ for 2 h to form amorphous Si-C-N-O followed by high energy milling for 1 h. Milled amorphous Si-C-N-O was sintered in hot pressing at 1600 and 1700 °C for 1 h in vacuum under the applied pressure of 50 MPa. Although no sintering additives were used, dense SiC-based composites were obtained with this method. Sintered density was 3.04 g/cm³, while only 2.57 g/cm³ for amorphous Si-C-N-O without milling. It is suggested that the liquid phase generated during the formation of Si₂N₂O facilitated the densification of the composite.

Abstrak

Pengaruh Penggilingan terhadap Densifikasi Komposit berbasis SiC dari Polysilazane. Komposit berkepadatan tinggi berbasis SiC dari polysilazane dibuat dengan penggilingan energi tinggi dan *hot pressing*. Setelah ikatan silang (*cross linking*) pada suhu 200 °C, polysilazane mengalami pirolisis pada suhu 1000 °C in N₂ selama 2 jam untuk membentuk amorf Si-C-N-O diikuti dengan penggilingan energi tinggi selama 1 jam. Gilingan amorf Si-C-N-O disinter pada *hot pressing* pada suhu 1600 dan 1700 °C selama 1 jam dalam vakum di bawah tekanan terapan 50 MPa. Meskipun tidak menggunakan aditif yang disinter, komposit padat berbasis SiC diperoleh dengan metode ini. Kepadatan sinter yang diperoleh adalah 3,04 g/cm³, sementara hanya 2,57 g/cm³ untuk amorf Si-C-N-O tanpa penggilingan. Terlihat bahwa fase cair yang dihasilkan selama pembentukan Si₂N₂O memfasilitasi densifikasi komposit.

Keywords: high energy milling, polysilazane, SiC-based composites, Si₂N₂O

1. Introduction

It is well known that SiC-based composite has excellent mechanical and thermal properties at high temperature. However, SiC has a high covalent bonding and low-self diffusivity, making it difficult to obtain dense material with normal sintering technique. Hot pressing sintering with temperature and pressure at 2500 °C and 5 GPa, respectively, is needed to obtain dense SiC [1]. Another effort to obtain SiC at lower temperature is reported by Xie *et al.* [2]. They succeeded in fabricating SiC with 96% of theoretical density at 1300°C with an applied pressure of 4-4.5 GPa. However, these processes are not suitable for industrial application due to high processing temperature and/or pressure. To overcome this problem, normally sintering additives are used to fabricate dense SiC. Moreover, the addition of sintering additives also decreases the sintering temperature of SiC. In liquid phase sintering, sintering additives react with thin layer SiO₂

that exists on the surface of SiC to form a liquid phase and enhance the densification of SiC. Although the sintering additives can increase the density of SiC, the grain growth can be enhanced with the addition of sintering additives [3], which might decrease the mechanical properties of SiC.

Polysilazane, one of the polymer derived-ceramics, has been applied in wide range of applications, such as synthesis of fibers and coatings [4-9]. According to manufacturer [10], polysilazane can be derived to Si-based ceramics such as SiC, SiC/Si₃N₄ or Si_xN_yO_z depend on the atmosphere of the pyrolysis. Nowadays, we can find a published report about fabrication of Si₃N₄ [11] or Si₃N₄/SiC [4,11-15] from polysilazane. However, to obtain fully dense ceramic composites from polysilazane, the sintering additives are still required [11-15]. Therefore, fabrication of SiC-based composites from polysilazane without the addition of sintering additives is still challenging.

In this study, we successfully fabricated high density SiC-based composites from polysilazane prepared by high energy milling without intentional addition of sintering additives. One hour of high energy milling using 0.45 mm ZrO₂ beads was performed for the milling of amorphous Si-C-N-O powder before sintering. It seems that the formation of Si₂N₂O in the sintered amorphous Si-C-N-O prepared by high energy milling played an important role in promoting densification. The phase generated during sintering, density, and microstructure of amorphous Si-C-N-O prepared by high energy milling were compared to amorphous Si-C-N-O without milling.

2. Experimental

Starting materials in this study were commercial polysilazane (KiON Ceraset Polysilazane 20, USA). Cross-linked polysilazane was obtained by heating at 200 °C for 90 min in hot plate followed by grinding in mortar and pestle. Cross-linked powder was pyrolysed at 1000 °C under N₂ atmosphere for 2 h to obtain amorphous Si-C-N-O powder. Although the pyrolysis was performed in N₂ atmosphere, oxygen element was found in the amorphous powder [9,15] with chemical composition of Si_{1.00}C_{1.55}N_{0.81}O_{0.17} [15]. High energy milling (MiniCer, Netzch, Germany) was used to reduce the particle size of amorphous Si-C-N-O powder for 1 h using 0.45-mm ZrO₂ beads at 3000 rpm. Milled powders were put in the graphite die and hot-pressed (ThermVac Engineering Inc., Korea) at 1600 and 1700 °C for 1 h in vacuum under the applied pressure of 50 MPa. The samples were named HEM1600 and HEM1700 for high energy milling of amorphous Si-C-N-O sinter at 1600 and 1700 °C, respectively. For comparison, amorphous Si-C-N-O was hot-pressed at 1600 and 1700 °C at same condition without milling step, named 1600 and 1700, respectively.

The Archimedes principle was used to measure the density of the sintered specimens. The phases generated after sintering was analyzed by X-ray diffraction (XRD: X'Pert-PRO MPD, PANalytical B.V., The Netherlands), using the Cu K α line, 40 kV and 30 mA, and Rietveld refinement were performed for quantitative phase verification after sintering. The microstructures of specimens and composition were examined by scanning electron microscopy (SEM: Hitachi S-4800, Japan) equipped with an energy dispersive X-ray spectrometer (Horiba EX-250).

3. Results and discussion

Figure 1 shows the particle size of amorphous Si-C-N-O powders before and after milling process. The amorphous Si-C-N-O before milling had an irregular shape, as shown in Figure 1 (a). One hour of high energy milling resulted in size decrease to less than 1,000 nm, as shown in Figure 1 (b), while the shape of particle did not change significantly after milling.

Figure 2 shows the XRD patterns of sintered composites with and without milling at different hot pressing temperatures. SiC, Si₂N₂O, Si₃N₄, and ZrO₂ phases were observed for milled amorphous powder at both temperatures, while SiO₂ and Si were only observed in 1600 and 1700 °C, respectively. ZrO₂ was present as

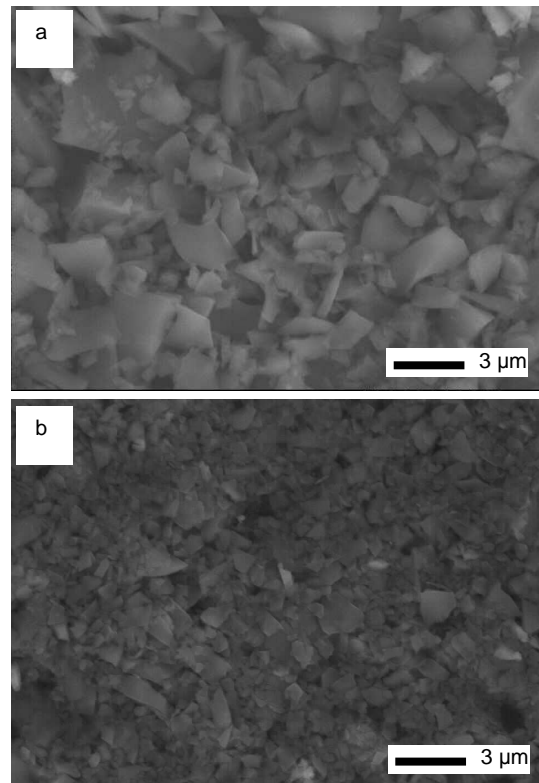


Figure 1. SEM Images of the Amorphous Si-C-N-O (a) before Milling and (b) after High Energy Milling for 1 Hour

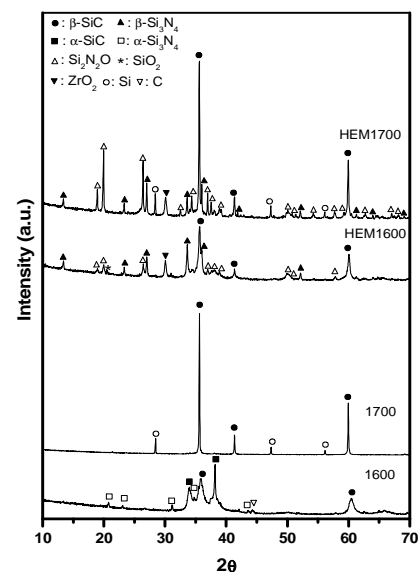


Figure 2. XRD Patterns of the Sintered SiC-based Ceramic Composite with Different Hot Pressing Temperature

impurity from milling media, which was inevitable. Since the amorphous powder composed of Si, C, N, and O, either SiO₂, SiC or Si₃N₄ can be formed depending on sintering condition. Based on Gibbs free energy at 1600 °C, SiO₂ has the lowest energy -576.020 kJ mol⁻¹ compared to Si₃N₄ (-37.868 kJ mol⁻¹) and SiC (-53.173 kJ mol⁻¹) [16]; hence, in the beginning of sintering the formation of SiO₂ was favorable, which was confirmed in the XRD results as shown in Figure 2.

The formation of SiO₂ along with Si₃N₄ led to the formation of Si₂N₂O follow the reaction equation (1) [17]:



It was reported that Si₂N₂O was only formed via liquid phase at the eutectic composition of 98 Si₃N₄- 2 SiO₂ mol % [17-18]. The greater amount of Si₂N₂O at 1700 °C than 1600 °C can be explained by the complete reaction between Si₃N₄ with SiO₂, thus no SiO₂ peaks could be observed at 1700 °C. One notable thing is the presence of β-Si₃N₄ without showing α-Si₃N₄. According to Tanaka *et al.* [19], the temperature of transformation α- to β- Si₃N₄ is 1750 °C, which is higher than this observation. In our case, the transformation of α- to β-Si₃N₄ was completed at <1600 °C. The lower α- to β-Si₃N₄ transformation temperature than the previous report might be attributed to the high-energy milling process as also reported in the case of lowering sintering temperature of Gd doped-Ceria [20].

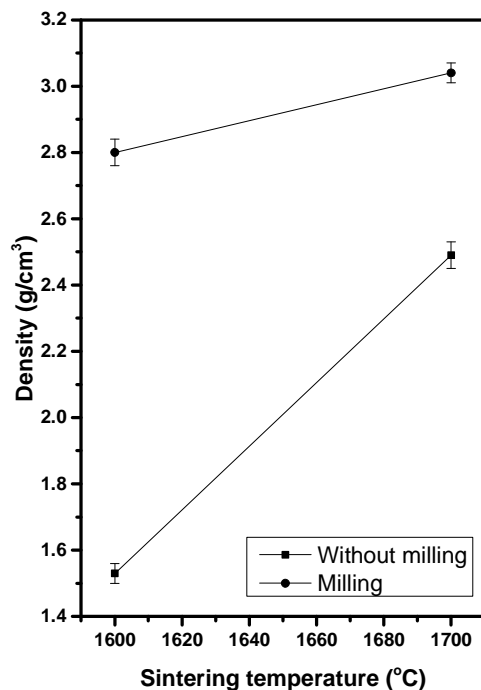


Figure 3. Densities of the Sintered SiC-based Ceramic Composite with Different Hot Pressing Temperature

Since β-Si₃N₄ is more energetically favorable than α-Si₃N₄ at high temperature, the transformation from α- to β-Si₃N₄ is irreversible. In contrast, no SiO₂ peaks were observed at 1600 °C for hot-pressed amorphous Si-C-N-O without milling as seen in Figure 2. Therefore, as expected, the formation of Si₂N₂O did not occur without the presence of SiO₂. It seemed either high energy milling or impurity ZrO₂ might be affected to the formation of SiO₂, as it occurred only in the milled amorphous Si-C-N-O. Only metastable α-SiC (2H) phase, α-Si₃N₄ and C were formed at 1600 °C.

At 1700 °C, all metastable α-SiC (2H) phase transformed to stable phase β-SiC and the decomposition of Si₃N₄ under the existence of free C [21] resulted in the excess Si.

Figure 3 shows the density of SiC-based composites with and without milling. Regardless of the milling process, the composite density increased with the increase of hot pressing temperature as shown in Figure 3. The densities of HEM1600 and HEM1700 were 2.80 and 3.04 g/cm³, respectively, and 1.53 and 2.47 g/cm³ for 1600 and 1700, respectively. There were two possibilities of liquid phase sintering mechanism in this study: the presence of ZrO₂ impurity that acted as sintering additives or the formation of Si₂N₂O that involved liquid. One of the important things in the liquid phase sintering was that the additives should not react with SiC or Si₃N₄ during sintering [22] since the reaction between additive and the matrix hindered the formation of liquid phase [23]. There are few studies that have reported ZrO₂ as sintering additives for Si₃N₄ [24-27], while the formation of ZrN was reported during sintering of Si₃N₄ with the addition of ZrO₂ as sintering additives [24-25]. Moreover, fully dense Si₃N₄ could not reach even ZrO₂ content which was increased up to 20 wt.% [27]. In order to investigate the effect of ZrO₂ impurity in the composites, we added intentionally 5 wt.% and 10wt.% of ZrO₂ (mean particle size: 200 nm) to the amorphous Si-C-N-O and hot pressed at 1700 °C in the same condition. The densities were 2.04 g/cm³ and 2.21 g/cm³ for 5 wt.% and 10 wt.% addition of ZrO₂, respectively. It seemed that the ZrO₂ introduced by the high energy milling created almost no effect to enhance the densification of HEM1600 and HEM1700. Moreover, the amount of ZrO₂ introduced by high energy milling was 3.2–3.4 wt. % based on the quantitative analysis of XRD, which meant that it was quite low to act as sintering additives. Therefore, enhancing sintering density of HEM1600 and HEM1700 might be explained with the existence of liquid phase associated with the formation of Si₂N₂O. This liquid phase acted as a high diffusivity path to enhance the density of the composites. Hence, the density of SiC-based composite increased with the existence of Si₂N₂O. In addition, the formation of Si₂N₂O was desirable because this phase conferred the excellent high temperature strength and oxidation

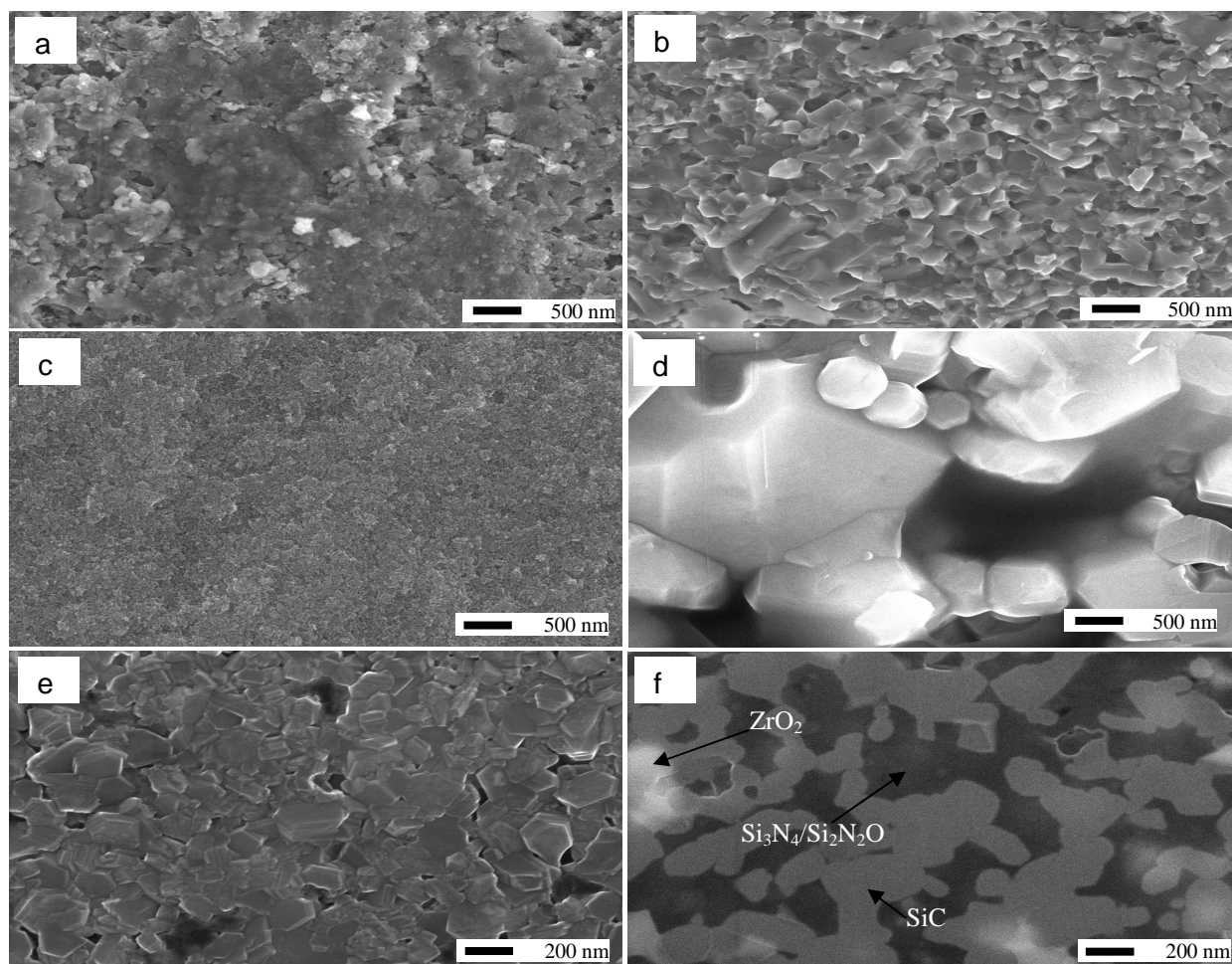


Figure 4. SEM Images of Fractured Surface of (a) HEM1600, (b) HEM1700, (c) 1600, (d) 1700, (e) Thermally-etched and (f) Polished Surface of HEM1700. Different Magnification was Used for (e) and (f) for Convenient

resistance [28-29]. Furthermore, the typical hot pressing temperature of $>1800\text{ }^{\circ}\text{C}$ for Si_3N_4/SiC composites can be used to achieve the density of $>3.00\text{ g/cm}^3$ with the addition of 8-15 wt. % sintering additives [13,30-32], which was higher compared to this study.

SEM images of the fractured surface of HEM1600, HEM1700, 1600 and 1700 are shown in Figure 4. Since no other phase such Si_2N_2O and ZrO_2 was found, the microstructure of 1600 (Figure 4 (c)) was very fine, and the grain size cannot be seen clearly with SEM. However, at 1700 (Figure 4 (d)), the grain grew tremendously without densification mechanism, resulting in density of only 2.47 g/cm^3 corresponding to 76.9% relative density (theoretical density of $SiC = 3.21\text{ g/cm}^3$). On the other hand, SiC -based composite with dense microstructure was obtained at $1700\text{ }^{\circ}\text{C}$ as seen in Figure 4 (b).

Although there was a grain growth in HEM1700 (Figure 4 (b)) compared to HEM1600 (Figure 4 (a)), the growth was not significant compared to 1700 (Figure 4 (d)), which meant that the densification mechanism took

place in the sintering of milled amorphous $Si-C-N-O$ as described before. The mean grain sizes for HEM1700 (Figure 4 (e)) was 293 nm, much finer than the typical grain size of submicron/micrometer with the conventional method [11,21-23]. Fine microstructure of HEM1700 was formed probably due to the high viscosity in liquid phase of Si_2N_2O . This result is in agreement with the sintering of SiC with the addition of AlN , whereas the liquid phase containing N_2 had higher viscosity [33]. Three phases were observed in the SEM image of Figure 4 (f); black, grey, and white. Energy dispersive X-ray spectroscopy analysis revealed that the grey and white phases were SiC and ZrO_2 , respectively, while the black area was Si_3N_4 and Si_2N_2O .

4. Conclusions

High density SiC -based composites from polysilazane were successfully prepared by high energy milling without the addition of sintering additives. The density of 3.04 g/cm^3 could be achieved by 1 hour hot pressing at $1700\text{ }^{\circ}\text{C}$ under an applied pressure of 50 MPa in

vacuum atmosphere for HEM1700, while 2.47 g/cm³ for 1700. The formation of Si₂N₂O that involved liquid phase in amorphous Si-C-N-O was imperative to achieve high density SiC-based composites from polysilazane. Moreover, the presence of Si₂N₂O played an important role in restraining the grain growth of the composites.

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