

Ceramic composites derived from polysilazane with the addition of silicon carbide

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Ceramic composites from the polysilazane with the addition of silicon carbide (SiC) was successfully sintered by a hot pressing furnace at 1,600-1,800 °C for 1 h under the applied pressure of 20 MPa in a nitrogen atmosphere. The addition of SiC did not influence the densification of sintered polysilazane. However, the phases generated during sintering were affected by the addition of SiC, resulting in the multi-phases of sintered polysilazane/SiC composite. The formation of SiC, Si₃N₄, Si₂N₂O, and SiO₂ phases were observed in the sintered polysilazane/SiC composite. The highest hardness of sintered polysilazane was obtained with the addition of SiC sinter at 1,700 °C, i.e., 24.3 ± 1.1 GPa, and decreased to 21.8 ± 0.7 GPa at 1,800 °C. This is due to the sintered polysilazane/SiC composite at 1,700 °C possess fine microstructure compared to 1,800 °C. Meanwhile, the sintered polysilazane experienced significant grain growth at 1,700 °C, thus the hardness of this sample was lower than sintered polysilazane/SiC composite.

Keywords: Polysilazane, Silicon carbide, Sintering, Phase, Microstructure.

Introduction

Polysilazane has been used extensively to synthesize Si-based ceramic composites, such as Si₃N₄ and SiC. In general, there are two steps for the sintering of ceramic composites from the polysilazane [1-7]; first the polysilazane was cross-linked and pyrolyzed at temperature 1,000-1,600 °C to obtain the amorphous powder. Subsequently, the amorphous powder was sintered at high temperatures to obtain a sintered body. The phase that generates during sintering depends on the sintering additives, sintering temperature, and sintering atmosphere that used for the densification of amorphous polysilazane. Moreover, the addition of sintering additives is still required to obtain the dense sintering body from polysilazane [1-3, 5, 6, 8] due to the high covalence bonding and low self-diffusivity of Si-based ceramic, such as Si₃N₄ and SiC, make them difficult to sinter to a high density. For instance, the sintering temperature of 2,500 °C and applied pressure are needed to densify SiC [9]. The other study reported the use of ultra-high pressure to achieve SiC with density near the theoretical study [10]. Liquid phase sintering is believed as the mechanism for the densification of amorphous polysilazane due to the presence of oxide sintering additives.

However, several studies showed that dense ceramics body from polymer precursor could be densified without the addition of sintering additives, which used mechanical milling to activate the amorphous polymer precursor [11-13].

SiC is a ceramic material that widely uses for the application at elevated temperature due to excellent thermal and mechanical properties, such as heat exchanger, gas turbine, and space shuttle [14, 15]. SiC composite is also considered as a structural material for nuclear reactor because of the low neutron irradiation of Si and C. In daily life, SiC is used as abrasive materials due to the high hardness of this material, which suitable for application as wear-resistant materials. SiC is also a promising material for application as electronic devices due to excellent electronic properties [16]. However, the addition of SiC into polysilazane is rarely reported, apart from the work of Noviyanto et al. [8] who reported the addition of SiC into polysilazane (weight ratio = 1) and studied the effect of sintering atmosphere on the microstructure and phase of the sintered ceramic.

In the present study, we investigated the effect of SiC addition on the phase formation and microstructure of Si-based ceramics from polysilazane prepared by a hot-pressing furnace. Three different sintering temperatures were used in this study. The data on phase, microstructure, and relation with the hardness of sintered polysilazane are examined to elucidate the effect of SiC in the

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polysilazane.

Experimental

Polysilazane (KiON Ceraset Polysilazane 20, USA) was dissolved in acetone and mixed with β -SiC powder (> 97.5% purity, 4620KE, NanoAmor Inc., USA) with a weight ratio of 5:1. The slurry was dried and subsequently cross-linked on a hot plate at 200 °C for 90 min. The cross-linked powder was pyrolyzed at 1,300 °C for 2 h in a nitrogen atmosphere using a tube furnace to form an amorphous powder. According to our previous study, the crystallization of amorphous powder starts at 1,450 °C [12]. Al_2O_3 (> 99.9% purity, Baikowski, Japan) and Y_2O_3 (> 99.9% purity, Acros Organics, USA) were used as sintering additives with the ratio were 60:40 in weight. Sintering additives were mixed with the pyrolyzed powder using ball milling for 24 h. The number of sintering additives was 5 wt.% in the total mass of mixed powder. The mixed powder was sintered at 1,600, 1,700 and 1,800 °C for 1 h under an applied pressure of 20 MPa in a nitrogen atmosphere using a hot pressing vacuum furnace. Polysilazane without the addition of β -SiC powder was also prepared for the comparison purpose.

Archimedes principle was used to estimate the density of sintered powder. The microstructure of sintered bodies was observed by scanning electron microscope (SEM: S-4800, Hitachi, Japan). The crystalline phases that formed during sintering were detected by room-temperature X-ray diffraction (XRD: X'Pert-PRO MPD, PANalytical, The Netherlands) using the $\text{Cu K}\alpha$ line. The samples were mirror-polished before measuring the hardness. The Vickers indentation method using a hardness tester (MVK-H1, Mitutoyo, Japan) with a 1 kg load and a loading time of 10 s were used to determine the hardness of sintered samples.

Results and Discussion

Fig. 1 displays the XRD patterns of polysilazane/SiC after sintering using the hot pressing furnace at different temperatures. SiC in the form of β -SiC and α -SiC were detected at the 1,600 °C (Fig. 1(a)). In terms of stability at high temperature, the transformation of β -SiC to α -SiC occurs at temperature > 1,600 °C [17], however, in our study, the formation of those phases appears simultaneously, as shown in Fig. 1(a). Comparing with polysilazane without the addition of SiC (Fig. 2(a)), it showed that the presence of α -SiC is dominant compared to β -SiC. Therefore, the occurrence of β -SiC in the polysilazane/SiC composite sinter at 1,600 °C originates from the β -SiC powder since the polysilazane tend to form α -SiC instead of β -SiC. The other phases that exist at 1,600 °C were $\text{Si}_2\text{N}_2\text{O}$, SiO_2 and β - Si_3N_4 . The origin of those phases came from the polysilazane, since the polysilazane consists of Si, C, N, and O [18],

which might form SiC, Si_3N_4 , SiO_2 . Fig. 3 shows the Gibbs free energy of SiC, Si_3N_4 , SiO_2 as a function of temperature. At 1,600 °C, the Gibbs free energy of SiC, Si_3N_4 , and SiO_2 were -50.981, -34.605, and -576.02 kJ mol⁻¹, respectively. Therefore, the formation of SiO_2 occurred in the beginning. Subsequently, Si_3N_4 started to form after the formation of SiO_2 completed, as observed in Fig. 1(a). However, at a temperature higher than 1,400 °C, SiC is more stable than Si_3N_4 , as shown in Fig. 3. The decomposition of Si_3N_4 to SiC can be suppressed by the use of a nitrogen atmosphere during sintering [19]. Therefore, the existence of Si_3N_4 at sintering temperature > 1,600 °C, as shown in Fig. 1(b) and (c), due to the sintering atmosphere that used in the present study. Interesting to note is that the formation of $\text{Si}_2\text{N}_2\text{O}$, which is the result of Si_3N_4 and SiO_2 reaction [8, 20]. It seems the formation of $\text{Si}_2\text{N}_2\text{O}$ complete at 1,700 °C due to the disappearance of SiO_2 peak at 1,700 °C, as shown in Fig. 1(b). The phase of polysilazane/SiC composite sinter at 1,700 and 1,800 °C is similar, as shown in Figs. 1(b) and (c), respectively.

Fig. 2 shows the XRD pattern of the sintered polysilazane at different temperatures. The crystalline phases that detected in sintered polysilazane were β -SiC, α -SiC, α - Si_3N_4 , and β - Si_3N_4 . At 1,600 °C (Fig.

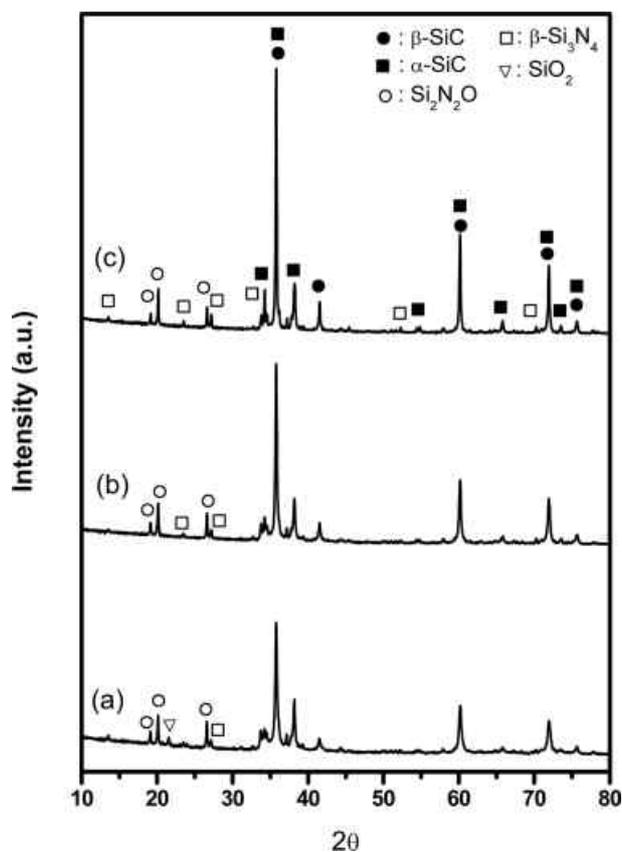


Fig. 1. XRD patterns of polysilazane/SiC composite after sintering at (a) 1,600, (b) 1,700, and (c) 1,800 °C, showing the formation of Si-based compound such as β -SiC, α -SiC, β - Si_3N_4 , $\text{Si}_2\text{N}_2\text{O}$ and SiO_2 .

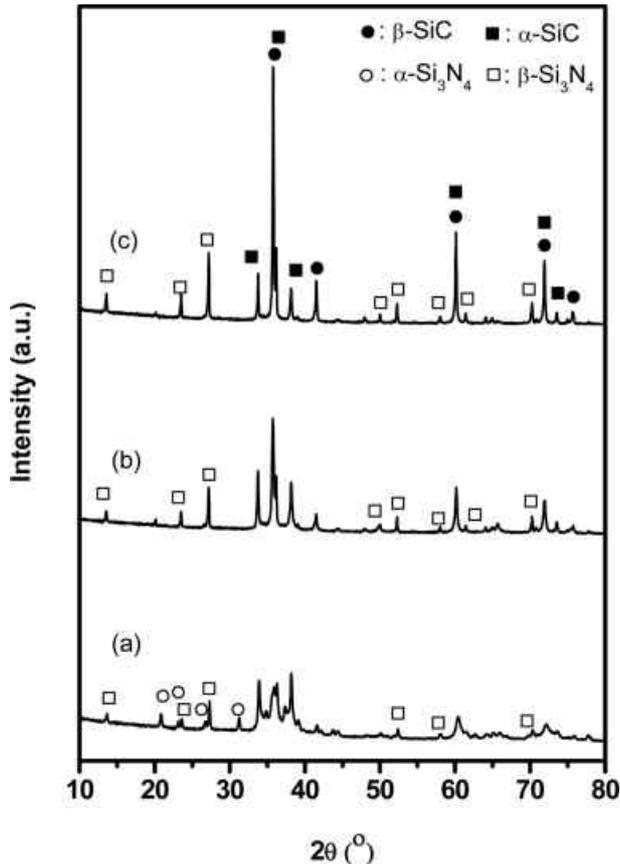


Fig. 2. XRD patterns of polysilazane after sintering at (a) 1,600, (b) 1,700, and (c) 1,800 °C, showing the formation of SiC and Si₃N₄.

2(a)), besides the formation of α -SiC, the other phases that detected were α -Si₃N₄, and β -Si₃N₄. Initially, α -Si₃N₄ formed in the beginning. However, since the α -Si₃N₄ is not stable at high temperatures [21-23], it transformed into β -Si₃N₄. Therefore, the presence of α -Si₃N₄ was not identified at 1,700 °C, indicates that all α -Si₃N₄ had already transformed into β -Si₃N₄, as shown in Fig. 2(b). Moreover, Fig. 2(b) revealed the existence of β -SiC at 1,700 °C compared to 1,600 °C, as indicated by the peak at 35.579°.

Table 1 shows the density and hardness of the sample sinter at different temperatures. It is clear that the density of all samples increased with increasing temperature. It seems the sintering temperature of 1,600 °C was too low for densification, both for the polysilazane with and without SiC, resulting in a density of 2.41 and 1.73 g/cm³ for the polysilazane/SiC and polysilazane, respectively. However, at 1,700 °C the density of both samples increased significantly to 3.03-3.05 g/cm³, corresponding to the relative density of 93-95%, if compared to the theoretical density of SiC. Moreover, the relative density higher than 98% was obtained at 1,800 °C, equal to the density of 3.15-3.17 g/cm³. These results are in agreement with the microstructure analysis, as shown in Fig. 4. The pores were observed

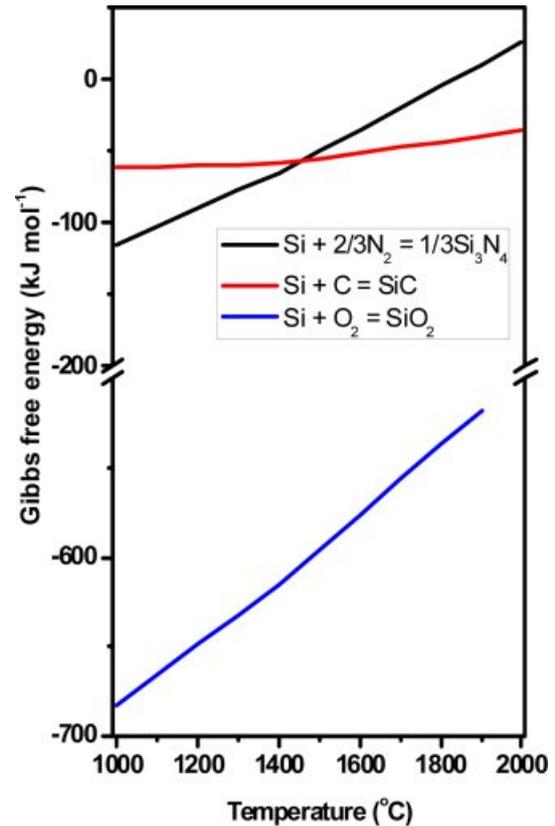


Fig. 3. Gibbs free energy of SiC, Si₃N₄ and SiO₂ as a function of temperature.

Table 1. Density and hardness of samples sinter at different temperature.

Samples	Sintering temperature (°C)	Density (g/cm ³)	Hardness (GPa)
Polysilazane/SiC	1,600	2.41	-
	1,700	3.03	24.3 ± 1.1
	1,800	3.15	21.8 ± 0.7
Polysilazane	1,600	1.73	-
	1,700	3.05	23.8 ± 0.9
	1,800	3.17	23.2 ± 0.2

in the polysilazane/SiC composite (Fig. 4(a)) and polysilazane (Fig. 4(b)), which indicated a low dense sintered body. However, the particle size of polysilazane sinter at 1,600 °C is much finer compared to polysilazane/SiC. Since the starting material of polysilazane is an amorphous powder, therefore, the crystallinity of this powder depends on the sintering temperature. As shown in Fig. 2(a), the crystallinity of sintered polysilazane is quite low, indicates that the sintered body in the first stage to form the crystalline phase, resulting in the very fine microstructure. On the other hand, the particle size of polysilazane/SiC was observed very clear. This particle was β -SiC powder, which is intentionally added into polysilazane. Moreover, the peaks of β -SiC were detected even though at 1,600 °C, as shown in Fig. 1(a). The tremendous change in microstructure was

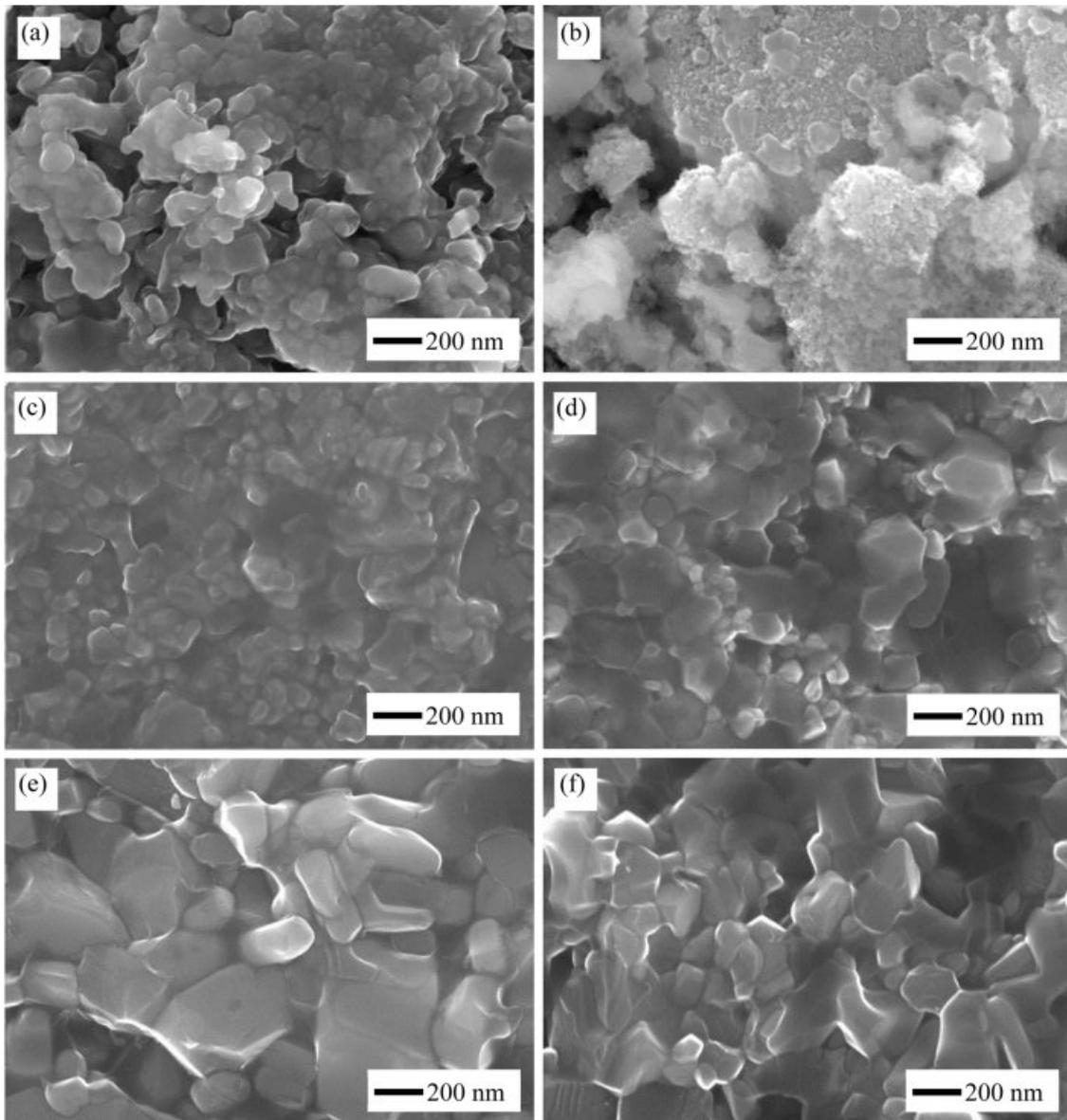


Fig. 4. SEM images of polysilazane/SiC composite after sintering at (a) 1,600, (c) 1,700, and (e) 1,800 °C, and polysilazane after sintering at (b) 1,600, (d) 1,700, and (f) 1,800 °C.

noticeable at 1,700 °C, as shown in Figs. 4(c) and (d). In particular, for the sintered polysilazane, the particle size increases from the very fine at 1,600 °C to several hundred nanometers at 1,700 °C, even though the distribution of the grain size broadens. In contrast, the sintered polysilazane/SiC composite did not show a significant change in the grain size. However, the dense body was obtained at 1,700 °C, as shown in Fig. 4(c). Furthermore, significant grain growth occurred at 1,800 °C for both polysilazane/SiC composite (Fig. 4(e)) and polysilazane (Fig. 4(f)).

The hardness of the samples is shown in Table 1. The hardness of polysilazane/SiC composites at 1,700 and 1,800 °C was 24.3 ± 1.1 and 21.8 ± 0.7 GPa, respectively. Meanwhile, sintered polysilazane at 1,700 and 1,800 °C was 23.8 ± 0.9 and 23.2 ± 0.2 GPa, respectively. The

difference of hardness polysilazane/SiC composite and polysilazane at 1,700 °C is more likely due to the difference in microstructure, which is the microstructure of polysilazane/SiC composite finer than polysilazane following the Hall-Petch equation. Moreover, the phases have also affected the hardness, while the major phases significantly contributed to the hardness of samples. Indeed, SiC plays an important role in the hardness of sintered samples.

Conclusions

The ceramic composite of polysilazane/SiC was successfully sintered by a hot pressing furnace for 1 h under an applied pressure of 20 MPa in a nitrogen atmosphere. Multi-phases, such as SiC, Si_3N_4 , $\text{Si}_2\text{N}_2\text{O}$,

were detected by XRD at any sintering temperature, while SiO₂ only observed at 1,600 °C. The disappearance of SiO₂ at sintering temperature > 1,600 °C was likely due to the reaction with Si₃N₄ to form Si₂N₂O. On the other hand, the sintered polysilazane without the addition of SiC showed only SiC and Si₃N₄ phases at any temperature. The density obtains after sintering for the polysilazane/SiC composite was 2.41, 3.03, and 3.15 g/cm³ for the sintering temperature of 1,600, 1,700, and 1,800 °C, respectively. Similar results are also achieved for the sintered polysilazane without the addition of SiC. However, the microstructure generates after sintering for the polysilazane/SiC composite significantly different compared to polysilazane, in particular for the sintering temperature of 1,600 and 1,700 °C. The existence of pores was observed for both samples at 1,600 °C, however, sintered polysilazane possesses a very fine microstructure. Furthermore, the tremendous increase in density and grain size was observed in the sintered polysilazane at 1,700 °C. In contrast, the sintered polysilazane/SiC composite only increases the density at 1,700 °C without a significant increase in the grain size. As the results of fine microstructure, polysilazane/SiC composite has the highest hardness, i.e., 24.3 ± 1.1 GPa, among the other samples.

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