Densification of SiC from Amorphous Polysilazane with The Addition of β-SiC as a Filler Prepared by Hot Pressing Furnace

Galuh Sukmarani¹, Alfian Noviyanto¹,²*, Retno Kusumaningrum¹, Alvin Muhammad Habieb¹, Fiqi Fauzi¹, Wahyu Bambang Widayatno³, Agus Sukarto Wismogroho³, Muhamad Ikhasul Amal³, and Nurul Taufiqu Rochman⁴

¹ Nano Center Indonesia, Jl. PUSPIPTEK, South Tangerang, Banten 15314 Indonesia
² Department of Mechanical Engineering, Mercu Buana University, Jl. Meruya Selatan, Kebun Jeruk, Jakarta 11650, Indonesia
³ Research Center for Physics, Indonesian Institute of Sciences, PUSPIPTEK, South Tangerang, Banten 15314, Indonesia
⁴ Research Center for Metallurgy and Materials, Indonesian Institute of Sciences, PUSPIPTEK, South Tangerang, Banten 15314, Indonesia

*a.noviyanto@nano.or.id

Abstract. Dense silicon carbide (SiC) was successfully sintered from amorphous polysilazane (PSZ) using hot pressing at 1750°C for 1 hour under an applied pressure of 20 MPa in Ar atmosphere. The effect of β-SiC powder as a filler on the density, phase, microstructure and hardness were examined. Al₂O₃ and Y₂O₃ were used as sintering additives through the liquid phase sintering mechanism. The phase analysis showed the formation of SiC after sintering of amorphous PSZ. However, α-SiC was a dominant phase and the amount of α-SiC decreased with the addition of β-SiC powder. The relative density of sintered SiC was obtained in range 99.6 – 99.7% regardless of the addition of β-SiC powder. Sintered SiC from amorphous PSZ revealed significant shrinkage compared to sintered SiC from β-SiC powder, while the minimum shrinkage was achieved by the addition of 70% β-SiC into amorphous PSZ. However, the hardness of sintered SiC did not correlate with the addition of β-SiC powder, with highest hardness of 26.4 GPa, which is SiC from solely β-SiC powder. This result indicates that amorphous PSZ is an alternative precursor to fabricate dense SiC.

Keywords: SiC, amorphous polysilazane, hot pressing, density, shrinkage.

1. Introduction
Silicon carbide (SiC) is a non-oxide ceramic material which has attracted enormous attention due to the excellent thermal, mechanical and chemical properties [1]. This material has been developed in many industrial application such as fusion reactor, semiconductor devices, optoelectronics, and heating elements in solar cell system [1–3]. However, a strong covalent bonding between Si and C leads to this material has a low diffusion which results in a great challenge to sintering SiC in high density [4]. Therefore, it requires a high temperature and pressure or using sintering additives. Dense SiC-based
ceramics are commonly prepared by powder sintering, carbothermal reduction [5], chemical vapour deposition [6], and polymer-derived sintering [7]. Because of the remarkable potential for low-temperature processing of both non-oxide and oxide ceramics, the polymer-derived sintering has gathered a great interest in producing high-density SiC-based ceramics [8].

Polysilazane (PSZ) is one promising polymer precursor which results in S/C/N ceramics include SiC. The used PSZ as the polymer-derived precursor for SiC₃N₃ has been reported by Obmann, et al. [9]. Moreover, Salameh et al. also reported the used PSZ to prepare SiAlCN ceramics [10]. Besides, effect milling and sintering atmosphere also have been studied by Noviyanto, et al. which showed that high density and purity SiC-based ceramic was obtained by milling and sintering in Ar atmosphere [11], [12]. However, due to large shrinkage of the PSZ, several infiltrations are needed to fabricate SiC/SiC composite using polymer impregnated and pyrolysis method [13].

Therefore, the aim of this study is to examine the effect of amorphous PSZ as a precursor to producing high-density SiC-based ceramic. Due to the importance of the SiC phase to improve its mechanical properties, β-SiC powders were used as a filler in various compositions to analyse its effect for SiC properties. The density, hardness, and shrinkage of the sintered samples from amorphous PSZ with/without the addition β-SiC were analysed to explain the influence of phase ratio and PSZ.

2. Experimental method
PSZ (KiON Ceraset Polysilazane 20, USA) and β-SiC powder (> 97.5 % purity, 4620KE, NanoAmor Inc., USA) were used in this study. PSZ was cured and cross-linked at 200°C for 90 minutes using a hot plate. The cross-linked powder was pyrolyzed in a nitrogen atmosphere at 1000°C for 2 h to produce amorphous PSZ powder. This amorphous powder was mixed with β-SiC powder and sintering additives (Al₂O₃ and Y₂O₃) using ball milling for 24 h. SiC ball was used to minimize the contamination during milling. Detail composition and sample name in this study are shown in Table 1. The mixed powder was sintered in argon atmosphere at 1750 °C for 1 h with pressure 20 MPa.

| Sample name | Amorphous PSZ (wt.%) | β-SiC (wt.%) | Sintering additives (wt.%) |
|-------------|---------------------|-------------|--------------------------|
| 100PSZ      | 90                  | 0           | 10                       |
| 30SiC70PSZ  | 63                  | 27          | 10                       |
| 50SiC50PSZ  | 45                  | 45          | 10                       |
| 70SiC30PSZ  | 27                  | 63          | 10                       |
| 100SiC      | 0                   | 90          | 10                       |

To evaluate the mechanical properties of the samples, Archimedes principle was used to measure the density while the hardness was measured by The Vickers indentation method using a hardness tester (MVK-H1, Mututoyo, Japan) with a 1 kg load and 10 s loading time. Scanning electron microscopy (SEM: S-4800, Hitachi at 15 kV and 10 μA) and high-resolution transmission electron microscopy (HR-TEM: Tecnai G2F20 S-twin, FEI operated at 200 kV) also were used to analysed the microstructure and particles of the sample. Meanwhile, X-ray diffraction (XRD: X’Pert-PRO MPD, PANalytical, The Netherlands) at room temperature using the Cu Kα line was used to identify phase generated during hot pressing.

3. Results and discussion
Table 2 shows the relative density of the sintered samples. The relative densities of 70SiC30PSZ, 50SiC50PSZ and 30SiC70PSZ were 99.7, 99.8 and 99.7%, respectively. The sintered sample of 50SiC50PSZ indicated the maximum density as high as 100SiC while the amorphous PSZ without the addition of β-SiC powder (100PSZ) showed the lowest density was 99.6%. The sintering condition in this study is quite mild, while the typical sintering condition for SiC using hot pressing furnace is temperature > 1800°C, pressure >25 MPa and sintering time > 1 h with the typical relative density 94–
99.4% [14]. In this study, although the sintering temperature only 1750 °C with the applied pressure of 20 MPa and only for 1 h, the relative densities achieved in this study was 99.6 – 99.8%. The result reveals that amorphous PSZ may be used as a precursor for SiC, and the addition of β-SiC powder as a filler on amorphous PSZ did not decrease the density of the samples. Since the sintering additives were used in this study, the liquid phase sintering mechanism is convinced to occur during sintering and help the densification of these samples. The liquid can be formed from the melting of sintering additives in eutectic formation, which are Al₂O₃ and Y₂O₃ in this study. Nature high covalent bonding of SiC hampers the diffusion of Si and C, thus sintering SiC without the addition of additives requires very high temperature and applied pressure. For instance, fully dense SiC could only be achieved at 2500 °C with an applied pressure of 5 GPa [15].

Table 2. The density of sintered amorphous PSZ with β-SiC filler

| Sample  | Density (g/cm³) | Relative density (%) |
|---------|-----------------|----------------------|
| 100SiC  | 3.205           | 99.8                 |
| 70SiC30PSZ | 3.202       | 99.7                 |
| 50SiC50PSZ | 3.204       | 99.8                 |
| 30SiC70PSZ | 3.201       | 99.7                 |
| 100PSZ  | 3.197           | 99.6                 |

Figure 1 shows the XRD pattern of the samples, which indicates the formation of SiC after sintering of amorphous PSZ. The phase analysis showed that there were two phases formed, namely α-SiC and β-SiC. No secondary phases observed in Figure 1, indicating that the high purity of SiC ceramic was obtained in this work. Although the elements in the amorphous PSZ were Si, C, N, and O [16], the formation of Si₃N₄ or SiO₂ or another Si-based material could be inhibited during sintering of these samples. Si₃N₄ is not a stable phase at high temperature and tend to decompose to another phase [12]. Therefore, the formation of SiC more likely from the decomposition of Si₃N₄, which reacts with C to form SiC. The similar condition also applied for the SiO₂. Consequently, single phase SiC was observed, as shown in Figure 1 (a), without the presence of secondary phases. Figure 1 (b) displays the variation of α- and β-SiC content in the samples. Indeed, the α-SiC phase was dominant in 100PSZ sintered sample, while SiC made from β-SiC powder revealed the β-SiC phase in the sintered sample. The formation was caused by high-temperature sintering about 1600 – 1900°C, which generally occurs the transformation of β- to α-SiC phase [17]. The transformation was also influenced by several factors such as sintering additive, sintering atmosphere, precursor, temperature and pressure [17, 18]. Moreover, the formation α-SiC on 100PSZ linked to the high number of entropy on amorphous PSZ, which caused the formation α phase instead β-SiC phase [19]. Furthermore, the phase analysis also reveals that the addition of β-SiC powder on amorphous PSZ leads to declining α-SiC phase on the sintered samples.
Figure 2 displays SEM images showing the microstructural of the samples after hot pressing sintering. The results demonstrated that 100SiC and 50SiC50PSZ had a tighter microstructure than 100PSZ, 70SiC30PSZ and 30SiC70PSZ. The result reveals that the addition of β-SiC powder produced denser the sintered samples, although it showed the large grain sizes, which is caused by PSZ as a precursor. The 100SiC indicated the finest microstructure, which is in contrast with 50SiC50PSZ that showed the largest grain sizes. Due to the phase difference in the samples where the high amount of β-SiC caused the smaller grain sizes. This results was consistent with previous work reported by Xu et al [17] whereby they explained that the α-SiC as a starting material would result in the larger grain grow rather than β-SiC. Moreover, the microstructure results of these samples also correspond to the hardness and density of the samples. A dense and fine microstructure leads to the sample had a high density and hardness [12].

![SEM images of sintered samples](image)

**Figure 2.** SEM images of sintered (a) 100SiC, (b) 70SiC30PSZ, (c) 50SiC50PSZ, (d) 30SiC70PSZ and (e) 100PSZ samples.

Figure 3 shows the shrinkage and hardness of the samples. The shrinkage was determined based on the sintered samples thickness, which was compared with sintered β-SiC thickness was 2.43 mm. The shrinkage of 70SiC30PSZ, 50SiC50PSZ, 30SiC70PSZ and 100PSZ were 4.9, 9.1, 10.3 and 13.6%, respectively. As a polymer precursor, shrinkage is one of a drawback which could not be prevented. Thus, to minimize the shrinkage, the β-SiC powder was added as a filler on the sintering of SiC from...
amorphous PSZ as a precursor. According to the results, it is clear that the rising portion of β-SiC powder produced a considerable decline of shrinkage in the sintered samples. The hardness of 70SiC30PSZ, 50SiC50PSZ and 30SiC70PSZ were 23.6, 22.4 and 25.3 GPa, respectively while 100SiC and 100PSZ were 26.4 and 24.5 GPa, respectively. Indeed, the highest hardness obtained by 100SiC due to fine grain size as explained in the previous paragraph, while the lowest hardness in the 50SiC50PSZ sample due to large grain, as shown in Figure 2 (c). As explained in the Hall-Petch equation, the fine grain size proportional with high hardness [20].

Figure 3. The shrinkage and hardness of the sintered amorphous PSZ with β-SiC as a filler in various composition.

4. Conclusion
Monolithic SiC was prepared by amorphous PSZ precursor and successfully sintered using hot pressing vacuum furnace. Certainly, the lowest shrinkage was obtained by the addition of 70% of β-SiC powder, while the highest shrinkage observes in the sintered SiC without the addition of β-SiC powder. It should be noted that the relative density of sintered SiC for all samples appeared very high, i.e., > 99%, which is near the theoretical density of SiC. Sintering SiC from amorphous PSZ causes the formation of α-SiC with minor β-SiC. This is due to the high number of entropies on amorphous PSZ, which caused the formation α phase instead of β-SiC phase. Finally, the addition of 50% of β-SiC powder into sintered SiC from amorphous PSZ generate large grain in the microstructure compared to sintered SiC without the addition of β-SiC powder. Thus, the lowest hardness was obtained in this sample. This study demonstrates that amorphous PSZ may be used as a precursor for SiC through the liquid phase sintering additives. The addition of β-SiC powder into amorphous PSZ succeed to minimize the shrinkage of amorphous PSZ without hampers the properties of sintered SiC.

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References
[1] M. Aizat, H. Mohd, M. Mustapha, and J. C. Kurnia, “Silicon carbide- from synthesis to application : a review,” MATEC Web Conf., vol. 131, pp. 1–6, 2017.
[2] H. Ou, Y. Ou, A. Argyraki, S. Schimmel, M. Kaiser, P. Wellmann, and K. Margareta, “Advances in wide bandgap SiC for optoelectronics,” *Eur. Phys. J. B.*, vol. 87, p. 58, 2014.

[3] M. Syväjärvi, Q. Ma, V. Jokubavicius, A. Galeckas, J. Sun, X. Liu, M. Jansson, P. Wellmann, M. Linnarsson, P. Runde, B. Andre, A. Thøgersen, S. Diplas, P. Almeida, O. Martin, D. Nilsen, A. Yu, and B. G. Svensson, “Solar Energy Materials & Solar Cells Cubic silicon carbide as a potential photovoltaic material,” *Sol. Energy Mater. Sol. Cells.*, vol. 145, pp. 104–108, 2015.

[4] C. Greskovitch and J. H. Rosolowski, “Sintering of Covalent Solids,” *J. Am. Ceram. Soc.*, vol. 59, no. 1, pp. 336–343, 1976.

[5] J. Xiong and Q. Huang, “Crystallization behavior of polymer derived silicon carbide sintered through microwave heating technique,” *J. Wuhan Univ. Technol. Sci. Ed.*, vol. 32, no. 6, pp. 1368–1373, 2017.

[6] H. Abderrazak, E. Selmane, and B. Hadj, “Silicon Carbide: Synthesis and Properties Silicon Carbide: Synthesis and Properties,” *Prop. Appl. Silicon Carbide*, pp. 361–388, 2011.

[7] C. Hwang, Q. Yang, S. Xiang, V. Domnich, A. U. Khan, K. Y. Xie, K. J. H. Kermer, and R. A. Haber, “Journal of the European Ceramic Society Fabrication of dense B 4 C-preceramic polymer derived SiC composite,” *J. Eur. Ceram. Soc.*, vol. 39, no. 4, pp. 718–725, 2018.

[8] Y. Li, L. Chen, L. Hong, K. Ran, Y. Zhan, and Q. Chen, “Fabrication of porous silicon carbide ceramics at low temperature using aluminum dihydrogen phosphate as binder,” *J. Alloys Compd.*, vol. 785, pp. 838–845, 2019.

[9] R. Obmann, S. Schörpf, C. Gorsche, R. Liska, T. Fey, and T. Konegger, “Porous polysilazane-derived ceramic structures generated through photopolymerization-assisted solidi fication templating,” *J. Eur. Ceram. Soc.*, vol. 39, no. 4, pp. 838–845, 2018.

[10] F. Salameh, C. Bernard, S. Gervais, C. Babonneau, A. Bruma, S. Malo, and P. Miele, “Aluminum-modified polysilazanes: synthesis, pyrolysis behaviour and microstructural evolution,” *J. Eur. Ceram. Soc.*, vol. 39, no. 2–3, pp. 183–194, 2018.

[11] A. Noviyanto and T. Nishimura, “Effect of Milling on the Densification of SiC-Based Composites from Polysilazane,” *Makara J. Technol.*, vol. 20, no. 3, pp. 109–113, 2016.

[12] A. Noviyanto, D. Yoon, Y. Han, T. Nishimura, D. Yoon, and Y. Han, “Effect of sintering atmosphere on the grain growth and hardness of SiC / polysilazane ceramic composites,” *Adv. Appl. Ceram.*, pp. 1–4, 2016.

[13] S. G. Lee, J. Fourcade, R. Latta, and A. A. Solomon, “Polymer impregnation and pyrolysis process development for improving thermal conductivity of SiCp / SiC – PIP matrix fabrication,” *Fusion Eng. Des.*, vol. 83, pp. 713–719, 2008.

[14] S.-G. Lee, W.-H. Shin, J.-Y. Kim, Y.-W. Kim, and W. T. Kwon, “Effect of sintering-additive composition on fracture toughness of liquid-phase-sintered SiC ceramics,” *J. Mater. Sci. Lett.*, vol. 20, no. 2, pp. 143–146, 2001.

[15] J. S. Nadeau, “Very high pressure hot pressing of silicon carbide,” *Am. Ceram. Soc. Bull.*, vol. 52, no. 2, pp. 170–174, 1973.

[16] D. Galusek, S. Reschke, R. Riedel, W. Dreszler, Sajgalk, Z. Lenčēš, and J. Majling, “In-Situ Carbon Content Adjustment in Polysilazane Derived Amorphous SiCN Bulk Ceramics,” *J. Eur. Ceram. Soc.*, vol. 19, Aug. 1999.

[17] H. Xu, T. Bhatia, N. P. Padture, A. L. Ortiz, and F. L. Cumbrera, “Microstructural Evolution in Liquid-Phase-Sintered SiC: Part I, Effect of Starting Powder,” *J. Am. Ceram. Soc.*, vol. 84, pp. 1578–1584, 2001.

[18] C. Ragaru, M. Lancin, and C. Marhic, “A Phase Transformation in SiC: Link between Polytypism, Dihedral Angle and Nucleation Mechanism of Twins,” *J. Eur. Ceram. Soc.*, vol. 19, pp. 2701–2709, 1999.

[19] K. A. Graeser, J. E. Patterson, J. A. Zeitler, and T. Rades, “The Role of Configurational Entropy in Amorphous Systems,” *Pharmaceutics*, vol. 2, no. 2, pp. 224–244, May 2010.

[20] R. Vaßen, A. Kaiser, J. Förster, H. P. Buchkremer, and D. Stöver, “Densification of ultrafine SiC powders,” *J. Mater. Sci.*, vol. 31, no. 14, pp. 3623–3637, 1996.