Journal of Metals, Materials and Minerals, 34(1), 1939, 2024

Possibility of using boric acid and glutinous rice flour as additive for producing silicon carbide ceramic via pressureless solid-state sintering

Apichart JINNAPAT[1], Auamporn RATTANASING[1], Nithiwach NAWAUKKARATHARNANT[2,3], Kritkeaw SOMTON[4], and Kannigar DATERAKSA[4,*]

[1] *Department of Military and Aerospace Materials, Navaminda Kasatriyadhiraj Royal Thai Air Force Academy, 999 Mittraphap, Muak Lek, Saraburi, 18180, Thailand*
[2] *Metallurgy and Materials Science Research Institute, Chulalongkorn University, 254 Phyathai Road, Pathum Wan, Bangkok 10330, Thailand*
[3] *Upcycled Materials from Industrial and Agricultural Wastes Research Unit, Department of Materials Science, Faculty of Science, Chulalongkorn University, Phyathai Road, Bangkok, 10330, Thailand*
[4] *National Metal and Materials Technology Center (MTEC), National Science and Technology Development Agency (NSTDA) 111 Thailand Science Park, Phahonyothin Road, Khlong Nueng, Khlong Luang, Pathum Thani, 12120, Thailand*

***Corresponding author e-mail**: Kannigd@mtec.or.th

Received date:
18 January 2024
Revised date
19 February 2024
Accepted date:
4 March 2024

Keywords:
Silicon carbide;
Ceramics;
Glutinous rice flour;
Boric acid;
Pressureless solid-state sintering

Abstract

This research aimed to investigate the possibility of using the mixture of boric acid and glutinous rice flour as a cost-efficient alternative additive for producing silicon carbide (SiC) ceramic sintered at 1800°C via pressureless solid-state sintering. The results indicated that the addition of boric acid–glutinous rice flour mixture (10 wt%) in an appropriate ratio (0.5 by molar ratio) into the SiC mixture (90 wt%) enhanced the densification and flexural strength of sintered SiC samples. However, increasing boric acid/glutinous rice flour ratio reduces density and flexural strength. The 5.45 wt% carbon content was sufficient to remove the oxide layer of the SiC surface and improve the properties of SiC ceramic. In summary, the boric acid–glutinous rice flour mixture has a high potential to be used as an additive for producing dense and porous SiC ceramics via pressureless solid-state sintering.

1. Introduction

Silicon carbide (SiC) is an ideal material for numerous applications, such as ceramic armor applications, turbine engines, nozzles, heat-conducting tubes, and aerospace applications, due to its superior properties such as low density, high strength, high hardness, high elastic modulus, high chemical stability, and high wear resistance [1-3]. However, sintering SiC without sintering aids or high external pressure is difficult because of its strong covalent bond structure and low self-diffusion coefficient [4]. To save energy in production, pressureless solid-state-sintered SiC using several sources of boron and carbon as the boron–carbon additive systems sintered at 1900°C to 2050°C have been reported [5,6]. The majority of boron can form solid solutions in the SiC grains, and carbon is used to remove silica (SiO_2) layers on the SiC surfaces, the boron-carbon additive system has already been shown to be effective for enhancing densification progress [3,5,7]. Prochazka produced 96% relative density of SiC ceramic with additions of 0.5 wt% boron and 1 wt% carbon after sintering at 2050°C to 2150°C in an argon atmosphere [8]. The SiC ceramics were fabricated via pressureless solid-state sintering at 2100°C for 2 h in argon atmosphere with additives, boron nitride as boron source in range of 0.45 wt% to 2.65 wt% and phenolic resin as carbon source [9]. The fabrication of SiC ceramic via pressureless solid-state sintering with boron carbide (B_4C) and carbon additives at temperatures between 1950°C and 2180°C for 1 h in a vacuum sintering furnace was studied by D. C., *et al*. [10]. The SiC ceramic has relative densities of 67.7% and 98.4% at 1950°C and 2150°C, repectively. Liu, *et al*. [11] fabricated a fully dense SiC ceramic via pressureless solid-state sintering at 2150°C for 0.5 h using boric acid and D-fructose as additives. The authors observed that both carbon and boron contents significantly affected the properties of the SiC sample. However, using boric acid and glutinous rice flour, which are inexpensive and environmentally friendly, as a boron–carbon additive for SiC sintering has never been reported. Glutinous rice flour is one type of flour that is mostly produced in the Northeast of Thailand. It is a biopolymer that is widely used in the textile, paper, plastic, food, cosmetic, and pharmaceutical industries due to its many advantages, including being biosourced, renewable, biodegradable, biocompatible, and inexpensive [12,13]. In addition, it is a readily available carbon source with high content of –OH functional groups in its structure. These –OH functional groups can interact with boric acid to enhance the formation of B_4C [14]. The densification of SiC ceramics can be promoted by B_4C as sintering aid.

Therefore, the challenge was to study the effect of using boric acid and glutinous rice flour as additives on the properties of SiC samples sintered at 1800°C. In this study, the SiC samples were created using SiC micron powder, with boric acid–glutinous rice flour mixture as additives. The effect of boric acid/glutinous rice flour ratio on the properties of the SiC sample was discussed. This research presents an inexpensive alternative additive to be used for dense SiC ceramics production in further work.

2. Experimental

2.1 Materials

Commercial SiC powders (>98.5%) in size of 5.49 µm, 1.79 µm, and 0.73 µm were purchased from Electro Abrasives Corp (USA). Boric acid (99.5%) was purchased from Fisher Chemical (England) and food-grade glutinous rice flour was purchased from Thai Wah (Thailand).

2.2 Preparation of boric acid and glutinous rice flour precursors

Boric acid and glutinous rice flour suspensions were prepared in molar ratios of 0.5:1, 1:1, and 2:1 using the method described in a previous work [14]. Boric acid and glutinous rice flour were separately dissolved in distilled water by continuously stirring at 80°C. The suspensions were mixed together and further stirred at 80°C for 2 h. The Boric acid-glutinous rice flour precursors were then obtained.

2.3 Preparation of SiC samples

The SiC powder in size of 5.49 µm, 1.79 µm, and 0.73 µm were mixed in weight ratios of 66, 20, and 14, respectively, to obtain a high-packing-fraction mixture [15]. After that, the SiC mixture was filled into the prepared precursors with 90 wt% and 10 wt%, respectively, and stirred by magnetic stirrer at 80°C for 2 h. According to the molar ratio of precursors, the samples were named 0.5B1G, 1B1G, and 2B1G, respectively. The mixed suspensions were dried at 100°C for 24 h and calcined at 700°C for 2 h in a closed alumina container under a normal atmosphere. Afterward, the calcined powders were ground and passed through a 100–mesh screen. The prepared SiC powders with and without additives (100SiC) were uniaxially pressed to form bar-shaped specimens (6 mm^3 × 4 mm^3 × 35 mm^3) at 190 MPa, followed by cold isostatic pressing at 350 MPa. The green specimens were contained in a graphite container and sintered at 1800°C for 2 h with argon flow rate of 5 mL·min^{-1} in graphite resistance furnace. The sample without additive was prepared to investigate the properties comparing with the samples with additive.

2.4 Characterization

To confirm the carbon content of calcined SiC mixtures with additive, the residual carbon value was determined by CHNS/O Analyzers (Thermo Scientific, flash 2000). The boron contents (wt%) of calcined SiC mixtures with additive were calculated by boric acid dehydration reaction as shown in Equation (1).

$$2H_3BO_3 \rightarrow B_2O_3 + 3H_2O \quad (1)$$

The flexural strength of sintered samples was determined using a universal testing machine (Instron, 8872) with span of 20 mm and crosshead speed of 0.05 mm·min^{-1}. The flexural strength value was calculated according to Equation (2).

$$Flexural\ strength\ (MPa) = \frac{3PL}{2bd^2} \quad (2)$$

where P is the maximum applied load at rupture (N), L is span between supports (mm), b is width of samples and d is depth of samples. Average value was calculated from five measurements.

The bulk density and apparent porosity of sintered samples were measured using Archimedes' method and were calculated according to Equation (3-4).

$$Bulk\ density,\ D_b\ (g{\cdot}cm^{-3}) = \frac{W_d}{W_{s1} - W_{s2}} \quad (3)$$

$$Apparent\ porosity,\ P_a\ (\%) = \frac{W_{s2} - W_d}{W_{s1} - W_{s2}} \times 100 \quad (4)$$

where W_d is dry weight of sample (g), W_{s1} is suspended weight of sample (g), and W_{s2} is saturated weight of sample. Average value was calculated from five measurements.

The relative density of sintered samples was calculated using the theoretical density (D_t) of SiC (3.21 g·cm^{-3}) and was calculated according to Equation (5).

$$Relative\ density,\ D_r\ (\%) = \frac{D_b}{D_t} \times 100 \quad (5)$$

The microstructure of the materials was observed using a scanning electron microscope (SEM: JOEL, JSM-6480LV). Phase analysis of materials was conducted through X-ray diffraction (XRD, Bruker, D8 Advance) operated at 40 kV and 30 mA with Cu–K$_\alpha$ radiation at a scanning rate of 6°·min^{-1} (20° to 80° of 2θ).

3. Results and discussion

The carbon and boron content contained in calcined precursors are important for the formation of B_4C during sintering process of SiC sample. The residual carbon values of calcined precursors (0.5:1, 1:1, and 2:1) were 5.45%, 4.31%, and 3.78%, respectively. The result confirms that the boric acid and glutinous rice flour precursors composed of carbon after calcined at 700°C in a closed alumina container under a normal atmosphere. The calculated boron contents of calcined precursors (0.5:1, 1:1, and 2:1) were 0.28%, 0.48%, and 0.76%, respectively. These results reveal that calcined precursors consisting of carbon and boron can be used as the precursor for synthesis of B_4C and as the sintering aid for preparing SiC ceramics.

The SEM images of prepared SiC powders after drying are shown in Figure 1(a-d). The result revealed that the small boric acid–glutinous rice flour mixture particles adhered to the SiC particle surface. Therefore, after forming, the additive could be allocated at the SiC particle boundary, providing the benefit to the sintering process.

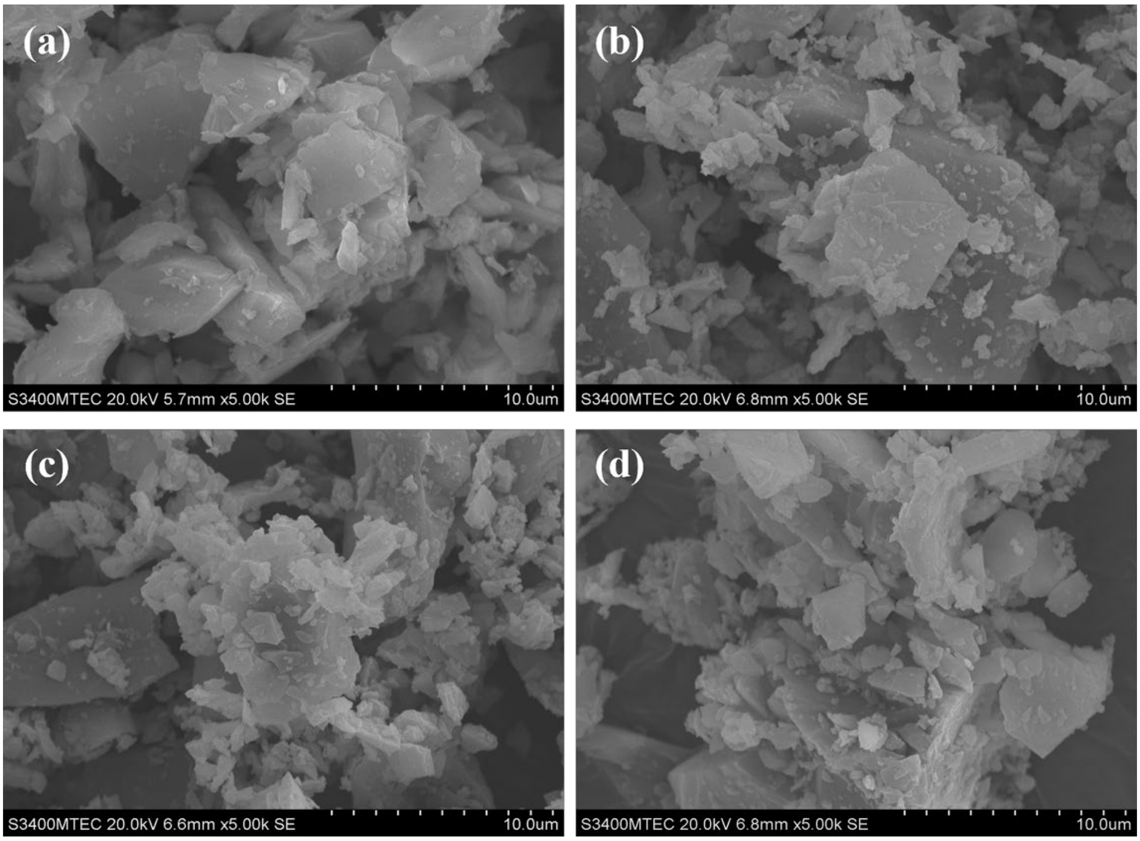

Figure 1. SEM images of prepared SiC powders after drying, (a) 100SiC, (b) 0.5B1G, (c) 1B1G, and (d) 2B1G.

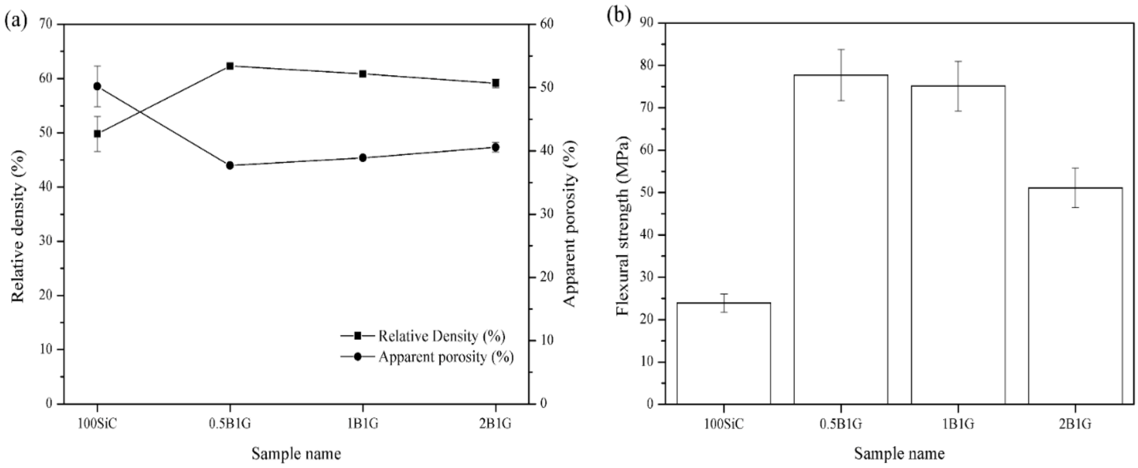

Figure 2. (a) Relative density and apparent porosity and (b) flexural strength of sintered SiC ceramics.

Figure 2(a) shows the relative density and apparent porosity of sintered ceramics with and without additives. The samples without additives had a relative density of 49.80%, which was lower than that of samples with additives. For sintered SiC samples with additives, the relative density of the samples tended to decrease with an increase in the boric acid/glutinous rice flour ratio. Thus, it can be implied that the relative density of the samples decreased with a decrease in carbon content. The 0.5B1G sample showed the highest relative density value (62.32%); this is because the free carbon content that remained in the mixture (5.45%) was sufficient to promote the removal of the oxide film from the SiC particles' surface as the reaction shown in Equation (6), thereby increasing surface energy and promoting sintering [16,17].

$$SiO_2\ (s) + 3C\ (s) \rightarrow SiC\ (s) + 2CO\ (g) \qquad (6)$$

Another reason that can support the enhancement of the sintering phenomenon, is the formation of sintering aid phase; B_4C, during sintering period [10]. From a previous work [14], B_4C can be synthesized by reaction of boric acid and glutinous rice flour at 1350°C to 1450°C.

According to Datta *et al*. work [18], the boron atom originating from B_4C has the ability to replace another atom within the SiC lattice, leading to an increase in the rate of diffusion. The increase in densification caused by the addition of boron can be attributed to the generation of additional vacancies in the lattice structure of the SiC compound, as described by Equation (7) [19].

$$B_4C \xrightarrow{SiC} 4B'''_{Si} + C^x + 4V_C^{\cdot\cdot\cdot\cdot} \quad (7)$$

Furthermore, the boron content of the mixture is an important factor that affects the densification of sinter samples [18]. When compared with the 100SiC sample, suitable content of boron atoms can promote the rate of material transport, leading to densification process. Based on these results, the boron content remaining in the mixture (0.28%) represented the SiC ceramic with highest density. This content is close to the literature, which contained 0.2 wt% to 0.5 wt% of boron content [20].

The apparent porosity result presented in Figure 2(a) also supports the explanation of the densification process. The apparent porosity of sintered samples with additives was higher than without additives. From these results, we can conclude that adding boric acid–glutinous rice flour mixture as boron–carbon sources, significantly can enhance the densification of SiC products. The relative density in this study (62.32%) can be compared with that of Jana *et al.*'s research [10]. The SiC ceramics with relative density of 67.70% were fabricated via pressureless solid-state sintering at 1950℃ for 1 h in argon atmosphere with B_4C and carbon additives.

Figure 2(b) displays the flexural strength of sintered samples with and without additives. The 100SiC sample had a strength value of 23.92 MPa, which was lower than that of samples with additives. The additive enhances the strength of SiC samples that accords with relative density and apparent porosity results due to densification. The maximum flexural strength (78 MPa) was observed in the 0.5B1G sample, which was the highest degree of densification. The strength value tended to decrease with an increasing boric acid/glutinous rice flour ratio. This is because an increase in boron content results in a decrease in the flexural strength of sintered samples. This result is consistent with that of Stobierski *et al.*'s work [20]. The reason is that the formation of a glassy phase reduces the strength of the sintered samples due to excess boron content.

Figure 3(a-c) and Figure 3(d-f) show the SEM images of sintered SiC samples with additives at 500× and 3000× magnification, respectively. The result agrees with the physical properties in that the amount and size of pores increased with the increasing boric acid/glutinous rice flour ratio. A dense structure with a low level of porosity and continuously connected grain was observed in the 0.5B1G sample, whereas a small number of discrete dense regions bounded by connected pores was observed in the 1B1G and 2B1G samples. An interconnection between the SiC particles was observed, especially in the 0.5B1G sample due to the distribution of carbon phases in the SiC sample that enhanced the densification process, as discussed earlier.

Figure 4 depicts the XRD patterns of 100SiC powder and sintered SiC samples. There were some differences between 100SiC and sintered SiC samples. The phase compositions of 100SiC powder were 6H-SiC (75–8914) and 4H-SiC (29–1127) as the major phases and 15R-SiC (39–1196), silicon (77–2107), and quartz (07–7344) as the minor phases. The peaks of quartz and silicon disappeared after sintering because quartz and silicon reacted with carbon to form the SiC during the sintering process [16,17]. This result supports the physical and mechanical properties of sintered SiC samples. There was no characteristic diffraction peak of graphite in XRD pattern. Moreover, evidence of boron compounds such as B_4C, was not observed for sintered SiC samples with additives. This is because of its low concentration and the fact that it is soluble in SiC structure [21]. This result confirms that the B_4C occurred from reaction between boric acid and glutinous rice flour act as the sintering aid that can improve the sintering behavior of SiC ceramic.

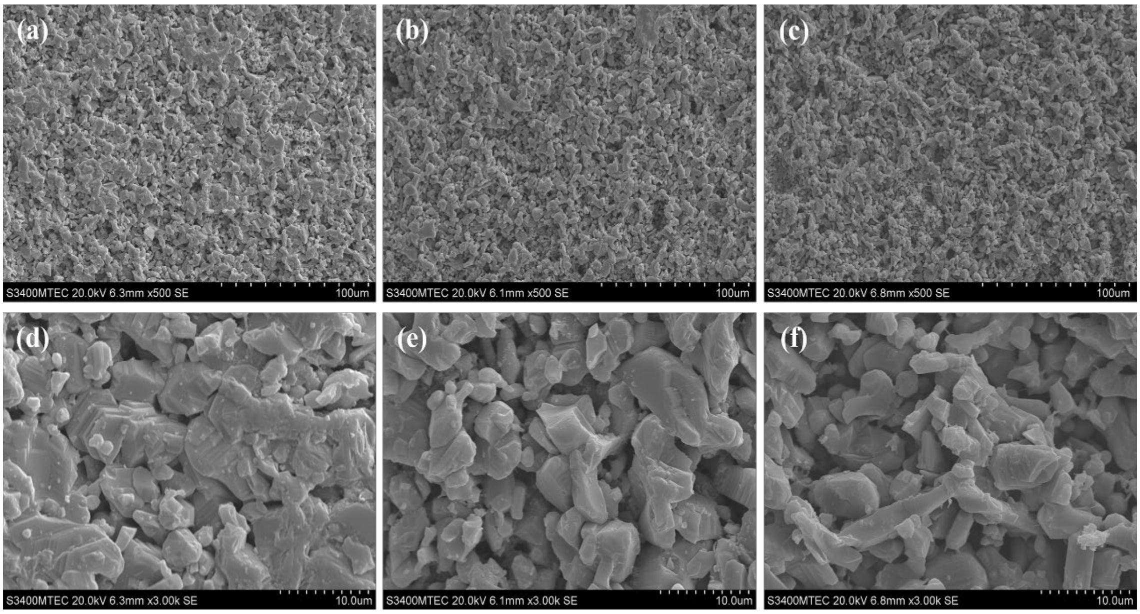

Figure 3. SEM images of sintered SiC ceramics at 500× magnification; (a) 0.5B1G, (b) 1B1G, and (c) 2B1G, and at 3000× magnification; (d) 0.5B1G, (e) 1B1G, and (f) 2B1G.

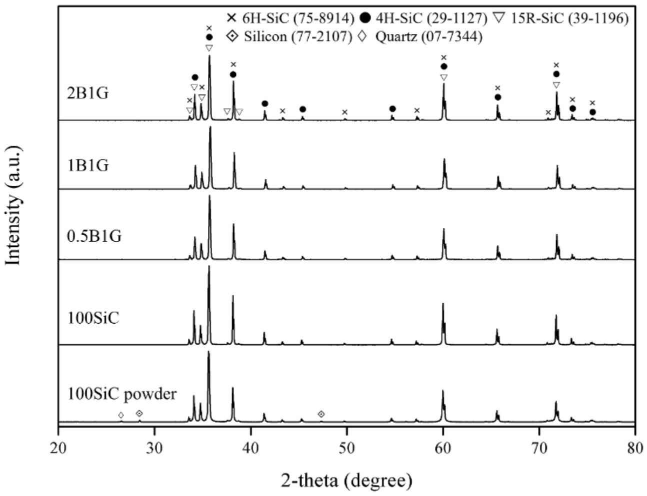

Figure 4. XRD patterns of 100SiC powder and sintered SiC samples.

4. Conclusions

This study assured the potential use of the boric acid–glutinous rice flour mixture as additive materials for sintering SiC ceramics via pressureless solid-state sintering. Boron–carbon derived from boric acid–glutinous rice flour had positive effects on the physical and mechanical properties of SiC ceramics sintered at 1800°C for 2 h in an argon atmosphere. The optimal boric acid/glutinous rice flour molar ratio for performing the highest relative density (62.32%) and flexural strength (78 MPa) was 0.5, which was attributed to 0.28 wt% boron and 5.45 wt% carbon content. Despite not achieving dense SiC ceramic, this study provided valuable insights and identified a cost-efficient alternative additive for SiC ceramic production.

Acknowledgements

The authors would like to thank the Royal Thai Air Force, for providing funding for this project. Highly thankful to the National Metals and Materials Technology Center (MTEC) and Metallurgy and Materials Science Research Institute for the characterization equipment.

References

[1] G. Magnani, A. Brentari, E. Burresi, and G. Raiteri, "Pressureless sintered silicon carbide with enhanced mechanical properties obtained by the two-step sintering method," *Ceramics International*, vol. 40, pp. 1759-1763, 2014.

[2] Z. Aygüzer Yaşar, V. A. DeLucca, and R. A. Haber, "Influence of oxygen content on the microstructure and mechanical properties of SPS SiC," *Ceramics International*, vol. 44, pp. 23248-23253, 2018.

[3] Q. W. Huang, and L. H. Zhu, "High-temperature strength and toughness behaviors for reaction-bonded SiC ceramics below 1400°C," *Materials Letters*, vol. 59, pp. 1732-1735, 2005.

[4] M. khodaei, O. yaghobizadeh, S. H. Naghavi Alhosseini, S. esmaeeli, and S. R. Mousavi, "The effect of oxide, carbide, nitride and boride additives on properties of pressureless sintered SiC: A review, " *Journal of the European Ceramic Society,* vol. 39, pp. 2215-2231, 2019.

[5] Z. Aygüzer Yaşar, V. A. DeLucca, and R. A. Haber, "Effect of boron carbide additive and sintering temperature - Dwelling time on silicon carbide properties," *Ceramics International*, vol. 47, pp. 7177-7182, 2021.

[6] G. D. Kim, Y. W. Kim, S. M. Yong, and W. K. Jung, "Improving specific stiffness of silicon carbide ceramics by adding boron carbide," *Journal of the European Ceramic Society,* vol. 42, pp. 6827-6835, 2022.

[7] A. Szkliniarz and W. Szkliniarz, "Effect of carbon content on the microstructure and properties of Ti-6Al-4V alloy," *Archives of Metallurgy and Materials*, vol. 65, pp. 1197-1204, 2020.

[8] S. Prochazka and R. M. Scanlan, "Effect of boron and carbon on sintering of SiC," *Journal of the American Ceramic Society*, vol. 58, pp. 72-72, 1975.

[9] R. Malik, and Y. W. Kim, "Pressureless solid-state sintering of SiC ceramics with BN and C additives," *Journal of Asian Ceramic Societies*, vol. 9, pp. 1165-1172, 2021.

[10] D. C. Jana, P. Barick, and B. P. Saha, "Effect of sintering temperature on density and mechanical properties of solid-state sintered silicon carbide ceramics and evaluation of failure origin," *Journal of Materials Engineering and Performance,* vol. 27, pp. 2960-2966, 2018.

[11] M. Liu, Y. Yang, Y. Wei, Y. Li, H. Zhang, X. Liu, and Z. Huang, "Preparation of dense and high-purity SiC ceramics by pressureless solid-state-sintering," *Ceramics International,* vol. 45, pp. 19771-19776, 2019.

[12] G. Liu, Z. Gu, Y. Hong, L. Cheng, and C. Li, "Electrospun starch nanofibers: Recent advances, challenges, and strategies for potential pharmaceutical applications," *Journal of Controlled Release,* vol. 252, pp. 95-107, 2017.

[13] P. Jaiturong, B. Sirithunyalug, S. Eitsayeam, C. Asawahame, P. Tipduangta, and J. Sirithunyalug, "Preparation of glutinous rice starch/polyvinyl alcohol copolymer electrospun fibers for using as a drug delivery carrier," *Asian Journal of Pharmaceutical Sciences*, vol. 13, pp. 239-247, 2018.

[14] K. Dateraksa and S. Sinchai, "Phase formation of boron carbide powder synthesized from glutinous rice flour," *Journal of Metals, Materials and Minerals,* vol. 29, pp. 48-53, 2019.

[15] R. McCuiston, S. Ngernbamrung, K. Dateraksa, K. Sujirote, J. Wannasin, and T. Sungkapun, "Fabrication of high-volume fraction SiCp/Al metal matrix composites," *Ceramic Engineering and Science Proceedings*, vol. 32, pp. 71-80, 2011.

[16] Y. Zhou, W. Sha, Y. Liu, Y. Lyu, and Y. Huang, "Influence of carbon source on microstructural and mechanical properties of high-performance reaction-bonded silicon carbide," *Materials*, vol. 15, pp. 5250, 2022.

[17] Z. A. Yaşar, and R. A. Haber, "Effect of carbon addition and mixture method on the microstructure and mechanical properties of silicon carbide," *Materials,* vol. 13, p. 3768, 2020.

[18] M. S. Datta, A. K. Bandyopadhyay, and B. Chaudhuri, "Sintering of nano crystalline α silicon carbide by doping with boron carbide," *Bulletin of Materials Science,* vol. 25, pp. 181-189, 2002.

[19] A. Maître, A. V. Put, J. P. Laval, S. Valette, and G. Trolliard, "Role of boron on the spark plasma sintering of an α-SiC

powder," *Journal of the European Ceramic Society,* vol. 28, pp. 1881-1890, 2008.

[20] L. Stobierski, and A. Gubernat, "Sintering of silicon carbide II. Effect of boron," *Ceramics International*, vol. 29, pp. 355-361, 2003.

[21] H. Skarpeid, "The effect of carbon and boron carbide additions in pressure assisted sintered silicon carbide," Master's thesis, Department of Materials Science and Engineering, Norwegian University of Science and Technology, 2017.