

Research Article

Densification and Microstructural Evolutions during Reaction Sintering of SiC-Si-C Powder Compacts

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Porous SiC-Si-C ceramics were produced by reaction sintering (RS) of silicon carbide, silicon, and carbon powder compacts in the temperature range of 1400–1600°C. The effects of chemical composition of the starting powder, initial SiC particle size, and reaction sintering temperature and duration on the densification and microstructure of ceramic materials were studied. The results showed that increasing the amount of Si and/or C powders in the starting powder mixture had a detrimental influence on the densification of ceramic material as a result of higher amount of remained silicon and carbon phases in the ceramic specimen. Increasing the RS temperature also degraded densification due to the melting of Si and coming out of it from compact during heating. Nevertheless, densification was improved by increasing the RS duration. Using nanometric SiC particles in the starting powder mixture improved the densification compared to that of micrometric ones especially at longer RS processing duration.

1. Introduction

Silicon carbide (SiC) was conventionally used in various industries as abrasive and cutting tools, structural materials, automobile parts, electric systems, electronic circuit elements, and heating elements. Nowadays, SiC is also attractive material for semiconductor production equipment parts, optical mirror devices in space, and fusion reactor structural applications [1]. The wide applications of SiC are attributed to the combination of low density, high stiffness, high hardness, high fracture toughness, high thermal and chemical stability, and good thermal and oxidation resistance [1, 2].

SiC parts have been principally produced by sintering method. However, the conventional sintering of SiC powders is considerably inhibited due to the strong covalent bonds that impose low values of self-diffusion of carbon and silicon within SiC structure [3, 4]. Therefore, SiC powders should be sintered at very high temperatures (>2000°C) for bulk fabrication of high-density ceramics. Using additives and/or applying pressure during sintering (hot pressing) can be employed to lower the sintering temperature. Gubernat et al. [4] have shown that SiC powders can be densified at temperatures between 1850 and 2000°C with the addition

of some oxides, for example, Al₂O₃, Y₂O₃, and MgO. Yano et al. [5] have produced SiC ceramics with high densities (95–99% theoretical) by hot pressing method at temperature range of 1700–1800°C, pressure of 30 MPa, and the use of aluminum, boron, and carbon dopant materials. Another promising method for production of SiC parts at lower temperatures is reaction sintering (RS) process. Employing RS can lower the processing temperatures to 1425–1500°C [2]. This has been attributed to the exothermic heat released during the reaction sintering between silicon and carbon to form SiC. Production of dense structure, good shape capability, low cost, and high purity are the other advantages of RS method [1]. The RS process is typically involving the infiltration of liquid silicon into a porous preform containing silicon carbide, and carbon has been extensively studied in the past [6–10]. An in situ reaction occurs between silicon and carbon to produce a secondary SiC phase, which then bonds the original SiC particles [3]. Residual pores and space not occupied by silicon carbide are filled with liquid silicon. It is well known [11, 12] that one limiting factor to obtain SiC parts with high strength is the amount of free silicon in the composites since the brittle free silicon phase and interfaces between SiC and Si are preferential paths for fracture.

Additionally, the mechanical properties, for example, strength, modulus of elasticity, and fracture toughness deteriorate due to increasing the amount of residual silicon phase especially at high temperatures [13–15]. Some studies [12, 16] have been performed in order to reduce the free silicon content in SiC-Si ceramics and enhance the mechanical properties. For instance, Blecha et al. [16] have suggested using SiC powders with different particle sizes.

The process chosen in this paper is a modification on reaction sintering process to reduce the free silicon content. The major difference between this approach and the typical reaction sintering process is that liquid silicon is not infiltrated into the porous SiC-C compact. Instead, the SiC parts are made by heating of compacts including SiC, Si, and C powder mixtures to promote reaction sintering. Therefore, the aim of the present study is to investigate the possibility of producing SiC ceramics through the RS of SiC, Si, and C powders. The reaction sintering temperature and time were optimized to get ceramics with minimum residual Si and C. The role of the chemical composition of the initial powder and the size of SiC particles on the microstructure and densification of ceramic parts are addressed.

2. Experimental Procedure

Silicon carbide, silicon, and carbon powders were used as starting materials. SiC powders with two different sizes, that is, micrometric SiC (μ -SiC, $\sim 15\ \mu\text{m}$, Zamin Tavana Co., Mashhad, Iran) and nanometric SiC (n-SiC, $\sim 50\ \text{nm}$, Alfa Aesar, Mass, USA) powders were employed. Powder batches with various weight ratios of Si/C in the range of 1–4 and (Si + C)/SiC between 0.8 and 19 were prepared. These powders were mixed by employing ball milling in methanol media for 1 h. Stainless steel balls with diameter of 4.8 mm and ball to powder weight ratio of 1 : 1 were utilized. After drying, a small amount of polyvinyl acetate (PVA) binder was added to powder. The powders were sieved to remove agglomerates and large particles. Then the powders were compacted in a steel die, 10 mm in diameter, at pressure of 125 MPa. The green compacts were heated at temperatures of 1400, 1500, and 1600°C. The heating duration was chosen to be 2 and 4 h. The process was performed under Ar atmosphere to protect the specimens from oxidation.

Density was measured by the Archimedes method according to the ASTM Standard B962 after sealing the surface pores with a water-resistant spray. Specimens for metallographic observations were prepared by the common procedure of grinding on emery papers and fine diamond polishing. The polished sections were studied by an optical microscope. X-ray diffraction (XRD) analysis by using $\text{Cu K}\alpha$ radiation (wavelength of 1.5406 Å) working at 40 kV and 30 mA was utilized for determination of the phases in the specimens. The step size was $0.05^\circ\ \text{s}^{-1}$.

3. Results

3.1. Effect of Reaction Sintering Temperature. Figure 1 shows the effect of reaction sintering temperature on the density of SiC-Si-C ceramics with different SiC particle sizes and

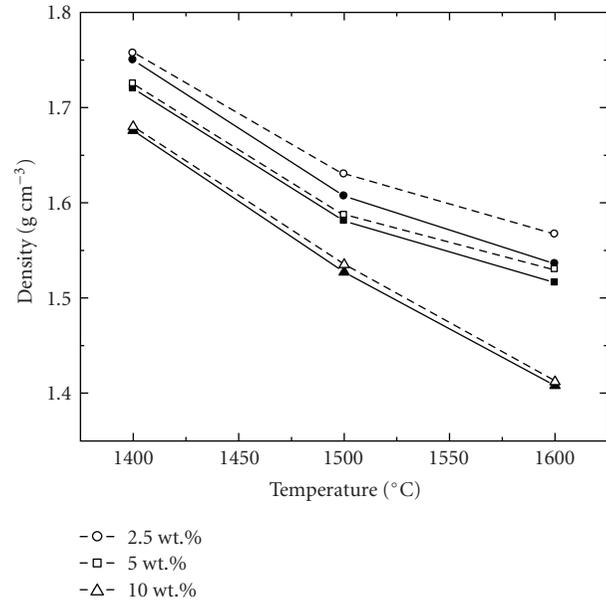


FIGURE 1: Density of SiC-Si-C ceramics as a function of RS temperature at different amounts of Si (2.5, 5 and 10 wt.%) by using μ -SiC (hollow symbols) and n-SiC (solid symbols) powders. RS time was 2 h, and Si/C ratio was 1.

Si powder contents. Si/C ratio of 1 and RS duration of 2 h were used. The density of specimens was decreased by increasing the RS temperature from 1400 to 1600°C, especially at higher amounts of Si powder. The microstructure of ceramic specimens at different RS temperatures is depicted in Figure 2. In general, the microstructure consists of SiC (light gray regions), C (dark gray regions), and Si (white regions) phases. Therefore, unreacted Si and C are present in the specimen, especially at 1400°C (Figure 2(a)). Additionally, high amounts of porosity can be observed (dark areas) in the microstructure. The amount of unreacted phases was decreased by an increase in the RS temperature (Figures 2(b) and 2(c)). Nevertheless, the porosity was significantly increased at the higher RS temperatures. Consequently, the specimens reaction-bonded at 1500 and 1600°C are very brittle and weak. XRD patterns of ceramic materials produced from n-SiC particles by RS at 1400 and 1600°C for 2 h are illustrated in Figure 3. As it can be seen, only β -SiC peaks appear in the diffraction patterns. The diffraction peaks were slightly intensified by increasing the RS temperature. Therefore, amplification of diffraction peaks is mainly attributed to the formation of new β -SiC phase via the RS of Si and C powders.

3.2. Effect of Reaction Sintering Time. The influence of RS duration on the density of SiC-Si-C ceramics is shown in Figure 4. The density of ceramics was increased by increasing the RS time. The rate of increasing in the density is higher for specimens prepared from n-SiC compared to that of μ -SiC. Again, the density was reduced by increasing the Si content. Figure 5 illustrates the microstructure of ceramic specimens processed for 2 and 4 h at 1400°C. It is clear that the amount of porosity was reduced at longer times of RS. It is important

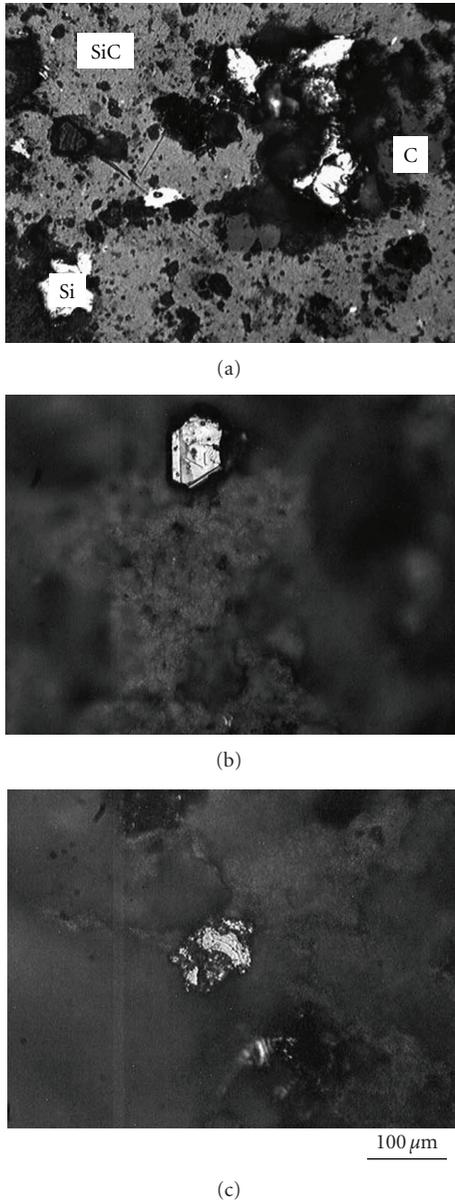


FIGURE 2: Optical micrographs from SiC-Si-C ceramics at RS temperatures of (a) 1400, (b) 1500, and (c) 1600°C. Si powder content of 10 wt.%, Si/C ratio of 1, initial SiC particle size of 50 nm, and RS time of 2 h were used.

to note that unreacted Si and C phases were present even after RS for 4 h (Figure 5(b)). As it can be seen in Figure 3, XRD patterns show β -SiC reflections only after 4 h RS at 1400°C.

3.3. Effect of Initial Si and C Content. Figure 6 shows the variation of density as a function of Si and C content for SiC-Si-C ceramics with Si/C ratio of 1. The density was decreased by increasing the amount of Si or C in the compacts. The rate of reduction is steeper for the specimens produced from micrometric SiC powders. This effect was also observed at different RS temperatures (Figure 1) and RS times (Figure 4). As shown in Figure 7, the porosity was increased at higher

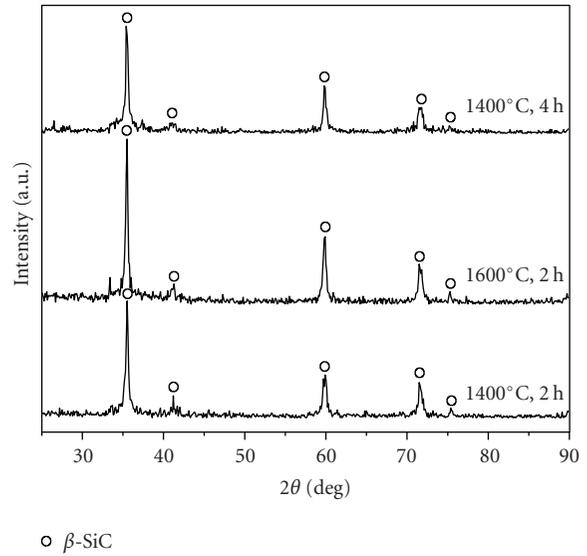


FIGURE 3: XRD patterns of SiC-Si-C ceramics at different RS temperatures and times. Si powder content of 5 wt.%, Si/C ratio of 1 and initial SiC particle size of 50 nm were used.

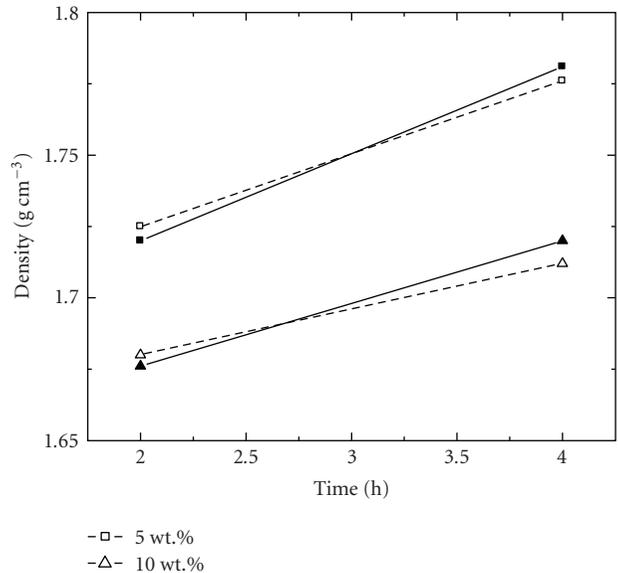


FIGURE 4: Changes of density of SiC-Si-C ceramics with RS time at different amounts of Si (5 and 10 wt.%) by using μ -SiC (hollow symbols) and n-SiC (solid symbols) powders. RS temperature was 1400°C and Si/C ratio was 1.

amounts of Si and C in the mixed powder. Moreover, the amounts of unreacted Si and C were significantly increased.

3.4. Effect of Si/C Ratio. Changes in the density of ceramic compacts with different Si/C ratios are depicted in Figure 8. At a fixed amount of C in the starting powder mixture, the density was reduced by an increase in the Si/C ratio, especially at higher C content (Figure 8(a)). The microstructure of SiC-Si-C ceramics at initial C content of 5 wt.% at Si/C ratios of 2 and 4 is shown in Figure 9. The porosity

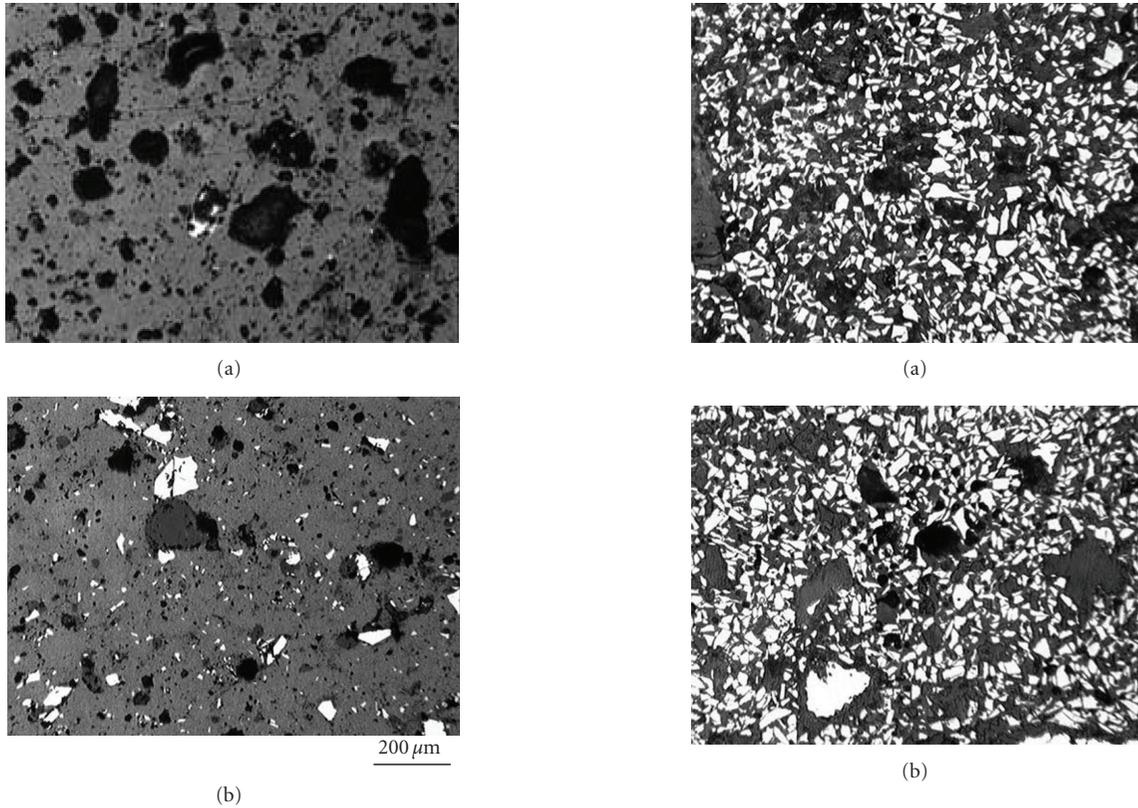


FIGURE 5: Microstructure of SiC-Si-C ceramics by using n-SiC powders at RS times of (a) 2 and (b) 4 h. RS temperature of 1400°C, Si/C ratio of 1, and Si amount of 5 wt.% were employed.

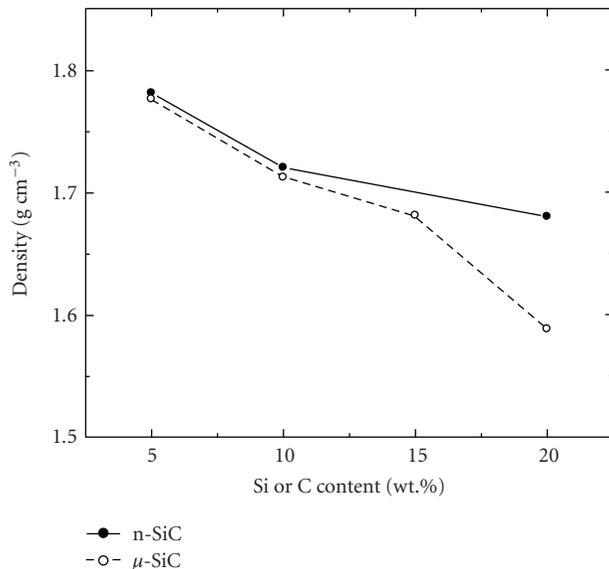


FIGURE 6: Effect of Si or C content on the density of SiC-Si-C specimens with Si/C ratio of 1. Ceramic compacts reaction-bonded at 1400°C for 4 h.

was not considerably changed by increasing the Si content from 5 to 10 wt.% (Figures 7(a) and 9(a)). Nevertheless, a large fraction of porosity and unreacted Si and C phases are

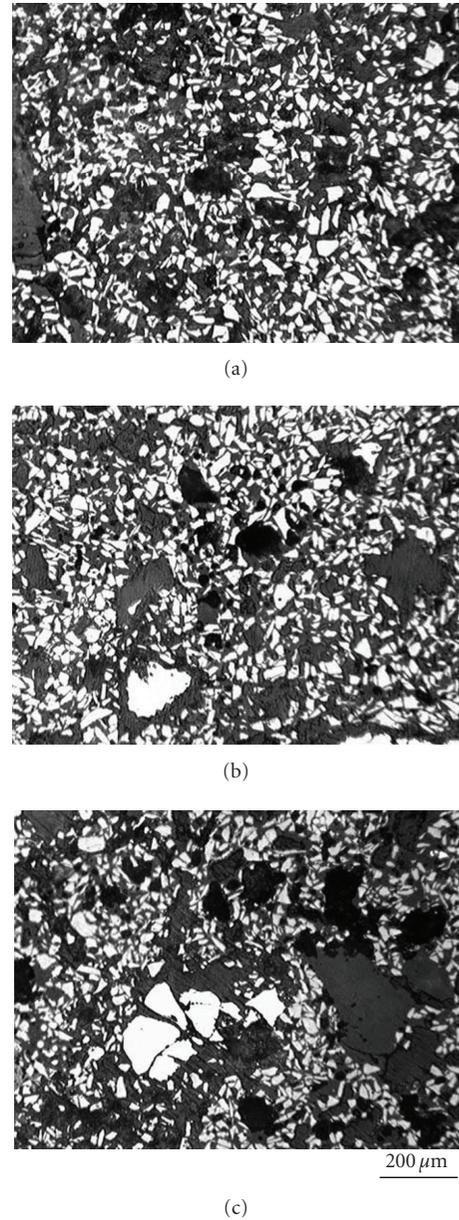


FIGURE 7: Microstructure of SiC-Si-C specimens by using μ -SiC powders at Si amount of (a) 5, (b) 10, and (c) 20 wt.%. Compacts with Si/C ratio of 1 were reaction-bonded at 1400°C for 4 h.

observable at Si/C ratio of 4 (Figure 9(b)). The presence of Si phase around SiC particles and microcracks within them is also noticed. XRD patterns of ceramic specimens produced from μ -SiC powders at two different Si/C ratios are shown in Figure 10. At Si/C = 1, α -SiC and β -SiC phases are detected. The appearance of weak SiO₂ reflections can be attributed to the presence of this phase in the initial powder. On the other hand, Si peaks appear in addition to α -SiC, β -SiC, and SiO₂ peaks in the diffraction pattern of ceramic with Si/C = 4. This is related to the remaining of unreacted Si in the specimen as shown in Figure 9(b).

At a fixed amount of Si in the starting powder, the density of SiC-Si-C specimens was increased by an increase in the

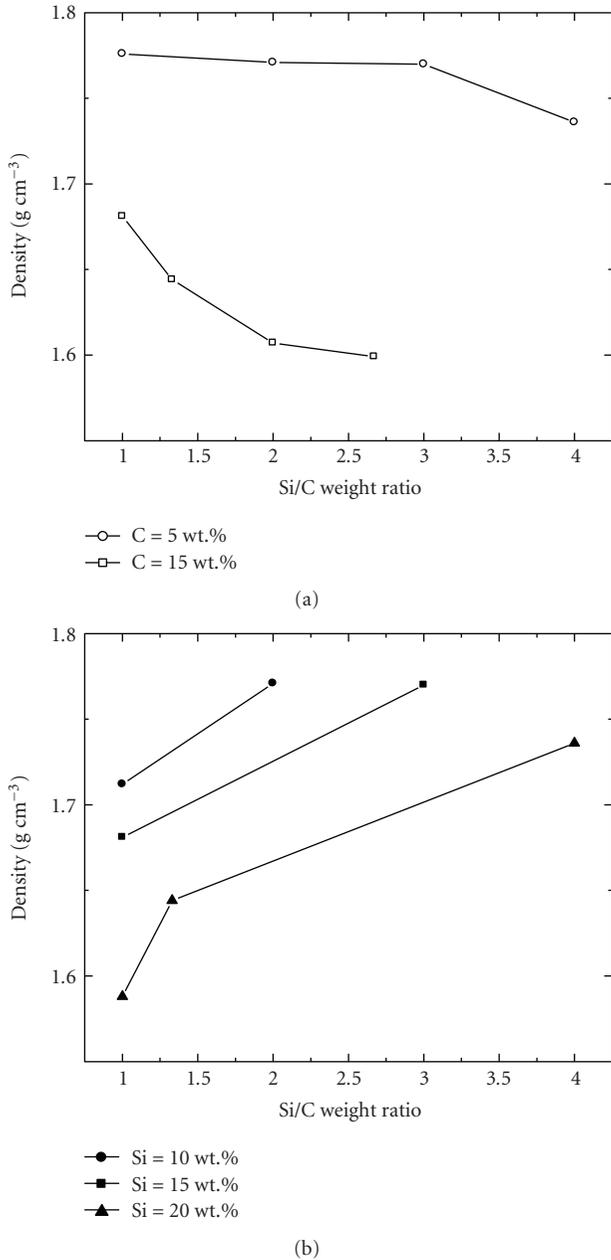


FIGURE 8: Density of SiC-Si-C compacts as a function of Si/C ratio at fixed amount of initial (a) C powder and (b) Si powder. Specimens were produced by RS at 1400°C for 4 h.

Si/C ratio (Figure 8(b)). In other words, the density was reduced at higher C contents.

3.5. Effect of SiC Particle Size. The role of initial SiC particle size on the density is related to the RS duration. The use of micrometric SiC particles resulted in higher density at shorter times of RS, that is, 2 h (see Figures 1 and 4). Nevertheless, at a longer RS duration, nanometric SiC particles were yielded to the higher densification (Figures 4 and 6). In addition, lower porosity and unreacted phases can be obtained (Figures 5(b) and 7(a)).

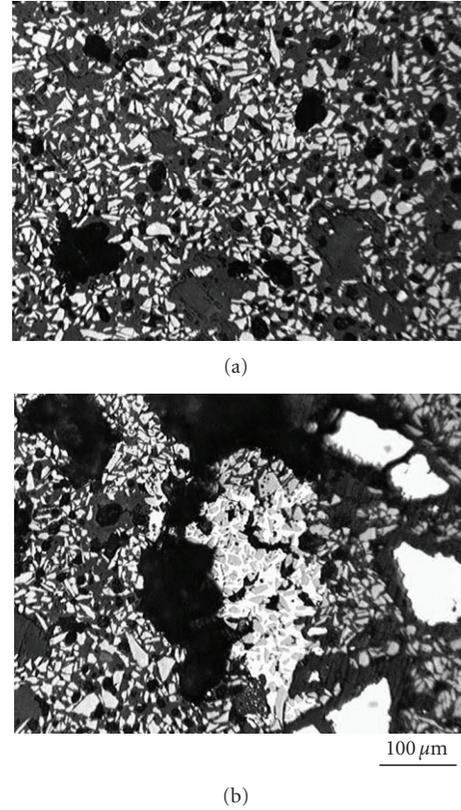


FIGURE 9: Optical micrographs from the microstructure of SiC-Si-C ceramics by using μ -SiC powders at initial C content of 5 wt.% and Si/C ratio of (a) 2, (b) 4. Specimens were reaction-bonded at 1400°C for 4 h.

4. Discussion

It was found that reaction sintering processing condition (temperature and time), chemical composition of the starting powder (Si/C ratio and amount of Si and C), and initial SiC particle size can significantly alter the densification behavior of SiC-Si-C ceramics during RS process. Therefore, the density and microstructure can be influenced.

During RS, the carbon reacts with silicon to form the new β -SiC phase which grows onto the original SiC (α -SiC for micrometric or β -SiC for nanometric particles) and hence bonds the compact together. While this reaction is a diffusion-controlled process, it is expected that higher temperature and longer time of RS can progress the reaction and improve the densification. Nevertheless, the results showed that the densification was degraded by increasing the RS temperature in the range of 1400–1600°C (Figure 1). Indeed, although higher β -SiC was formed (Figure 3), there was no evidence of densification at 1500 and 1600°C (Figures 2(b) and 2(c)). Since the melting point of pure silicon is \sim 1410°C [17], silicon melted during the RS at 1500 and 1600°C. Some of the silicon reacted with carbon to form β -SiC. However, most of the silicon phase came out of the compact during RS. As a result, the amount of porosity was grown and compact lost its integrity. Nevertheless, RS was performed in solid state at 1400°C, and better densification

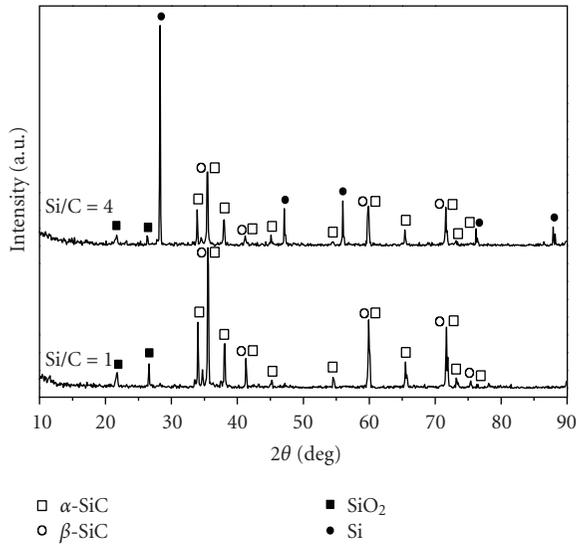


FIGURE 10: XRD patterns of SiC-Si-C ceramics at Si/C ratio 1 and 4 by using μ -SiC powders. C powder content of 5 wt.%, RS temperature of 1400°C, and RS time of 4 h were used.

was achieved by applying prolonged RS (Figure 4). While there were some unreacted carbon and silicon phases within the compacts, it can be concluded that using longer RS times can lead to enhanced reaction and superior densification.

The results showed that increasing the amount of Si and/or C powders in the starting powder mixture at stoichiometric ($\text{Si/C} = 1$) or nonstoichiometric ($\text{Si/C} \neq 1$) ratio has a detrimental influence on the densification of ceramic material (Figures 1, 4, 6 and 8). As SiC-Si-C ceramics consisted of α -SiC or β -SiC (density of 3.21 g cm^{-3}), residual Si (density of 2.33 g cm^{-3}), and residual C (density of 2.67 g cm^{-3}) in the ceramic body, the density was proportional to the amount of unreacted Si and C phases [6]. The amount of free silicon and carbon phases was significantly increased by an increase in the amount of Si and/or C in the starting powder mixture (Figures 7 and 9). Therefore, the density of ceramic compacts was reduced at higher contents of Si and/or C. On the other hand, since the interfaces between SiC and Si as well as the brittle free silicon phase are preferential paths for fracture, the presence of free silicon is detrimental for production of SiC ceramics [18]. Additionally, the strength and creep resistance deteriorate at temperatures above 1400°C due to existing free silicon [11]. Microcracks were found within some of the free silicon phase at high amount of Si in the starting material (see Figure 9(b)). These microcracks can be generated due to the crystallographic mismatch and differences in thermal expansion coefficient of SiC and silicon phases [11]. It is pertinent to point out that one of the ways to reduce the free silicon content in the reaction-bonded SiC ceramics produced via infiltration of Si into SiC/C preforms is increasing the carbon content in the preform. Wilhelm et al. [12] reported that the free silicon content reduced from 26 to 12 vol.% by increasing the phenol formaldehyde resin from 15 to 25 wt.% in the SiC/C preform. Nevertheless, the results of this study showed that increasing the carbon

content in the initial powder mixture reduced the density of sintered compacts (Figure 8(b)). This is mainly attributed to the difference in the mechanism of RS process in this study (solid-state reaction) with conventional infiltration of silicon into a carbon-contained preform (liquid-phase reaction).

The results demonstrated that using nanometric SiC particles instead of micrometric ones in the starting powder mixture improved densification at longer RS duration and higher amount of Si or C (Figures 4 and 6). It is well known that reduction of the initial powder particle size leads to an increase in the surface area of the powder. Therefore, it is estimated that higher amount of newly formed SiC phase is required for bonding the nanometric SiC powders compared to micrometric ones. Consequently, RS for longer time and higher amount of Si and C can result in higher density and lower amount of unreacted phases.

5. Conclusions

The density and microstructure of porous SiC-Si-C ceramics produced by reaction sintering were investigated. The most important findings can be summarized as follows.

- (1) Increasing the reaction sintering temperature higher than 1400°C degraded the densification, and specimens had low strength due to numerous and large porosities remaining within them.
- (2) Increasing the RS time from 2 to 4 h improved densification and less unreacted silicon and carbon phases were remained.
- (3) Using the higher amount of silicon and/or carbon powders in the initial powder mixture had a detrimental influence on the densification. Additionally, higher amount of free silicon and carbon phases remained in the specimens.
- (4) Superior densification was achieved by using nanometric SiC particles in the initial ceramic powder mixture compared to micrometric powders especially at longer RS durations and higher amount of Si and C in the starting powder mixture.

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