High mechanical properties of $\beta$-SiAlON/TiC$_{0.3}$N$_{0.7}$ ceramic composite prepared by pressureless spark plasma sintering

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1. Introduction

Silicon nitride ceramic is an advanced ceramic material with low density, high strength, good friction and oxidation resistance and high chemical corrosion resistance, which is widely used in cutting tools, bearings, reciprocating engine parts, wear and metal forming components [1–4]. $\beta$-SiAlON is a $\beta$-Si$_3$N$_4$ solid solution by substitution of a silicon-nitrogen bond with aluminum-oxygen bond [5–7], named after the elements they contain silicon (Si), aluminum (Al), oxygen (O) and nitrogen (N). SiAlON shows similar physical and mechanical properties to those of Si$_3$N$_4$ ceramics, but better thermal shock resistance because of its lower thermal expansion. However, the SiAlON matrix composites still exhibit some inadequacies such as the inherent brittleness of ceramic [8–10]. Many efforts have been made to improve the brittleness properties of the ceramics via well-definable composition and microstructure by carefully controlling the process parameters and methods [11–13].

The dispersion of the second phases has been regarded as an effective way for ceramic toughening. It is reported that TiN particulates improve the fracture toughness of Si$_3$N$_4$ and SiAlON composites at room temperature [8,10,14–18]. The Si$_3$N$_4$/TiN nanocomposites containing 10 wt.% TiN obtained by hot pressing show a fracture toughness of ~6.7 MPa m$^{1/2}$ [19]. The fracture toughness of 5.52 MPa m$^{1/2}$ was obtained in $\alpha$-$\beta$-SiAlON/TiN composites with 5 wt.% TiN prepared by microwave sintering at 850°C [20]. Spark plasma sintering (SPS) shows high efficiency for the densification of ceramics, including Si$_3$N$_4$, at relatively low temperatures under a pressure [21]. Compared to the traditional sintering processes, the SPS technology achieves the same sintering effect at lower temperatures within a shorter sintering time for Si$_3$N$_4$-based ceramics [22]. The fully dense nanocomposite containing 10 wt.% TiN, fabricated successfully by SPS at 1600°C for 3 min under a pressure of 30 MPa using Si$_3$N$_4$ and TiN nanopowders, exhibits the highest fracture toughness of ~4.9 MPa m$^{1/2}$ [17]. Fully dense $\beta$-SiAlON/TiN composites are produced by spark plasma sintering (SPS) at 1750°C under a pressure of 30 MPa for 30 min, using Si$_3$N$_4$, Al$_2$O$_3$, AlN and TiO$_2$ powders. The fabricated composite with 15 wt.% micronized TiO$_2$ possesses a high toughness of 6.3 MPa m$^{1/2}$ [10]. However, the Si$_3$N$_4$-based ceramics or SiAlONs may be easily reacted with the graphite mold during pressurized SPS at high temperatures. In this work, we successfully prepared $\beta$-SiAlON/TiC$_{0.3}$N$_{0.7}$ composites with high mechanical properties by means of pressureless SPS, which could avoid the above-mentioned reaction between the sample and the graphite mold. The densification of $\beta$-SiAlON/TiC$_{0.3}$N$_{0.7}$ composites could...
take place by intrinsic pulsed electric field effects on the mass transport in the pressureless SPS process, forming highly densified microstructures of interlock β-SiAlON lath grains + dispersed TiC$_3$N$_{0.7}$ particles without the oriented ununiform stress distribution caused by uniaxial pressure in normal pressurized SPS. Consequently, the high density, hardness and fracture toughness would be achieved.

2. Experimental procedures

The starting materials were Si$_3$N$_4$ (SN-E10 grade, 0.6 µm, 95% α-phase, UBE Industries, Japan), Al$_2$O$_3$ (Meyer, 100 nm, Germany), AlN (Meyer, 50 nm, Germany), Y$_2$O$_3$ (Meyer, 100 nm, Germany), and TiC$_3$N$_{0.7}$ (Xing Rong Yuan, 2 µm, China) powders. According to the weight ratios of the samples with different TiC$_3$N$_{0.7}$ contents, as listed in Table 1, the powders were mixed by wet ball-milling with ethanol for 48 h (zirconia balls and high-density polyethylene jar). The weight ratio of the balls to the powders was kept at about 10:1. The zirconia balls with 3.5 and 5.0 mm in diameter with the weight ratio of 8:2 were used. The milled powders were then dried in a drying box at 80°C for 12 h, sieved with 140 meshes, and cold isostatic pressed (~270 MPa) into pellets with 28 mm in diameter.

The pellets were sintered by pressureless SPS (lab-made SPS system) under a nitrogen atmosphere using a special cylindrical graphite mold with an inner diameter of 30 mm (see Figure 1). The samples with different TiC$_3$N$_{0.7}$ contents, namely 1-SNT0, 1-SNT2, 1-SNT5 and 1-SNT7.5 (see Table 1), were heated to the sintering temperature between 1500°C and 1650°C at a rate of 100°C/min, held at each temperature for 20 min, and then cool down to room temperature at a rate of 70°C/min. All the samples pressureless SPSed at 1550°C exhibited the best properties in density, hardness, fracture toughness. Therefore, they were selected for further improvement by further pressurized SPS under a pressure of 24 MPa at 1400, 1425 and 1450°C, respectively, for 5 min. These samples were named 2-SNT0, 2-SNT2, 2-SNT5 and 2-SNT7.5 (also see Table 1).

The as-prepared samples were polished with diamond paste up to 1.0 µm for phase and microstructure analyses, and also for the density, hardness, fracture toughness, and thermal conductivity measurements.

The phases were analyzed by X-ray diffraction (XRD) using Bruker D8 Advance SS/18 kW with Cu Kα radiation and Jade 6.5 software. The Rietveld refinements of XRD patterns were performed with the aid of Topas 3.1 software to estimate the theoretical density of the samples. The microstructures were observed by scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) (Su-70, Hitachi). The bulk density of the samples was measured by the Archimedes method. Vickers hardness and fracture toughness were determined using the indentation technique. The Vickers hardness was measured with a hardness tester (Micro-586 Vickers Hardness Tester, Shanghai Taiming Optical Instrument Co., Ltd.) with an indentation load of 10 kg (98 N) and a dwell time of 15 s. The Vickers hardness (H V in GPa) is given by [23]

$$HV = 0.001 \frac{2F \sin \alpha}{d^2} = 0.001854 \frac{F}{d^2}$$

(1)

where $F$ is the test force in Newton (N), $\alpha$ is the angle between two opposite faces of a regular quadrilateral pyramid diamond indenter (136°±0.5° in this work), and $d$ is the mean value of the two diagonals of the indentation in mm.

The fracture toughness ($K_{IC}$ in MPa m$^{1/2}$) is determined by [24]

$$K_{IC} = 0.016 \left( \frac{E}{HV} \right)^{1/2} \frac{1000F}{C^{3/2}}$$

(2)

where $E$ is Young’s modulus in GPa (300 GPa for Si$_3$N$_4$ in this work [24]) and $C$ is the mean crack length from the center of indentation in µm.

The thermal diffusivity ($\lambda$) was measured by the laser flash technique (NETZSCH LFA 467) and the heat capacity $C_p$ was determined using differential scanning calorimetry (NETZSCH DSC 404F3). The total thermal conductivity ($\kappa$) is calculated using the equation $\kappa = \rho \lambda C_p$, where $\rho$ is the mass density of the sample.
3. Results and discussion

3.1. Phases and microstructures

In this investigation, the \( \beta \)-SiAlON/TiC\(_{0.3}\)N\(_{0.7} \) composites were prepared with 6 Al\(_2\)O\(_3\)-3 AlN-6 Y\(_2\)O\(_3\) or 5 Al\(_2\)O\(_3\)-2.5 AlN-5 Y\(_2\)O\(_3\) additives (wt.%) and different TiC\(_{0.3}\)N\(_{0.7} \) contents. The \( \beta \)-SiAlON ceramics were formed by the following reaction [10]:

\[
\frac{(6 - z)}{3} \text{Si}_3\text{N}_4 + \frac{z}{3} \text{Al}_2\text{O}_3 + \frac{z}{3} \text{AlN} \\
\rightarrow \text{Si}_{(6 - z)}\text{Al}_z\text{O}_z\text{N}_8 (0 \leq z \leq 4.2)
\]

Based on the Al\(_2\)O\(_3\)-AlN-Y\(_2\)O\(_3\) phase diagram, the Y\(_2\)O\(_3\) additive can decrease the forming temperature of the transient liquid phase and thus reduce the sintering temperature [25]. The pulsed electrical current with 10 ms on/10 ms off period and about 2000 A was used in this work. As a result of particle rearrangement due to the Si\(_3\)N\(_4\)-dissolution to \( \beta \)-SiAlON precipitation, the densification of the \( \beta \)-SiAlON/TiC\(_{0.3}\)N\(_{0.7} \) composites can also occur by intrinsic pulsed electric field effects on the mass transport without pressure during the pressureless SPS process, forming the highly densified microstructures, showing similar sintering behavior as comparing to the normal pressurized SPS.

Figure 2a represents the typical XRD patterns for the mixed powder and the pressureless SPSed sample 1-SNT5 at different temperatures. The mixed powder contains \( \alpha \)-Si\(_3\)N\(_4\) phase mainly, together with minor \( \beta \)-Si\(_3\)N\(_4\) and TiC\(_{0.3}\)N\(_{0.7} \) phases, and Al\(_2\)O\(_3\), AlN and Y\(_2\)O\(_3\) additive phases. As the mixed powder pressureless SPSed at 1500–1650°C for 20 min, the crystalline phases are \( \beta \)-SiAlON and minor TiC\(_{0.3}\)N\(_{0.7} \) phases. Almost all the \( \alpha \)-Si\(_3\)N\(_4\) phase has reacted with the additives Al\(_2\)O\(_3\) and AlN and transforms to \( \beta \)-SiAlON ceramic completely.

Figure 2. XRD patterns for (a) the mixed powder and the 1-SNT5 sample with 5.0 wt.% TiC\(_{0.3}\)N\(_{0.7} \) after pressureless SPS at different temperatures 1500–1650 °C and (b) the 1-SNT0, 1-SNT2, 1-SNT5 and 1-SNT7.5 samples with 0, 2.0, 5.0 and 7.5 wt.% TiC\(_{0.3}\)N\(_{0.7} \), respectively, after pressureless SPS at 1550 °C.
The Al₂O₃, AlN and Y₂O₃ react chemically with Si₃N₄ on the surface of Si₃N₄, forming a transient liquid phase during the sintering and finally become glass phases along the grain boundaries of the β-SiAlON/TiC₀.₃N₀.₇ crystalline phases. Therefore, both the formation of the liquid phase and the phase transformation of α-Si₃N₄ to β-SiAlON in the liquid phase also occur during the pressureless SPS process. As the sintering temperature increases to 1650°C, the minor impurity crystalline phases, seeming Y₂SiAlO₃N and Y₁₀Al₂Si₁O₁₆N₄, appear in the sample, which may arise from the crystallization from the glass phases. Similar phase formation is also found in the other samples with different TiC₀.₃N₀.₇ contents as shown in Figure 2b. The β-SiAlON/TiC₀.₃N₀.₇ composites with 0, 2.0, 5.0 and 7.5 wt.% TiC₀.₃N₀.₇, containing β-SiAlON and TiC₀.₃N₀.₇ crystalline phases, along with the grain boundary glass phases, can be fabricated by the pressureless SPS at ~1550°C. As the TiC₀.₃N₀.₇ content increases, the intensity of the TiC₀.₃N₀.₇ peak increases (see Figure 2b).

Figure 3 shows the backscattering electron micrographs of the polished surfaces of the representative sample 1-SNT5 pressureless SPSed at different temperatures. Clearly, the micrographs consist of the dark gray, bright white, white and dark regions. The dark regions in Figure 3a are pores, which reveal that the pressureless SPS temperature of 1500°C is too low for sample 1-SNT5 to obtain dense ceramic due to the high viscosity of the liquid phase along the grain boundary. Based on the compositions obtained by EDS analysis and the XRD results, it is confirmed that the dark gray region belongs to the β-SiAlON phase and the bright white phase region to the TiC₀.₃N₀.₇ phase, while the white region is of the glass phase or minor impurity Y₂SiAlO₃N phase formed from the residual additives along the grain boundaries of the β-SiAlON phase. As the sintering temperature is increased to 1550°C, there are no pores present in the samples whose microstructures are mainly composed of interlock elongated β-SiAlON grains uniformly dispersed with TiC₀.₃N₀.₇ particles (see Figure 3b). As the sintering temperature is further increased to 1600°C, no obvious change is found in the microstructure (see Figure 3c). However, when sintering at 1650°C, the long columnar grains begin seemingly to grow larger (see Figure 3d).

Figure 4 shows the typical EDS spectra for elongated β-SiAlON phase (dark gray region, marked 1 in
Figure 4. EDS results for (a) the elongated dark gray region (β-SiAlON phase), (b) the bright region (TiC<sub>0.3</sub>N<sub>0.7</sub> phase) and (c) the white region (glass phase) in the micrograph of the polished surface of the 1-SNT5 sample with 5.0 wt.% TiC<sub>0.3</sub>N<sub>0.7</sub> after pressureless SPS at 1550°C (see Figure 3b).

Figure 3b), TiC<sub>0.3</sub>N<sub>0.7</sub> phase (bright white region, marked 2 in Figure 3b) and glass phase (white region, marked 3 in Figure 3b) in the micrograph on the polished surface of the sample 1-SNT5 pressureless SPSed at 1550°C for 20 min. The dark gray region is of the β-SiAlON phase formed by the reaction of Si<sub>3</sub>N<sub>4</sub>, Al and O, which mainly contains Si and N together with a small amount of Al and O but not Y (see Figure 4a). The bright white region is the TiC<sub>0.3</sub>N<sub>0.7</sub> phase, which mainly contains Ti, N and C, along with a small amount of Si, O and Al but not Y (see Figure 4b) affected from the β-SiAlON matrix. The element Y distributes mainly in the glass phases or in the minor impurity Y<sub>2</sub>SiAlO<sub>5</sub> N (see Figure 4c). The large amount of Si and N in the glass phase should be affected by the β-SiAlON matrix since the glass layer is very thin (about 80 nm).

The elemental mapping on the polished surface of the 1-SNT5 sample pressureless SPSed at 1550°C is illustrated in Figure 5. It is clearly seen that TiC<sub>0.3</sub>N<sub>0.7</sub> particles are uniformly distributed in the β-SiAlON matrix. It can be envisaged that the oriented ununiform stress distribution, caused by uniaxial pressure in

Figure 5. Microstructures (a) and elemental mapping of Si (b), Al (c), O (d), Ti (e), N (f), C (g) and Y (f) on the polished surface of the 1-SNT5 sample with 5.0 wt.% TiC<sub>0.3</sub>N<sub>0.7</sub> after the pressureless SPS at 1550°C.
normal pressurized SPS, can be disappeared in the pressureless SPSed samples, which would be beneficial to the enhancement of fracture toughness.

### 3.2. Density, hardness, and fracture toughness

The high density, hardness and fracture toughness can be obtained by the pressureless SPS. Figure 6 shows the density, hardness and fracture toughness for the samples pressureless SPSed at different temperatures. The values of density and hardness for the sample 1-SNT0 without TiC$_{0.3}$N$_{0.7}$ increase sharply with increasing the sintering temperature from 1500°C to 1600°C, and then decrease slightly with further increasing sintering temperature to 1650°C, which may be due to the larger grain size and the slight decomposition of Si$_3$N$_4$ created at this higher sintering temperature. The 1-SNT2, 1-SNT5 and 1-SNT7.5 samples containing different TiC$_{0.3}$N$_{0.7}$ contents exhibit a similar trend as the 1-SNT0 sample with increasing the sintering temperature. The densities for the 1-SNT2, 1-SNT5 and 1-SNT7.5 samples containing TiC$_{0.3}$N$_{0.7}$ are somehow higher than that of the 1-SNT0 sample due to the higher density of the TiC$_{0.3}$N$_{0.7}$ phase. The highest densities for the 1-SNT2, 1-SNT5 and 1-SNT7.5 reach 3.18, 3.25, 3.28 and 3.26 g cm$^{-3}$ respectively. The theoretical density of the pressurized SPSed sample 2-SNT5 is ~3.27 g cm$^{-3}$, estimated based on XRD Rietveld refinement and EDS analysis, considering the crystalline phases β-SiAlON and TiC$_{0.3}$N$_{0.7}$ only without taking account of the glass phase, which lower than the

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**Figure 6.** (a) Density ($\rho$), (b) hardness ($HV$) and (c) fracture toughness ($K_{1C}$) of the samples after both pressureless SPS and further pressurized SPS at different temperatures ($T$).
highest density 3.32 g cm$^{-3}$ of its further pressurized SPSed sample (see in section 3.4). Therefore, the highest densities, 3.24, 3.29, 3.32 and 3.32 g cm$^{-3}$ for the further pressurized SPSed samples 2-SNT0, 2-SNT2, 2-SNTS and 2-SNT7.5 with 0, 2.0, 5.0 and 7.5 wt.% TiC$_{0.3}$N$_{0.7}$ were taken as their theoretical density. The relative densities for the pressureless SPS samples are also plotted in Figure 6a. One can see that all the pressureless SPS samples show high relative densities around 98% and slightly higher with the introduction of the conductive TiC$_{0.3}$N$_{0.7}$ phase. The conductive TiC$_{0.3}$N$_{0.7}$ phase uniformly distributed in the β-SiAlON matrix increases the electrical conductivity of the composite materials and consequently affects their sintering behavior by the electric current passing through the sample in SPS [26]. As the result, it promotes the sample sintering at relatively lower temperatures, and thus leads to obtain the higher density, hardness and fracture toughness as well as the complete phase transformation of α-Si$_3$N$_4$ to β-SiAlON.

For the pressureless SPS at 1550°C and 1600°C, all the samples show better density, hardness and fracture toughness, shown in Figure 6. For example, the density, hardness and fracture toughness for the 1-SNT5 are 3.27 g cm$^{-3}$, 14.48 GPa and 7.20 MPa m$^{1/2}$ as the sample sintered at 1550°C, while 3.28 g cm$^{-3}$, 14.78 GPa and 7.06 MPa m$^{1/2}$ as the sample sintered at 1600°C. The fracture toughness of 7.20 MPa m$^{1/2}$ obtained for the β-SiAlON with 5.0 wt.% TiC$_{0.3}$N$_{0.7}$ sintered at 1550°C is higher than 6.7 MPa m$^{1/2}$ for the 10 wt.% TiN-Si$_3$N$_4$ nanocomposite obtained by hot pressing [19], 5.52 MPa m$^{1/2}$ for the 5 wt.% TiN-α-β-SiAlON composite achieved by microwave sintering at 850°C [20], and 6.2 MPa m$^{1/2}$ for the 10 wt.% TiN-β-SiAlON composite prepared by SPS at 1600°C for 10 min under a pressure of 30 MPa [18]. The β-SiAlON/TiC$_{0.3}$N$_{0.7}$ composites pressurized SPSed at 1550°C exhibit the best fracture toughness, which were selected for further pressurized SPS at temperatures between 1400°C and 1450°C for 5 min under a pressure of 24 MPa. The related results will be presented later.

The higher fracture toughness for the samples prepared by the pressureless SPS may be mainly ascribed to the highly dense microstructures with the interlocking of the lath β-SiAlON grains and the uniformly distributed TiC$_{0.3}$N$_{0.7}$ particles, and the disappearance of the oriented ununiform stress distribution caused by uniaxial pressure in normal pressurized SPS. The toughening mechanisms of the β-SiAlON/TiC$_{0.3}$N$_{0.7}$ composites fabricated in this work should be a crack deflection, branching and bridging, penetration and impedancing. Figure 7 shows a typical Vickers fingerprint and the crack propagation on the polished

![Figure 7](image-url)

*Figure 7.* Back scattering electron micrographs for the typical Vickers fingerprint (a) and crack propagation observations (b-i) near the indentation at the polished surfaces of the 1-SNT5 sample.
surfaces of the 1-SNT5 sample. A large number of interlocking lath \( \beta \)-SiAlON grains aligned in various directions are distributed inside the matrix. The TiC\(_{0.3}\)N\(_{0.7}\) particles distribute uniformly in the \( \beta \)-SiAlON matrix. When a crack encounters the lath \( \beta \)-SiAlON grains or TiC\(_{0.3}\)N\(_{0.7}\) particles of a certain specific orientation during the propagation process, the crack has to deflect around the \( \beta \)-SiAlON lath, leading to an increase in the resistance of crack propagation, shown in Figure 7 (b)-d) and (f). For some elongated lath \( \beta \)-SiAlON grains or TiC\(_{0.3}\)N\(_{0.7}\) particles with specific orientation and distribution, the crack is difficult to deflect and can only cut through or penetrate the \( \beta \)-SiAlON grain, hereby consuming more energy, shown in Figure 7 (g)-(h). The crack bridging occurs as the hardness of TiC\(_{0.3}\)N\(_{0.7}\) is higher than that of \( \beta \)-SiAlON and the TiC\(_{0.3}\)N\(_{0.7}\) particles can bridge at the ends of two cracks, shown in Figure 7. The oriented uniform stress distribution caused uniaxial pressure in normal pressurized SPS also decreases fracture toughness. The pressureless SPS avoids this problem.

### 3.3. Thermal properties

The value of thermal conductivity, shown in Figure 8, decreases from 14.3 W\( \text{m}^{-1}\text{K}^{-1}\) at 25°C to 12.3 W\( \text{m}^{-1}\text{K}^{-1}\) at 500°C for the sample 1-SNT0, from 14.8 W\( \text{m}^{-1}\text{K}^{-1}\) to 12.5 W\( \text{m}^{-1}\text{K}^{-1}\) for the 1-SNT2 sample, from 15.1 W\( \text{m}^{-1}\text{K}^{-1}\) to 13.1 W\( \text{m}^{-1}\text{K}^{-1}\) for the 1-SNT3 sample, and from 15.5 W\( \text{m}^{-1}\text{K}^{-1}\) to 13.7 W\( \text{m}^{-1}\text{K}^{-1}\) for the 1-SNT7 sample. The increase of thermal conductivity with the increase of TiC\(_{0.3}\)N\(_{0.7}\) is mainly due to the more conductive TiC\(_{0.3}\)N\(_{0.7}\) phase with a higher thermal conductivity. The phonon scattering resulting from the glass phases formed along the grain boundaries may somewhat decrease the thermal conductivity. No doubt, a high thermal conductivity of the ceramic composites is beneficial for their practical applications.

### 3.4. Further modification of pressurized SPS

The samples pressureless-sintered at 1550°C for 20 min were sintered again by SPS at different temperatures under a pressure of 24 MPa for 5 min. Figure 9a shows the typical XRD patterns for the 2-5N5T sample with 5.0 wt.% TiC\(_{0.3}\)N\(_{0.7}\) (see Table 1) after pressurized SPS at different temperatures. After further pressurized SPS at 1400°C, 1425°C and 1450°C, the phases in the samples have no apparent change, showing the main crystalline \( \beta \)-SiAlON phase and minor TiC\(_{0.3}\)N\(_{0.7}\) phase as well as some glass phases. As the TiC\(_{0.3}\)N\(_{0.7}\) content increases, the intensity of the TiC\(_{0.3}\)N\(_{0.7}\) peak increases (see Figure 9b).

![Figure 8](image8.png)

**Figure 8.** The thermal conductivity (\( \kappa \)) as a function of temperature (T) for the 1-SNT0, 1-SNT2, 1-SNT5 and 1-SNT7.5 samples after pressureless SPS at 1600°C for 20 min.

![Figure 9](image9.png)

**Figure 9.** XRD patterns for the \( \beta \)-SiAlON/TiC\(_{0.3}\)N\(_{0.7}\) composite samples: (a) 2-SNT5 with 5.0 wt.% TiC\(_{0.3}\)N\(_{0.7}\) after further pressurized SPS at different temperatures and (b) 2-SNT0, 2-SNT2, 2-SNT5 and 2-SNT7.5 with 0, 2.0, 5.0 and 7.5 wt.% TiC\(_{0.3}\)N\(_{0.7}\), respectively, after further pressurized SPS at 1400°C.
After further pressurized SPS, the samples exhibit much denser microstructure as compared with those of the pressureless-sintered samples, containing β-SiAlON phase (dark gray regions), TiC$_{0.3}$N$_{0.7}$ phase (bright white regions), and glass phase (white regions), as shown in Figure 10. It is anticipated that these samples could have a higher performance. As demonstrated in Figure 6, the density, hardness and fracture toughness of the samples are somewhat enhanced. The density increases from 3.18 to 3.22–3.24 g cm$^{-3}$ for the 2-SNT0 sample, from 3.25 to 3.28–3.29 g cm$^{-3}$ for the 2-SNT2 sample, from 3.28 to 3.31–3.32 g cm$^{-3}$ for the 2-SNT5 sample, and from 3.26 to 3.31–3.32 g cm$^{-3}$ for the 2-SNT7.5 sample. The density increases slightly with increasing TiC$_{0.3}$N$_{0.7}$ content because of the higher-density TiC$_{0.3}$N$_{0.7}$. The theoretical density of the 2-SNT5 sample is ~3.27 g cm$^{-3}$, estimated based on XRD Rietveld refinement and EDS analysis. A small number of Al and O are considered to replace Si and N, respectively, in β-Si$_3$N$_4$, thereby leading to the formation of β-SiAlON. The samples after further pressurized SPS can be considered to be fully dense.

As reported in [27], the density of 3.25 g cm$^{-3}$ is obtained for the Si$_3$N$_4$ ceramics by pressurized SPS at 1650°C for 10 min using 9.0 wt.% Al$_2$O$_3$ and 6.0 wt.% Y$_2$O$_3$ as additives. The silicon nitride ceramics fabricated by pressurized SPS exhibit the density of 3.08 g cm$^{-3}$ for sintering at 1500°C, 3.23 g cm$^{-3}$ for sintering at 1600°C, and 3.23 g cm$^{-3}$ for sintering at 1650°C using 2.0 wt.% Al$_2$O$_3$ and 5.0 wt.% Y$_2$O$_3$ as additives [22]. A study by Hayashi et al. [28] indicates that the Si$_3$N$_4$-based ceramic material prepared by sintering in a graphite resistance furnace at 1900°C for 2 to 48 h under a nitrogen pressure of 0.9 MPa with MgSiN$_2$ as additive possesses a density ranging from 3.20 to 3.26 g cm$^{-3}$. Thus, the density of the present samples fabricated by further pressurized SPS or even merely by pressureless SPS is comparable with or higher than those reported in literature.

After the further pressurized SPS, the Vickers hardness increases from 14.00 GPa to 15.50–15.92 GPa for the 2-SNT0 sample, from 14.77 GPa to 15.73–15.86 GPa for the 2-SNT2 sample, from 14.78 GPa to 15.39–15.87 GPa for the 2-SNT5 sample, and from 13.87 GPa to 15.08–15.48 GPa for the 2-SNT7.5 sample. The hardness for 2-SNT0, 1-SNT2 and 2-SNT5 is not apparently different at different TiC$_{0.3}$N$_{0.7}$ contents after the further pressurized SPS, while the hardness of 2-SNT7.5 is slightly lower, which may be due to the less sintering aids of Al$_2$O$_3$-AIN-Y$_2$O$_3$.

The second-stage pressurized SPS can also enhance the fracture toughness of β-SiAlON/TiC$_{0.3}$N$_{0.7}$ composites. It is increased from 6.40 to 7.00 MPa m$^{1/2}$ for the 2-SNT0 sample, from 6.65 to 6.98 MPa m$^{1/2}$ for the 2-SNT2 sample, from 7.20 to 7.44 MPa m$^{1/2}$ for the 2-SNT5 sample, and from 6.94 to 6.92 MPa m$^{1/2}$ for the 2-SNT7.5 sample. The

**Figure 10.** Typical back scattering electron micrographs on the polished surfaces of the representative samples: (a) 2-SNT0, (b) 2-SNT2, (c) 2-SNT5, (d) 2-SNT7.5 after further pressurized SPS at 1400°C for 5 min, which consist of the dark gray, bright white and white phase regions.
relatively low fracture toughness of 6.12 MPa m$^{1/2}$ for the 2-SNT0 sample after pressurized SPS may be because the sintering temperature is too low to obtain higher density for the sample due to its lower fluidability. This implies that the secondary phase TiC$_{0.3}$N$_{0.7}$ in the β-SiAlON matrix may increase the fluidability of the composite at high temperature. Consequently, pressureless SPS along with further pressurized SPS can fabricate β-SiAlON/TiC$_{0.3}$N$_{0.7}$ ceramic composites with excellent mechanical properties and meanwhile the reaction between the sample and the graphite mold can considerably be restrained.

4. Conclusions

The β-SiAlON/TiC$_{0.3}$N$_{0.7}$ ceramic composites with excellent mechanical properties have been fabricated by pressureless spark plasma sintering (SPS) at relatively low sintering temperatures. The mechanical properties of the composites can be further improved by a further SPS at 1400 °C for 5 min under a pressure of 24 MPa. This technique can avoid the oriented uniform stress distribution, caused by uniaxial pressure in normal pressurized SPS and simultaneously minimize the reaction between the sample and the graphite mold.

The formation of the liquid phase and the phase transformation of α to β-SiAlON occurs in the pressureless SPS process. The prepared β-SiAlON/TiC$_{0.3}$N$_{0.7}$ composites have an interlock microstructure formed by lath β-SiAlON grains with TiC$_{0.3}$N$_{0.7}$ particles dispersed uniformly in the matrix. The composite with 5 wt.% TiC$_{0.3}$N$_{0.7}$ exhibits a high density of 3.28 g cm$^{-3}$, high hardness of 14.53 GPa, and high fracture toughness of 7.20 MPa m$^{1/2}$. The high fracture toughness may mainly arise from the highly densified microstructures with the interlocking of the lath β-SiAlON grains and the uniformly distributed TiC$_{0.3}$N$_{0.7}$ particles, and the disappearance of the oriented uniform stress distribution caused by uniaxial pressure in normal pressurized SPS.

With a further SPS at 1400°C under a pressure of 24 MPa for 5 min, the fully dense β-SiAlON/TiC$_{0.3}$N$_{0.7}$ composites are obtained and their mechanical properties are somewhat enhanced. For the composite with 5 wt. % TiC$_{0.3}$N$_{0.7}$, the Vickers hardness is enhanced to 15.87 GPa and the fracture toughness to 7.44 MPa m$^{1/2}$. The present fracture toughness is well comparable with its publically available values. Therefore, the pressureless SPS may be a promising technique for the fabrication of the high-performance β-SiAlON matrix composites.

Disclosure statement

No potential conflict of interest was reported by the authors.

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