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The Effect of La-silicon Oxynitride on the Densification of Si_3N_4 Ceramics by Spark Plasma Sintering

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ABSTRACT

Silicon nitride-La-silicon oxynitride ceramics were fabricated by Spark Plasma Sintering (SPS). The density, crystalline phase and microstructure were compared with those obtained by Hot Pressing (HP). The full density was achieved within 40 min by spark plasma sintering at 1650 °C, whereas the same result was required by hot pressing with a dwell time of 500 min at higher temperature. There were some differences in the microstructure and second phases in the sintered ceramics, which are attributed to the rapid densification in the spark plasma sintering. The fine and acicular grain microstructure appeared in spark plasma sintering.

Key words : Spark plasma sintering, Hot pressing, Silicon nitride, Oxynitride, Densification, Microstructure

1. Introduction

Silicon nitride (Si_3N_4) contains a high degree of covalent bonding and does not decompose until 1880. Therefore, it is impossible to densify Si_3N_4 without sintering additives. Densification is achieved by liquid-phase sintering usually using metal oxides (MgO, Al_2O_3, Y_2O_3 etc.) as the sintering additives. These oxides react with SiO_2, which inherently exists at the surface of Si_3N_4 particles, to form an oxide melt at high temperature. With increasing temperature, an oxynitride melt is formed due to further dissolution of Si_3N_4. A problem associated with the use of the additives is the resultant degradation of high temperature properties of Si_3N_4 due to residual grain boundary glassy phase.[1,2] Several attempts to prevent the degradation in the high temperature properties have been reported.[3] These include the tailoring of the grain boundary glassy phases,[4-6] crystallizing the grain boundary glassy phases,[7] and using transient liquid phase sintering.[8,9]

Work performed by Lange *et al.*[10] on the Si_3N_4-SiO_2-Y_2O_3 system has shown that the high temperature properties of Si_3N_4 can be improved by choosing compositions in the Si_3N_4-Si_2N_2O-$Y_2Si_2O_7$ compatibility ternary system, since Si_2N_2O and $Y_2Si_2O_7$ phases are in equilibrium with SiO_2. On this basis, various rare earth oxides have been studied as potential sintering additives, since Si_3N_4-SiO_2-rare earth oxide systems would also exhibit good high temperature characteristics. It has been shown that rare earth oxides are as effective as Y_2O_3 in the densification of Si_3N_4.[7,11,12] Furthermore, refractory disilicate, $Re_2Si_2O_7$ (Re refers to the cation of a rare earth oxide), can be crystallized at grain boundaries, thereby resulting in improved high temperature properties.[7,13-15] These results make the Si_3N_4-$Re_2Si_2O_7$ system attractive for the high temperature application of Si_3N_4.

Recently, a Si_3N_4-$Yb_4Si_2N_2O_7$ system also has been investigated due to the superior stability of the $Yb_4Si_2N_2O_7$ phase at high temperature.[16,17] Other rare-earth oxides have similar phase relationship with the Si_3N_4-SiO_2-Yb_2O_3 system[7,10,18-20] and therefore, the Si_3N_4-$Re_4Si_2N_2O_7$ system could be considered as a candidate for high temperature application of Si_3N_4.[17,20-22]

Spark Plasma Sintering (SPS) is a new technique, which makes it possible to obtain fully dense ceramics due to rapid sintering process.[19-31] It is similar to Hot Pressing (HP). In the conventional hot pressing, the main driving forces promoting the densification are Joule heat and applied pressure; i.e., the sample is heated by an external source, which implies that the rate of densification is strongly dependent on the rate of heat transfer to the specimen located in a pressure die. Using this type of sintering equipment, it is almost impossible to prevent grain growth and to produce ceramic compacts consisting of submicrometer-sized or even nano-sized grains. On the other hand, in SPS, the heating is carried out by means of several thousands of DC pulse. The powder compacts are heated initially by spark discharge between particles. As a new compacting process, SPS can overcome these problems associated with HP.

The objective of this experiment is to investigate the difference in densification behavior between SPS and HP using the Si_3N_4-$La_2Si_2O_7$ and Si_3N_4-$La_4Si_2N_2O_7$ systems of the same batch.

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Table 1. Compositions of the Si_3N_4-$La_2Si_2O_7$ and Si_3N_4-$La_4Si_2N_2O_7$ Ceramics

Nomination	Composition (vol%)	Si_3N_4-SiO_2-La_2O_3 (mol%)
SNLa227	88 Si_3N_4-12 $La_2Si_2O_7$	84.4-11.2-5.4
SNLa4227	88 Si_3N_4-12 $La_4Si_2N_2O_7$	87.8-1.8-10.4

2. Experimental Procedure

Commercially available Si_3N_4 powder (SN-E10, Ube Industries, Tokyo, Japan) and the oxide additives were used for fabricating Si_3N_4 ceramics from the systems of Si_3N_4-$La_2Si_2O_7$ and Si_3N_4-$La_4Si_2N_2O_7$, which are called SNLa227 and SNLa4227, respectively, later in this work. The oxide additives were SiO_2 (99.9%, Arosil 200, Degussa Corp., NJ., USA) and La_2O_3 (99.9% Johnson Matthey, Seabrook, NH, USA). The SiO_2 content present on the surface of the Si_3N_4 particles was 2.6 wt% (3.1 vol%) according to the manufacturer's data. The total amount of the sintering additives was fixed to 12 vol%, as shown in Table 1. The powder mixture was milled in methanol for 24 hrs using Si_3N_4 grinding balls. The milled slurry was then dried and sieved for the Si_3N_4-$Re_2Si_2O_7$ and Si_3N_4-$Re_4Si_2N_2O_7$ sintering.

In both SPS and HP processing, the sample preparation procedure, such as the die setting, the powder loading into the graphite mold and the application of mechanical pressure, was almost same, as shown in Fig. 1. The additive effects on the densification of Si_3N_4 in SPS process were enhanced by both the mechanical pressure (P_m) and spark impact pressure (P_s). However only mechanical pressure was applied in the case of hot pressing process. The SPS processing (Dr Sinter 1050, Sumitomo Coal Mining Co. Ltd., Japan) was carried out in a vacuum (0.7×10^{-2} Pa) in the temperature range of 1500~1650°C for 5 min, as shown in Fig. 2. The heating was conducted by DC pulse (pulse duration=12 sec, 85.7% duty, 2000 A), which was applied through electrodes located on the top and bottom of the die punch. The temperature was monitored and controlled with

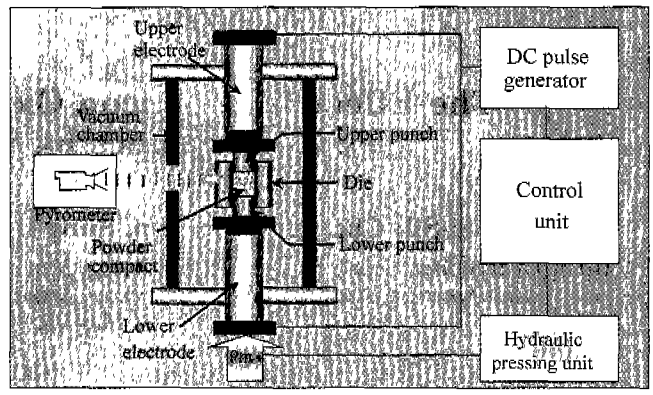

Fig. 2. Schematic diagram of spark plasma sintering apparatus.

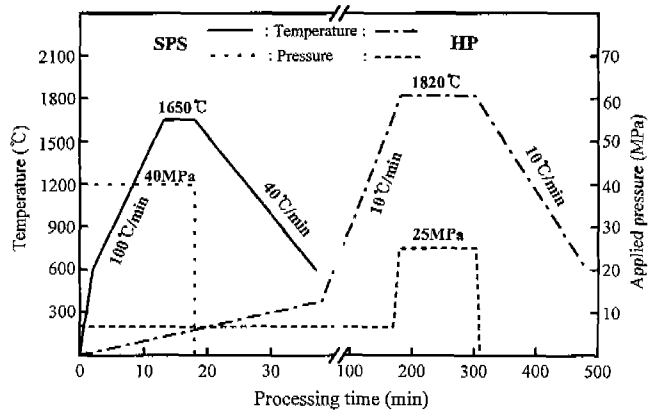

Fig. 3. Schematic showing the thermal and pressure schedules of spark plasma sintering and hot pressing.

an optical pyrometer focused on the surface of the graphite die. The mechanical pressure was applied at 40 MPa. The hot pressing (HP20-3560-FP20, Astro, U.S.A.) was carried out at 1820°C for 120 min with pressure of 25 MPa under nitrogen atmosphere.

Typical heating and pressing schedules of SPS and HP are shown in Fig. 3. SPS processing had 10 times faster heating

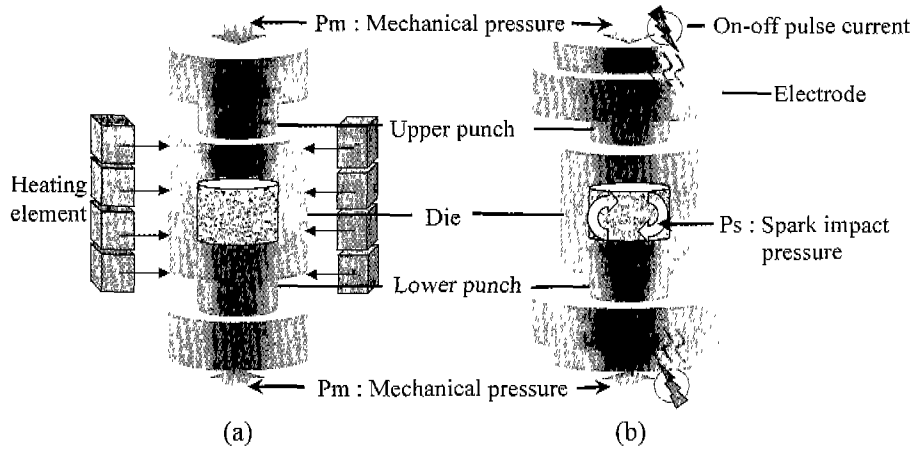

Fig. 1. Assisted effects on densification for pressure sintering : (a) external heating type of hot pressing and (b) internal heating type of spark plasma sintering.

rate (100°C/min) and shorter sintering time (5 min) compared to HP process (10°C/min and 120 min). The whole processing for SPS including heating, sintering and cooling was finished within 40 min, but it was lasted over 500 min for HP process. Mechanical pressure of 40 MPa for SPS was applied from the start of operation at room temperature to the end of sintering, and in the case of HP, the sample was first heated to 1000°C and then mechanical pressure of 25 MPa was applied.

Sample densities were measured using the Archimedes method. The theoretical densities of the specimens were calculated according to the rule of mixtures. Crystalline phases in the sintered specimens were determined by X-Ray Diffraction (XRD) using Co Kα radiation. The amounts of α- and β-Si_3N_4 phases were calculated from the fraction of the relative integrated intensities of 102(α) and 101(β) peaks using the method similar to that used by Perera. [36] The sintered specimens were cut, polished, and then plasma-etched by CF_4 containing 7.8% O_2. The microstructure was observed by Scanning Electron Microscopy (SEM).

3. Results and Discussion

Relative densities of silicon nitride ceramics are shown in Fig. 4. The relative density of 99.0% was obtained by spark plasma sintering after holding for 5 min at 1650 °C. However, in hot pressing, the equivalent value of relative density was achieved with longer time and higher temperature (for 120 min at 1820°C). It was found that spark plasma sintering had a greater effect on the densification of silicon nitride ceramics than hot-pressing. This is probably due to the factors such as self-heat generation by microscopic electric discharge between powder particles, activation of the particle surface, and high speed mass transfer, effectively exerting an influence on specimens. [23]

Table 2 contains the crystalline phases identified by X-ray diffraction. Both of α-, and β-phase of Si_3N_4 were detected as the major phases in the spark plasma sintered specimens, whereas only β-phase as a result of complete transformation from α to β-Si_3N_4 was seen in the hot-pressed materials. The

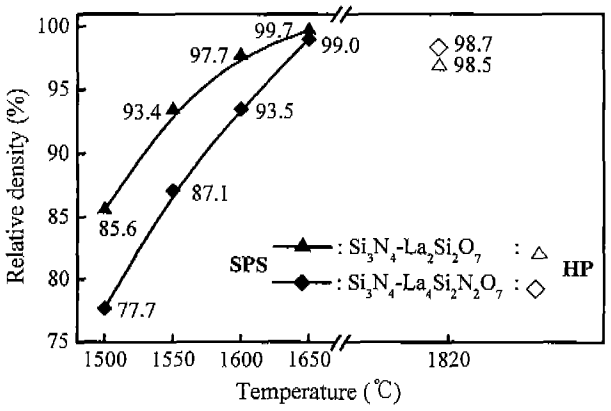

Fig. 4. Density variation with temperature of silicon nitride ceramics processed by SPS and HP.

Table 2. Crystalline Phase for SPS and HP Specimens by X-ray Diffraction Analysis

Nomination	Process and Temperature (°C)	Identified Crystalline Phase	
		α : β ratio of Si_3N_4	Re-silicon oxynitride*
SNLa227	SPS-1500	92 (α) : 8 (β)	Not detected
	SPS-1550	87 (α) : 13 (β)	"
	SPS-1600	62 (α) : 38 (β)	"
	SPS-1650	19 (α) : 81 (β)	"
	HP-1820	0 (α) : 100 (β)	$La_2Si_2O_7$
SNLa4227	SPS-1500	94 (α) : 6 (β)	$La_5(SiO_4)_3N$
	SPS-1550	86 (α) : 13 (β)	$La_5(SiO_4)_3N$
	SPS-1600	73 (α) : 27 (β)	$La_5(SiO_4)_3N$
	SPS-1650	53 (α) : 47 (β)	$La_4Si_2N_2O_7$, $La_5(SiO_4)_3N$
	HP-1820	0 (α) : 100 (β)	$La_5(SiO_4)_3N$

*Re-silicon oxynitride : Re refer to the cation of a rare earth oxide

difference in phase ratio of Si_3N_4 was attributed to the temperature and time dependent nature of the transformation. And there are differences in the formation of the minor phases between SPS and HP process.

For SNLa227 series, hot pressing resulted in the $La_2Si_2O_7$ phase, but the spark plasma sintering did not yield this phase. $La_2Si_2O_7$ as a second phase present at the Si_3N_4 grain pockets or along the two-grain boundaries is common in hot-pressed Si_3N_4. [7,10,15,21] The rate of cooling in SPS is much faster than HP, accounting for the absence of $La_2Si_2O_7$ phase under SPS.

For SNLa4227 series, $La_5(SiO_4)_3N$ phase was formed in hot pressing, whereas $La_4Si_2N_2O_7$ phase, besides $La_5(SiO_4)_3N$ phase, was found in spark plasma sintering. The heating/cooling rates and reaction temperature/time, i.e. short processing time with low temperature, may be responsible for this. Although $Yb_4Si_2N_2O_7$ was found in Si_3N_4, [16,17] it is known that $La_4Si_2N_2O_7$, $Y_4Si_2N_2O_7$ or $Er_4Si_2N_2O_7$ phase cannot coexist with Si_3N_4. [10,22] Mitomo *et al.* [37] reported the

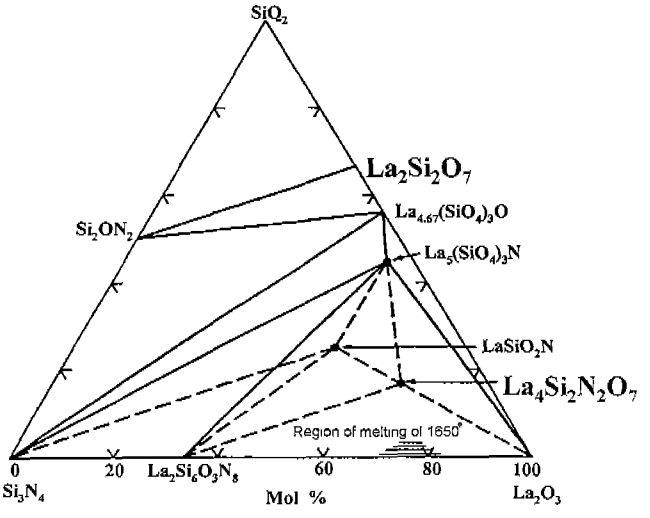

Fig. 5. Phase diagram of Si_3N_4-La_2O_3-SiO_2 system at 1700°C. The dashed lines represent compatibility at 1550°C. [33]

phase relationships in the system Si_3N_4-SiO_2-La_2O_3 at 1700 °C, as shown in Fig. 5. Because the relationships were obtained using specimens cooled to room temperature, Fig. 5 is not a true equilibrium diagram at 1700°C. Solid lines show compatibility at 1700°C and dashed lines represent compatibilities at 1550°C. The $La_4Si_2N_2O_7$ was found to be dissociated to $La_5(SiO_4)_3N$ phase and a glass easily after cooling from 1700°C. It is expect that some of $La_4Si_2N_2O_7$ was not dissociated to $La_5(SiO_4)_3N$ and glass in the fast cooling process of SPS, but that was almost dissociated in the

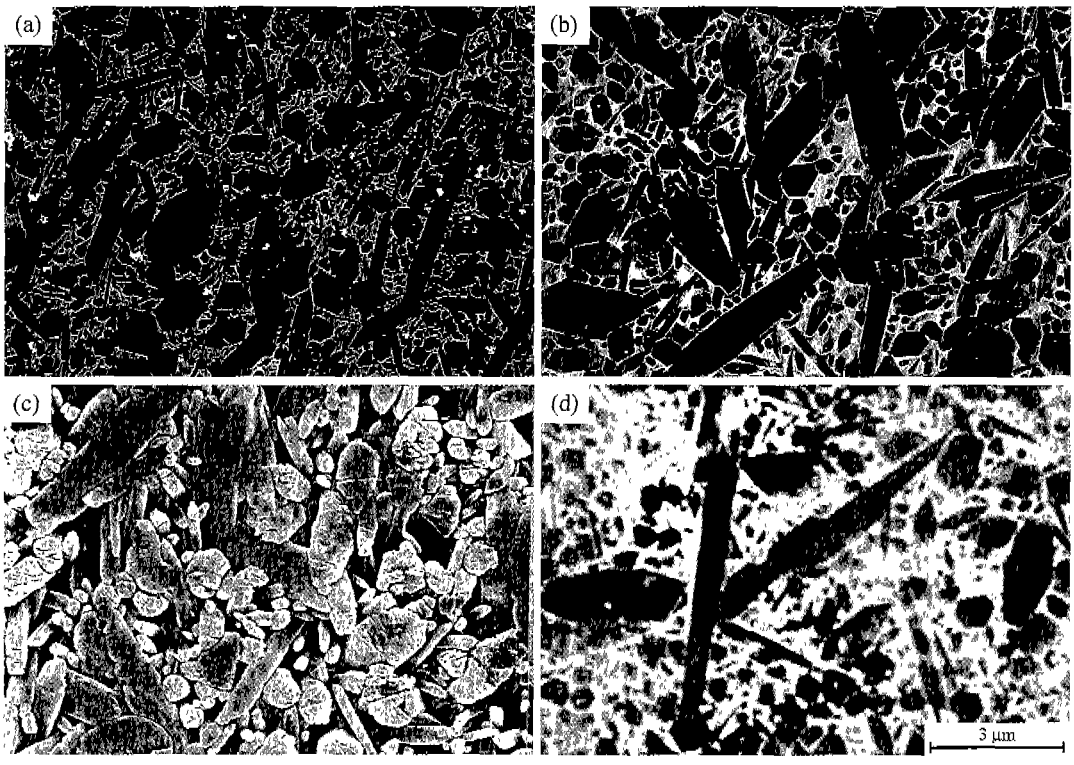

Fig. 6. SEM microstructures of silicon nitride ceramics : (a) SNLa227, (b) SNLa4227 prepared by SPS at 1650°C and (c) SNLa227, (d) SNLa4227 prepared by HP at 1820°C.

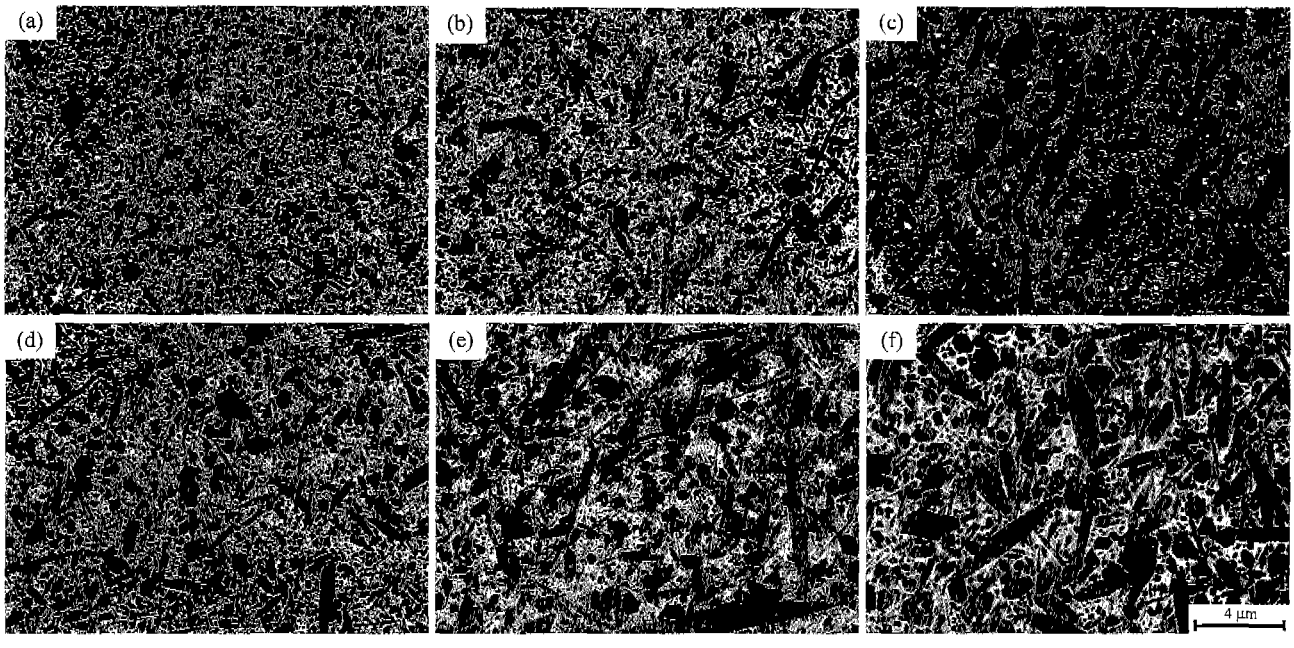

Fig. 7. SEM microstructures of silicon nitride ceramics processed by spark plasma sintering: SNLa227 sintered at (a) 1500°C, (b) 1600°C, (c) 1650°C and SNLa4227 sintered at (d) 1500°C, (e) 1600°C, (f) 1650°C.

slow cooling HP process.

The microstructure of Si_3N_4 ceramics prepared by both SPS and HP were similar, as shown in Fig. 6. The elongated β-Si_3N_4 grains in fine matrix grains were observed in both SPS and HP processing in spite of different sintering histories. SNLa4227 and SNLa227 compositions appear to be particularly effective in promoting the fine acicular microstructure because the radius of La^{3+} is larger than those of other lanthanide oxides(Y^{3+}, Yb^{3+}, Er^{3+}).[15,21,22] The elongated grains with the composition SNLa4227 are larger and longer than those with the composition SNLa227. And the size of fine matrix grains in the composition SNLa4227 is much greater than in the composition SNLa227. As a result, the mean grain size for the composition SNLa4227 is larger than that for the composition SNLa227. This result is consistent with the findings by Hirao *et al.*[38] and Kitayama *et al.*[39] that extensive grain growth of β-Si_3N_4 was observed when an amount of Y_2O_3 additive exceeded SiO_2 amount. Because the phase relationship of Si_3N_4-La_2O_3-SiO_2 system is similar to that of Si_3N_4-Y_2O_3-SiO_2, it is expected that their grain growth behaviors are also similar. An important aspect drawn from the relationships in the Si_3N_4-SiO_2-La_2O_3 system, as shown in Fig. 5, is that the solubility of Si_3N_4 in the liquid phase with the SNLa4227 composition is much larger than that with the SNLa227 composition at both temperatures.

4. Summary

The results show that spark plasma sintering can rapidly sinter silicon nitride-La-silicon oxynitride ceramics to high density. For example, full density was achieved within 40 min by heating to 1650°C for 5 min, whereas the same result was required by hot pressing with a dwell time of 500 min at higher temperature. There were some differences in the Si_3N_4 and second phases detected in the sintered ceramics, which are attributed to the faster processing in the spark plasma sintering. The finer and acicular grain microstructure appeared in spark plasma sintering.

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