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# Low-temperature spark plasma sintering of calcium stabilized alpha sialon using nano-size aluminum nitride precursor



REFRACTORY METALS & HARD MATERIALS

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## ABSTRACT

Calcium stabilized alpha-sialon ceramic was synthesized using spark plasma sintering (SPS). The size effect of aluminum nitride precursor (1 µm and 50 nm) on the phase analysis, microstructural and mechanical characteristics of the processed sialon was studied. Alongside the size of AlN precursor, holding time and sintering temperature were also varied in order to assess the degree of densification, phase transformation and its subsequent effect on the mechanical properties of these materials. The development of alpha phase was found to be strongly dependent on the particle size of the aluminum nitride (AlN) precursor. Interestingly, this novel approach of changing particle size from micro to nano-level combined with the SPS process resulted in the formation of alpha-sialon ceramic at much lower than previously reported sintering temperature i.e. 1500 °C as compared to 1700/1800 °C. Surface oxide layer associated with AlN particles resulted in the formation of additional beta phase along with major alpha phase in the final product. The sialon product synthesized from micron-size AlN particles (1 µm) at a sintering temperature of 1500 °C exhibited Vickers hardness value HV10, of 18 GPa and moderate fracture toughness of 5.6 MPa vm. However, sialon materials synthesized from nano-size AlN particles (50 nm) showed a hardness value of 14 GPa while displaying an improved fracture toughness of 7 MPa vm. Increase in holding time resulted in a slight increase in densification of these materials, however its influence on mechanical properties was less significant as compared to the effect of particle size of aluminum nitride staring powder precursor.

#### 1. Introduction

Ceramics have been long known as ideal materials that can withstand extreme operating conditions such as high temperature, loads and wear. Silicon nitride is an example of a ceramic that exhibits exceptional thermal and mechanical properties [1]. However, the strong covalent nature of its bonds, makes it difficult to achieve completely densified silicon nitride materials. While very high temperatures have been used to help achieve completely densified silicon nitride materials [2], performing operations at such high temperatures and carrying out sintering for necessarily long periods of time present practical complexities. In order to avoid these problems and to synthesize completely dense silicon nitride materials at lower temperatures, metal oxide additives have been used as densifying agents [1–3]. This modification resulted in the formation of sialon materials [4–6].

Sialon materials, which are solid solutions of silicon nitride, form generally two main phases, alpha sialon and beta sialon, which have different microstructure and crystal structure and thermo-mechanical characteristics. Beta sialon is formed by concurrent identical replacement of silicon by aluminum and nitrogen by oxygen. Its chemical formula has been commonly defined as  $Si_{6-z}Al_zO_zN_{8-z}$ . The chemical formula of the alpha-sialon, which embraces four units of  $Si_3N_4$ , is generally described by  $M_x^vSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$  where x < 2, x = mv, and m (Al–N) bonds and n (Al–O) replace (m + n) (Si–N) bonds [4,6–8]. Alpha and beta sialon have been intensely investigated in the course of the last couple of decades because of their outstanding mechanical properties, explicitly the better fracture toughness due to elongated morphology of beta phase and the high hardness of alpha phase [9,10].

Higher hardness as well as better sinterability of sialon materials in comparison to silicon nitride make them a desirable candidate material for cutting tools [11–13]. Company named CeramTec provides special tool materials composed of alpha/beta sialons specifically for boring, turning and milling of cast iron in interrupted along with uninterrupted machining mode [14].

Although rare-earth metallic ions have been used as stabilizers in

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the synthesis of sialons for decades, the higher solubility of calcium oxide as well as its relative stability have recently made it a preferred additive [15–20]. Moreover, the greater availability of Ca-based compounds, and hence their lower costs, make them advantageous as sintering aids [21,22]. A study by Wang et al. on phase formation of calcium alpha-sialons at 1750 °C using hot pressing technique concluded that maximum calcium content in alpha-sialons is about 70% of x value in  $M_x$  [23]. Conventional sintering techniques in combination with micron sized precursors require long sintering duration as well as a temperature > 1700 °C for the synthesis of well densified Ca-sialons [24–26]. SPS is a powder sintering process, which has gained focus in the consolidation of powder materials due to its novel pulsed-current-based heating allowing higher heating rate and short synthesis duration [27,28].

In the present work, we used SPS sintering technique and we studied the effect of AlN precursor powder size (1  $\mu$ m versus 50 nm), on the formation of calcium alpha-sialon phase at a low sintering temperature of 1500 °C. We used precursors in amounts that typically form Ca-stabilized alpha sialon. We also studied the effect of holding time during sintering on the mechanical properties of the produced sialon ceramics.

### 2. Experimental procedure

The alpha sialon having the chemical formula  $\text{Ca}_{0.8}\text{Si}_{9.2}\text{Al}_{2.8}\text{O}_{1.2}\text{N}_{14.8}$  was selected for the synthesis. This formula corresponds to m value of 1.6 and n value of 1.2 in the chemical formula of alpha sialons indicated above. Precursors employed for this synthesis included alpha-Si<sub>3</sub>N<sub>4</sub> with a particle size of  $\sim$  300 nm (Ube Industries, Japan), SiO<sub>2</sub> with a particle size of  $\sim$  20 nm (Sigma Aldrich, Germany), AlN with particle sizes shown in Table 1 (Sigma Aldrich, Germany) and CaO with a particle size  $\sim 160$  nm (Aldrich, Germany). These precursors were processed via SPS at sintering temperatures of 1400 °C and 1500 °C with holding times of 10, 20 and 30 min and uniaxial pressure of 50 MPa. Classification based upon size of initial powder mixture as well as that on processing conditions is summarized in the Table 1. The sample ID used in Table 1 and the rest of the manuscript starts with the numeric digit '5', which represents the alpha sialon composition dictated by the "m" and "n" values used, followed by the sintering temperature, holding time and aluminum nitride particle size. For instance an alpha sialon sample having the composition of  $Ca_{0.8}Si_{9.2}Al_{2.8}O_{1.2}N_{14.8}$  (m = 1.6, n = 1.2) sintered at 1500 °C with 30 min of holding using 50 nm AlN starting powder precursor is named as 5-15003050.

The masses of the various precursors were chosen to satisfy the target Ca<sub>0.8</sub>Si<sub>9.2</sub>Al<sub>2.8</sub>O<sub>1.2</sub>N<sub>14.8</sub> formula for the product and for each product to have a total mass of 5 g. These weighed out precursors were homogenously mixed for 30 min, using ethanol as a sonicating medium in an ultrasonic probe-sonicator. Furthermore, the sonicated powder mixture was desiccated at 80 °C for 24 h. to remove ethanol.

These sonicated powder mixtures were sintered into 20 mm diameter pellet using the consolidation temperatures and holding times

#### Table 1

Sets of conditions used to synthesize the sialon ceramics. In all cases, a constant cooling rate in the range of 200  $^\circ C$  was used.

S/no.	Sample ID	Sintering temp (°C)	Holding time (min)	AlN particle size
1	5-15001050	1500	10	50 nm
2	5-15002050	1500	20	50 nm
3	5-15003050	1500	30	50 nm
4	5-1500101	1500	10	1 µm
5	5-1500201	1500	20	1 µm
6	5-1500301	1500	30	1 µm
7	5-14003050	1400	30	50 nm
8	5-1400301	1400	30	1 μm

listed in Table 1, and by applying a uniaxial pressure of 50 MPa. The heating rate used for the synthesis was 100  $^{\circ}$ C/min. The samples were then quickly brought back to the room temperature within 5 min.

The sintered samples were then cleaned of graphite, mounted, and ground and polished using diamond disks. Phase identification analysis was performed using X-ray diffractometer (Rigaku MiniFlex, Japan) with Cu K $\alpha$ 1 radiation ( $\gamma$  = 0.15416 nm). The accelerating voltage of 30 kV and tube current of 10 mA was maintained during the entire scan. The software UnitCellWin was used to calculate the lattice parameters. Field emission scanning electron microscope (FESEM, Lyra 3, Tescan, Czech Republic) with an accelerating voltage of 20 kV was used for microstructural studies. Densities of the sintered disks (after removal of graphite) was calculated using Archimedes' principle. Vickers hardness (HV<sub>10</sub>) was measured on the surface of the polished samples by means of a universal hardness testing machine (Zwick-Roell, ZHU250, Germany). The indentation load of 10 kg was adopted for the hardness test. Indentation technique was employed to calculate the fracture toughness (K<sub>1c</sub>) of the prepared ceramic samples [27–29].

#### 3. Results and discussion

#### 3.1. Powder mixture and densification

To prepare a homogenous powder distribution, the starting precursors ( $Si_3N_4$ ,  $SiO_2$ , AlN, CaO) were mixed for 30 min in ethanol using ultrasonic probe-sonicator. The EDXS mapping performed on the powder mixture (using elemental mapping for Si, Al, Ca, O, N) did not reveal agglomeration as the elemental distribution was fairly homogenous, as depicted in Fig. 1.

Table 2 shows the density values of the Ca-sialons synthesized from aluminum nitride particle sizes of 1  $\mu$ m and 50 nm for various holding times at the relatively lower sintering temperatures of 1400 °C and 1500 °C. The alpha sialon sample 5-1500301 showed the highest density of 3.15 g/cm<sup>3</sup>. The increase in density value was prominent when the holding time was increased from 10 to 20 min for the sialon sample synthesized from the aluminum nitride precursor with a particle size of 1  $\mu$ m. This increase was primarily due to creation of more amount of liquid phase with the increased holding time for the sample having aluminum nitride of larger particle size. The comparatively lower density value for the samples synthesized from aluminum nitride with a particle size of 50 nm was due to the substantial nucleation and growth of beta-sialon crystals at the expense of a significant amount of liquid phase during the synthesis process.

In contrast to the samples sintered at 1500 °C, sialon material sintered at 1400 °C, from aluminum nitride with particle size of 1  $\mu$ m (5-1400301), relatively poor densification, with density values of 2.89 g/ cm<sup>3</sup> was observed. However, the sample synthesized from aluminum nitride with a particle size of 50 nm (5-14003050) displayed a density of 3.00 g/cm<sup>3</sup>, suggestive of the high reactivity of AlN and hence the creation of a sufficient quantity of the oxi-nitride liquid even at a temperature of 1400 °C. This observation is in line with the large surface area associated with a nano-sized powder acting as the driving mechanism for sintering [30].

It was observed that with the increase in sintering temperature from 1400 °C to 1500 °C there was an obvious increase in shrinkage primarily due to dissolution of nitride precursors and formation of oxinitride liquid phase (1298 °C) followed by precipitation (1480 °C) of sialon phase (Fig. 2a & b). A similar sort of behavior was observed by J. D. Bolton & A. J. Gant for the ceramic reinforced high speed steel metal matrix composites, where the densification was seen to increase as sintering temperature surpassed the solidus temperature [31]. However, in our case the shrinkage rate became independent of time after an approximate holding time of 10 min (due to high heating rate). Another aspect worth noting is that the shrinkage rate was higher for the samples synthesized from nano-sized AlN, due to the higher reactivity of the nano-sized particles. The relatively lesser shrinkage for the micron-

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