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A comparison of sintering techniques using different particle sized β-SiAlON powders

Onur Eser [a], Semra Kurama [b,*]

[a] Graduate Department of Advanced Technologies, Anadolu University, Eskisehir, Turkey
[b] Department of Materials Science and Engineering, Anadolu University, Eskisehir 26555, Turkey

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Abstract

In the present study sintering behavior and mechanical properties of β-SiAlON ceramics were investigated using different sintering techniques (gas pressured sintering (GPS), pressureless sintering and spark plasma sintering (SPS)) and different particle sized powders (with D_{BET} 216 and 130 nm). After sintering of the microstructure and phase characterization were carried out using a scanning electron microscope (SEM) and the X-ray diffraction (XRD) method, respectively. All the samples, prepared using fine powder, were sintered at lower temperatures than samples prepared by conventional powder, by two sintering techniques (GPS and pressureless). Additionally, the results showed that cooling rates had an important effect on the formation and the amount of intermediate phase in the sample. As a result, it was shown that the particle size of starting raw materials, the amount of additive, the sintering temperature and the technique had a significant effect on the microstructure and mechanical properties of the SiAlON samples.

Keywords: SiAlON; Sintering; Mechanical properties; Milling; Particle size

1. Introduction

Silicon nitride (Si_3N_4) and its solid solutions have attracted intensive attention because of their excellent mechanical properties, such as strength, fracture toughness and hardness. SiAlONs are Si_3N_4 based solid solutions with various structures, such as α-, β-, O- and X-SiAlON. The β-SiAlON phase is a derivative of β-Si_3N_4, formed due to the simultaneous replacement of Al and O with Si and N elements. The general formula of β-SiAlON is $Si_{6-z}Al_zO_zN_{8-z}$, where z ranges from 0 to 4.2. The β-SiAlON phase has more oxide additives than α-SiAlON and, because of this, β-SiAlON has a lower sintering temperature and elongated grains. There should be a sufficient liquid phase to obtain fully dense SiAlON ceramics. However, Al_2O_3 alone cannot supply this sufficient liquid phase. Therefore, additional metal (Y, Mg, etc.) and rare earth oxides (Yb, Nd, Sm, etc.) are used as sintering additives to promote densification through the liquid phase sintering.

Pressureless, gas pressuring (GPS), hot pressing (HP), hot isostatic pressing (HIP) and spark plasma sintering (SPS) are the common sintering techniques used in the production of SiAlON ceramics. Pressureless sintering, which allows complicated shapes to be mass produced economically, is a most attractive fabrication process for SiAlONs.[1] However, this technique requires a longer dwell time at the target temperature and sometimes the temperature is insufficient to obtain high density in compositions with less additives due to an absence of pressure. Also, higher temperatures without pressure assist may result in the decomposition of nitrides. The GPS technique is another industrial method for the mass production of SiAlON ceramics through the use of nitrogen pressure up to 20 MPa. However, nitrogen consumption makes this method more expensive compared to pressureless sintering.[2] The SPS technique is very similar to conventional hot pressing. Instead of an external heating source, the raw powders are heated from inside and outside in the SPS using of a pulsed, direct current passing through the electrically conducting pressure die and also through the sample.[3,4] SPS is a rapid densification technique that promotes neck growth between particles, thereby efficiently increasing the sinterability of particles.[5] The main advantage of this technique is full densification at relatively lower temperatures within minutes. However, limited production and the impossibility of

* Corresponding author. Tel.: +90 222 321 3550 ext 6346; fax: +90 222 323 9501.
E-mail addresses: skurama@anadolu.edu.tr, semra.kurama@gmail.com (S. Kurama).

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producing complex shapes make this technique unsuitable for mass production.

In the present work the aim was to find sintering behavior, mechanical properties (hardness and fracture toughness) and microstructural differences among β-SiAlON samples sintered by pressureless, GPS and SPS techniques. Also, we investigated the effect of the particle size of starting raw materials on these sintering techniques.

2. Experimental procedure

The β-SiAlON composition, $Si_{6-z}Al_zO_zN_{8-z}$, where the z value is 2, is prepared from a mixture of Si_3N_4 (UBE-10, containing 1.6% oxygen), AlN (Tokuyama, containing 1% oxygen), Al_2O_3 (99.99%, Sumitomo AES IIC) and Y_2O_3 (99.99% HC Starck) doped with different amounts of (3.5 and 5 wt.%) Y_2O_3. The conventional powder denoted as Y-5, contained 5 wt.% Y_2O_3 and was prepared by ball milling (Pulverisette 6 Fritsch, Germany) in isoproponal alcohol for 1,5 h at 300 rpm using the Si_3N_4 balls inball to powder ratio of 1:1,5. The contamination caused by the milling balls and/or vial was calculated by weighting them before and after the milling process. The results showed that during milling process weight loss of balls about 0.0036 wt.% and so that the wearing of balls can be ignored. In the high energy milling process the ball to powder ratio was determined as 12:1 according to the filling of 10 vol.% suspension in a closed packed system of Si_3N_4 balls (of 5 mm radius and 9 mm length). The milling studies for this mixture were carried out at 450 rpm for 5 h. The mixture doped with 3.5 wt. % Y_2O_3 and sample is denoted as Y-3.5.

The particle size of the prepared powders Y-5 and Y-3.5 was measured using the BET method. According to the results of this analysis D_{BET} of Y-5, prepared by the conventional method, and Y-3.5, prepared with the high energy milling method, the powders were calculated as 216 and 130 nm, respectively.

The sintering of the samples was carried out using three different techniques (GPS, pressureless and SPS). The dried powders were pressed into pellets of 15 mm diameter and 4–5 mm in thickness using uniaxially pressing at 1.96 MPa and then by cold isostatic press (CIP) under 250 MPa, before pressureless and gas pressured sintering.

The gas pressure sintering experiments were performed using a gas pressure sintering furnace FPW 180/250-2-220-100PS (FCT GmbH, Germany) in a nitrogen atmosphere (2.2 MPa) at different temperatures between 1675–1825 °C for 1 h. The heating and cooling rates were approximately 10 °C/min. The samples were heated up to 150 °C lower temperature than target temperature under atmospheric nitrogen pressure. The pressure was increased at 0.5 MPa and samples were kept under this pressure about 30 min. (pore closing process). After that pressure and temperature increased to 2.2 MPa and target temperature, respectively.

The pressureless sintering experiments were performed using a graphite resistance furnace (Thermal Technology Inc.) in an N_2 atmosphere at different temperatures between 1750–1850 °C for 1 h. During the sintering, the heating and cooling rates were 10 °C/min and 60 °C/min, respectively.

For sintering using the spark plasma sintering technique a 4 g powder mixture was used. The powders were put into a 20 mm diameter graphite die and sintered using a spark plasma sintering system (FCT GmbH, Germany) under vacuum with a uniaxial pressure of 30 MPa. In order to prevent sticking, due to the reaction of the powders with the graphite die, graphite foil was placed between the powders and the die. The samples were sintered at different temperatures ranges (from 1450 to 1550 °C) and the sample was kept for 5 min at the maximum temperature and the furnace was cooled at a 100 °C/min. cooling rate.

The densities of the sintered samples were measured by the Archimedes method in distilled water. The phase composition of the sintered samples was analyzed using the X-ray diffraction method (Rigaku Rint 2200). The microstructure of the sintered samples was characterized by scanning electron microscopy (Zeiss, Evo 50). The hardness and fracture toughness of the samples were determined using the Vickers indentation method with a load of 10 N for duration of 10 s on a polished surface.

3. Results and discussion

3.1. Gas pressured sintering

Fig. 1 shows the effect of the sintering temperature on the densities of the samples, sintered by the GPS technique. Although sample Y-3.5 has a lower amount of additives (wt.% 3.5 Y_2O_3) than sample Y-5 (wt.% 5 Y_2O_3), it had theoretically densified at 1725 °C, whereas Y-5 reached an almost theoretical density (99.4%) at 1825 °C. It is obvious that decrease of particle size of the raw materials from 216 nm (D_{BET}) to 130 nm (D_{BET}) has a significant effect on the sintering temperature due to its high specific surface area which is a driving force for easy densification. According to the XRD results, β-SiAlON as a dominant phase and 12H polytype as a secondary phase were observed in both samples. It is well known that a slow cooling rate leads to partial crystallization of the grain boundary glassy phase. Therefore, the formation of the 12H polytype can be related to a slow cooling rate (10 °C/min) in GPS. Fig. 2 shows the microstructures of the Y-5 and Y-3.5 samples sintered at 1825 °C and 1725 °C, respec-

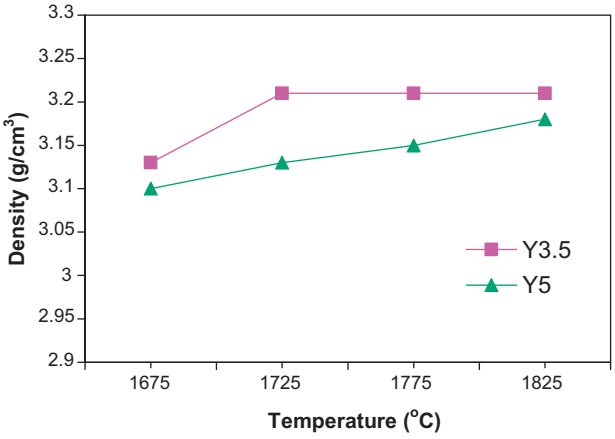

Fig. 1. Relationship between sintering temperature and density of samples sintered by GPS.

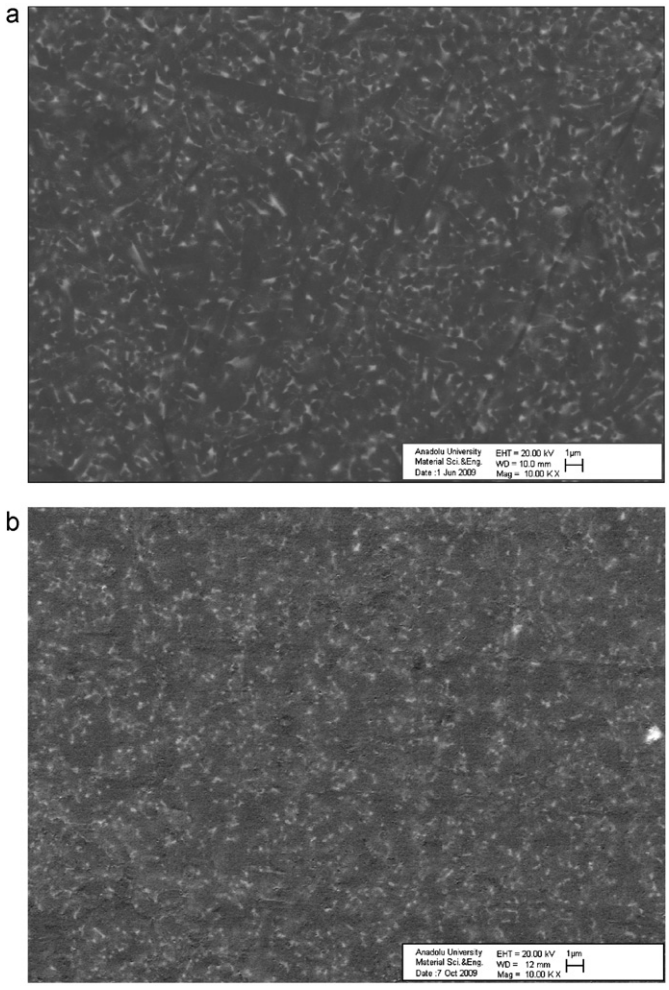

Fig. 2. SEM micrographs of (a) sample Y-5 gas pressure sintered at 1825 °C; (b) sample Y-3.5 gas pressure sintered at 1725 °C.

tively. Sample Y-5 has coarser and longer β-SiAlON grains than Y-3.5. The results show that decrease of particle size (130 nm) of the raw materials promoted a decrease in the sintering temperature (about 100 °C), the amount of additive and the grain size (Fig. 2(b)). Therefore, such an alteration in grain morphology could change the mechanical properties which will be discussed later.

3.2. Pressureless sintering

The effect of the sintering temperature on the densities of the samples, sintered by the pressureless sintering technique, is given in Fig. 3. Sample Y-3.5 reached an almost theoretical density (~99.1%) at 1775 °C whereas Y-5 had not fully densified (~96.6%) at 1850 °C. The results show that pressureless sintering is insufficient for the sintering of conventional powders (216 nm). However, it is possible to produce fully densified β-SiAlON ceramics by decreasing the particle size of the starting raw materials from 216 nm to 130 nm using a high energy milling method and an optimum medium.[6–8] The XRD results show that low amounts of 12H polytype phase, which formed during cooling, was observed. The amount of 12H polytype was

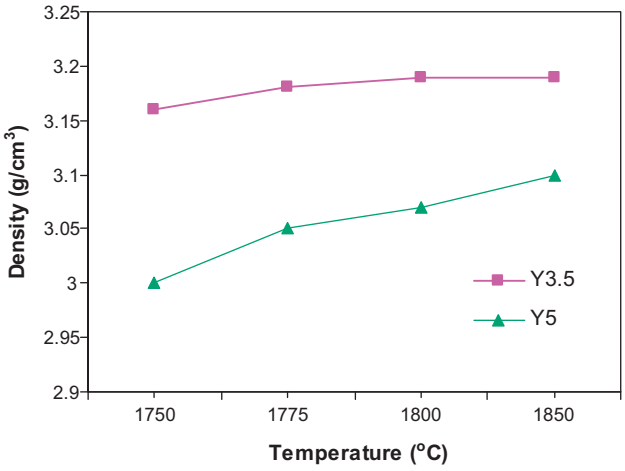

Fig. 3. Relationship between sintering temperature and density of samples sintered by pressureless sintering.

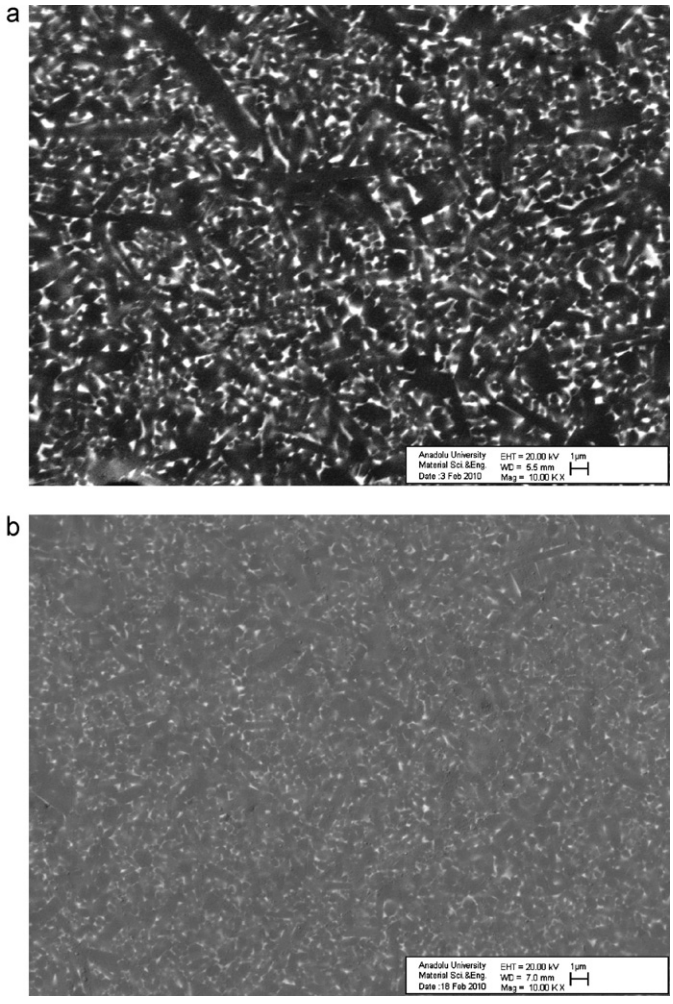

Fig. 4. SEM micrographs of (a) sample Y-5 pressureless sintered at 1850 °C; (b) sample Y-3.5 pressureless sintered at 1775 °C.

Table 1
Density, phase ratios and amount of Si of samples according to the SPS temperature.

Sample	Sintering temperature (°C)	Density (%)	Phase ratios (α:β)	Amount of Si (%)
Y5	1450	73	–	–
Y3.5	1450	75	–	–
Y5	1500	100	–	15
Y3.5	1500	100	–	20
Y5	1550	100	–	–
Y3.5	1550	100	–	–
Y5	1600	100	15:85	–
Y3.5	1600	100	10:90	–

lower than those produced by GPS. The reason is related with cooling rates (60 °C/min).

The SEM micrographs of the Y-5 and Y-3.5 samples are given in Fig. 4, sintered at 1850 °C and 1775 °C, respectively. Although the heating rate of both sintering techniques (pressureless and GPS) was the same (10 °C/min), the grain size of the pressureless sintered samples was higher and more elongated than the other. This means that gas pressure assist hinders grain growth.

3.3. Spark plasma sintering

Table 1 shows changes in the density and the phase ratios according to sintering temperature for the SPS samples. It is clear that decreasing the particle size of raw materials from 216 nm to 130 nm has no significant effect on the density of the samples (unlike GPS and pressureless). It was observed that by decreasing the sintering temperature below 1500 °C the density of both samples (Y-3.5 and Y-5) also decreases. This is directly related with an absence of liquid phase which will be formed by Y_2O_3/Al_2O_3 close to 1500 °C. Thus, smaller particle sized Y_2O_3 and/or Al_2O_3 starting powders should be used to form a liquid phase at lower temperatures. Another important point is the presence of Si in the samples sintered at 1500 °C. Salamon et al.[4] report that an absence of silicon indicates that during the sintering process, the SiAlON formation is faster than the decomposition of Si_3N_4 and/or any formed free silicon immediately reacts the with carbon source to form SiC. Thus, an absence of silicon over 1500 °C is related with the SiAlON formation rate. Additionally, the content of β-SiAlON increased with an increased sintering temperature, as α-Si_3N_4 converted to β-SiAlON in the presence of oxynitride liquid phase above 1400 °C.[9] Fig. 5 shows the SPS samples sintered at 1550 °C. It is well known that the grain size after sintering with SPS will be

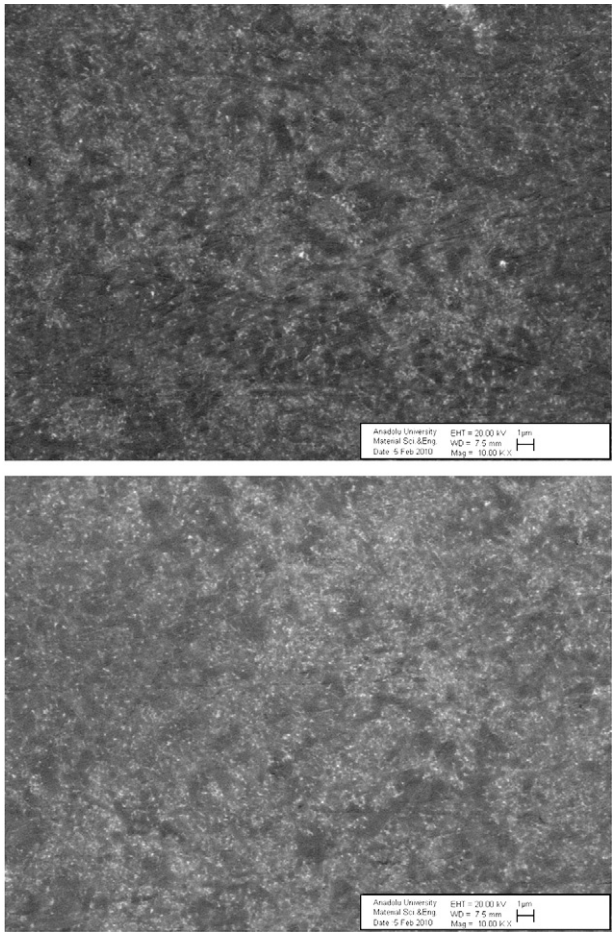

Fig. 5. SEM micrographs of (a) sample Y-5 spark plasma sintered at 1550 °C; (b) sample Y-3.5 spark plasma sintered at 1550 °C.

Table 2
Density and mechanical properties of samples sintered by various sintering techniques at different temperatures.

Sintering technique	Sample	Sintering temperature (°C)	Density (%)	Fracture toughness (MPa m$^{1/2}$)	Hardness (HV10)
GPS	Y5	1825	99.4	6.4 ± 0.4	14.2 ± 0.1
	Y3.5	1725	100	4.4 ± 0.3	16.5 ± 0.3
Pressureless	Y5	1850	96.6	5.7 ± 0.21	12.6 ± 0.16
	Y3.5	1775	99.4	5.8 ± 0.07	15.6 ± 0.1
SPS	Y5	1550	100	5.7 ± 0.05	15.8 ± 0.7
	Y3.5	1550	100	4.8 ± 0.05	16.7 ± 0.5

smaller when compared to other sintering techniques (pressureless and GPS) due to a high heating rate and a short sintering time. Although the particle sizes of starting raw materials were different for samples Y-5 and Y-3.5, it is very difficult to see any difference in grain size of both samples, unlike in GPS and pressureless sintering.

3.4. Mechanical properties

Table 2 gives the mechanical properties (hardness and fracture toughness) of densified samples sintered by various techniques. Although the spark plasma sintered samples fully densified at 1500 °C, because of the presence of silicon which could affect the mechanical properties samples sintered at 1550 °C were chosen for comparison.

When the sintering results are reviewed, the highest aspect ratio is observed in samples sintered by the pressureless sintering technique (Fig. 4). If we review the mechanical properties of these samples, it is clear that the toughness of the Y-5 samples, prepared as a reference, is the same as the sample Y-3.5 which has more fine elongated grains. However the reason for the low hardness of sample Y-5 is related to the use of a large amount of additive (5 wt.% Y_2O_3). This excess resulted with in a more amorphous grain boundary phase in the sample.

The second sintering technique in which elongated grains are observed is GPS (Fig. 2). However, the toughness of the sample Y-3.5, sintered by GPS under 2.2 MPa nitrogen gas pressure is the lowest of all the Y-3.5 samples, sintered using the other sintering techniques, (SPS and pressureless) due to the applied gas pressure and a decrease in the amount of additive (3.5 wt. Y_2O_3). On the other hand, the hardness value of the sample is almost the same as the others (sintered by pressureless and SPS).

The last sintering technique is SPS and both samples (Y-3.5 and Y-5) have very fine elongated grain morphology with a low aspect ratio (Fig. 5). The SPS sintered samples Y-3.5 and Y-5 have some amount of the α-SiAlON phase in their composition, at 30% and 40%, respectively. Although the sample Y-3.5 has a low amount of this phase during the sintering process an insufficient liquid phase hinders the formation of elongated grains with a high aspect ratio. This result clearly supports the lower toughness of sample Y-3.5 compared to sample Y-5.

4. Conclusion

In this study it was observed that a decrease of sintering temperature (for dense materials) is possible using a low particle size of the starting raw materials (130 nm). This result was investigated for both sintering methods, pressureless and GPS, but not SPS. Additionally, it is shown that without using high amounts of additive, it is possible to sinter β-SiAlON ceramics ($z = 2$) using high energy milled powders by pressureless sintering.

The particle size of starting raw materials, low amounts of additive and low sintering temperatures resulted in finer and equiaxed grains and decreased the fracture toughness of the samples. However, the use of low amounts of additive increases the hardness of these ceramics related to low amounts of the amorphous grain boundary phase. Additionally, the effect of cooling rates on sintering was investigated. By using different sintering techniques, GPS, pressureless and SPS, the cooling rate changes were 10, 60 and 100 °C/min, respectively. The sintering results show that by decreasing the cooling rate, some intermediate phase (12H) in samples sintered by GPS and pressureless sintering techniques is observed. To avoid the formation of an intermediate phase, the cooling rate should be increased (such as ∼100 °C/min). As a consequence, when smaller particle sized powders were used, pressureless sintering could be the best candidate for the production of these ceramics according to the mechanical properties and capability of mass production.

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