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The production of β-SiAlON ceramics with low amounts of additive, at low sintering temperature

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Abstract

In the present work nano-sized powder of β-SiAlON was produced using a wet milling process. Different milling times and mediums (methyl ethyl keton, ethanol and toluene as solvents, polyethyleneglicol, oleic acid, sodium tripolyphosphate and polyvinylpyrrolidon as dispersants) were performed for the determination of the most efficient milling system. The powders were produced using a conventional process (the ball to powder ratio was 1:1.5, at 300 rpm, for 1.5 h) having a few hundred nanometer particle size, and these were used as standard powders in this study. The nano-sized β-SiAlON starting powders (<100 nm) were sintered at lower temperatures than that of the conventional powders. The amount of Y_2O_3 in powders (∼130 nm), produced by high energy milling process, was fewer than conventional powders (5 wt.%). The results of the powder size, sintering behavior and mechanical properties of this sample were compared to those of the standard powder and its sintered sample. This sample, produced using the nano-powder, was investigated, and densified at 150 °C lower than that of the standard sample. Even though the amount of Y_2O_3 was decreased, the hardness of the samples was better than that of the standard sample.

Keywords: Wet milling; Sintering; SiAlON; Mechanical properties; Suspensions

1. Introduction

Silicon nitride and its solid solutions have superior physical and mechanical properties, such as excellent strength, fracture toughness, hardness and wear resistance. Also, these ceramics have good high temperature oxidation and corrosion resistance when compared to other structural materials. SiAlONs can be produced by various sintering methods, such as pressureless, gas pressured, hot isostatic pressured or spark plasma sintered. However, the sintering of Si_3N_4 ceramics is very difficult because of the strong covalent bonding between the Si and N atoms. Therefore, there should be pressure assist and/or sufficient amounts of sintering additive to obtain fully dense SiAlON ceramics. As a result, the elimination of the glassy phase is important to improve the high temperature properties.

In recent years, many investigations have been focused on the preparation of nano-sized SiAlON powders to decrease the sintering temperature and increase the mechanical properties.[1–5] Previous studies show that it is possible to densify SiAlON ceramics at 1500 °C using plasma-chemical synthesized starting powders with a specific surface area of 65 m^2/g.[1] However, plasma-chemical synthesis would increase the cost of the initial powder.[6] Alternatively, Xu et al. produced SiAlON starting powders with a nano-sized average particle size which was obtained by high energy mechanical milling.[3] Although this method promises very low particle sizes (∼40 nm) it could damage milling equipment.[5–7] Wet milling can be used to prevent the wear on milling equipment, but it decreases the efficiency of the milling. However, the efficiency of the milling might be increased. Agglomerates formed during the milling could exhibit a critical effect on the milling performance because the energy produced by the vial and balls process is used to break up the agglomerates. Thus, relatively in an agglomerate-free system, energy will be transferred to the powder to decrease the particle size. However, only a few published papers relate the solvent and dispersant type to the well-dispersed suspension system in order to decrease the starting particle size.[4,8–10] In our previous study we explain this relationship in the α-SiAlON materials.[11] However, there is no information relating to this in the β-SiAlON system. Therefore, the optimization of the well-

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dispersed suspension in the β-SiAlON composition is still a matter for research.

In this study, various types of solvent (methyl ethyl keton, ethanol and toluene) and dispersant (polyethyleneglicol, oleic acid sodium tripolyphosphate and polyvinylpyrrolidon) were used in different ratios for the optimization of a well-dispersed system. The aim of this study is to produce nano-powder using the wet milling process and to compare the results of the influence of the starting particle size on sintering behavior, and on the amount of additive and mechanical properties of the β-SiAlON ceramic to that of the standard sample.

2. Experimental procedure

β-SiAlON described as $Si_{6-z}Al_zO_zN_{8-z}$, where the z value is 2 and the composition doped with 5 wt.% Y_2O_3, was prepared from the starting powder 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). The weighed powders were planetary ball milled (Pulverisette 6 Fritsch, Germany) with Si_3N_4 balls for 2 h in different solvent compositions (toluene, methyl ethyl keton, ethanol) and in different ratios. The solvent ratios were determined as given in the literature.[11] The level of agglomeration, a critical parameter for the efficiency of the milling process, was determined using the sedimentation method. As explained in a previous study of Eser and Kurama, the most dispersed solvent composition was determined for α-SiAlON system in three kinds of dispersant (*oleic acid* (Codex, Carlo Erba), *polyethyleneglicol* (PEG, M.W.: 8000, Aldrich) *sodium tripolyphosphate* (STPP, Esan, Turkey)).[11] In the present study *polyvinylpyrrolidon* (PVP, Sigma–Aldrich) was also investigated as an alternative to the other three in the β-SiAlON system.

In the milling process the ball to powder ratio was determined as 12:1 according the filling of 10 vol.% suspension in a closed packed system of Si_3N_4 balls (with 5 mm radius and 9 mm length). The milling studies for this mixture were carried out at 450 rpm for different milling times (5–50 h). The samples are called *NX*, with *X* representing the milling time of the powders. The conventional powder mixture, called standard in later parts of this study, was prepared using a ball to powder ratio of 1:1.5, at 300 rpm, for 1.5 h, and is denoted as *C*. 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.

During milling process of powders in medium can be caused to oxidation on non-oxide powder surface and this oxidation can play a role on sintering behavior of SiAlON materials. Therefore, the oxidation amount of starting powder was calculated as 10.80 wt.%. For the milled powders oxidation characterization was carried out by using EDX analyze on scanning electron microscope (Zeiss, Evo 50) (Table 2).

The samples 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. Afterwards, the samples were sintered in a gas pressure sintering furnace (in FPW 180/250-2-220-100SP, FCT) in a nitrogen atmosphere (2.2 MPa) at different temperatures (1625–1825 °C) for 1 h. Using the dynamic light scattering (Malvern Nano ZS) the particle size distribution of the milled powders was determined. In addition, the specific surface area of the milled powders was determined using the BET nitrogen method (Quantachrome Instruments Autosorb-1). The equivalent grain size (D_{BET}) was calculated according to the following equation, based on the BET specific surface area:

$$D_{\mathrm{BET}} = \frac{6}{\delta \times S} \tag{1}$$

in this equation, δ represents the theoretic density (g/cm^3) of the powder.[12] The density of the starting mixture (δ) was calculated as 3.12 g/cm^3. The phase composition of the milled powder and the sintered samples was analyzed using the X-ray diffraction method (Rigaku Rint 2000). The bulk density of the sintered samples was measured using the Archimedes method. The microstructure of the sintered samples was characterized by scanning electron microscopy (Zeiss, Evo 50). The hardness and fracture toughness of the samples were measured using a Vickers diamond indenter on a polished surface with a load of 10 kg. The K_{IC} values were calculated using the following equations[13–14]:

$$K_{\mathrm{IC}}\,[\mathrm{MPa}^{1/2}] = k\left(\frac{E}{H}\right)^{1/2} \times F \times c^{-3/2} \times 0.0316 \tag{2}$$

E = Young's modulus (320 GPa), H = hardness (GPa), F = load (N), c = crack length (μm), k = dimensionless constant 0.016 ± 0.004.

$$H_V\,(\mathrm{GPa}) = \frac{0.47 \times P}{a^2} \tag{3}$$

P = applied force (10 kg), a = half of the length of the diagonal indentation.

3. Results and discussion

3.1. Preparation of a well-dispersed suspension and the milling process

The level of agglomeration was evaluated using the settling of powder (sedimentation height) for different types of solvent at 10 vol.% solid content (Fig. 1). As seen in Fig. 1, the optimum solvent ratio was investigated in an ethanol:toluene system of 70:30 vol. ratio with the highest sedimentation height. Because this system indicates the most dispersed solvent composition, it was selected for further investigation of the most efficient dispersant. The effect of the dispersant in the selected solvent composition was investigated by addition of oleic acid, STPP (*sodium tripolyphosphate*), PEG (*polyethyleneglicol*, M.W. 8000) and PVP (*polyvinylpyrrolidon*) as dispersants (Fig. 2). According to the result, the binary solvent system of ethanol and toluene (at a volume ratio 70:30) with 3 wt.% addition of PVP shows the most dispersed behavior and is used as a milling medium for milling studies.

After the milling process, the X-ray diffraction (XRD) characterization of the milled powders is shown in relation to the

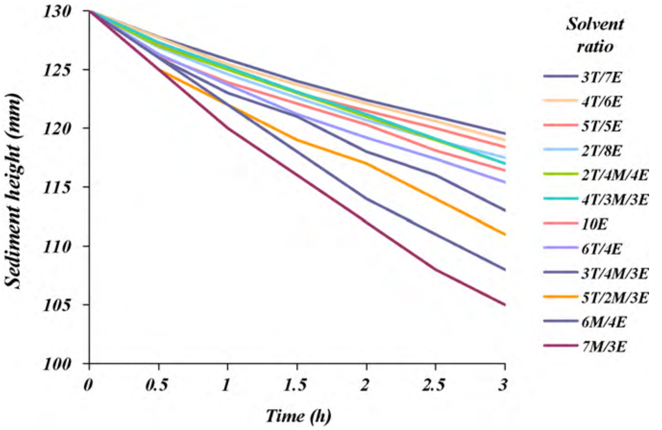

Fig. 1. Sedimentation height as a function of time for different kinds of solvent.

milling time in Fig. 3. The AlN peak, observed in the *C* powder, was widened by increasing the milling time and this indicates a reduced particle size. The cause of this behavior is explained in detail in a previous study of Eser and Kurama[11] and it is in agreement with the literature.[6]

For the characterization of the particle size of the milled powders, two different types of method were used in this study. One of these is the dynamic light scattering method, and the average particle size of the milled powders is given in Table 1. According to the results, a 45% decrease in particle size between the *C* and *N5* powders is observed, whereas this value is too low among the other samples. This result shows that a 5 h milling time has the most effect on particle size. However, further verification of these results is needed. The second method, BET, was used to measure the surface area of the powders and the mean particle size of (D_{BET}) the powders was calculated (Table 2). Comparison of the dynamic light scattering and the BET meth-

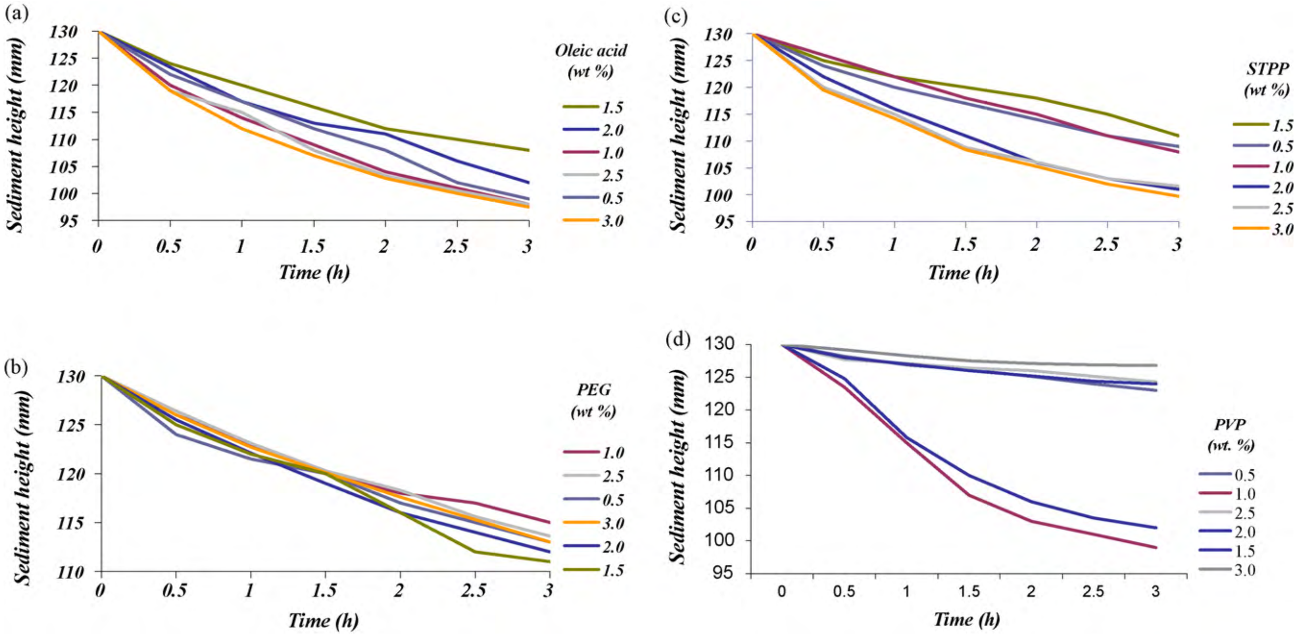

Fig. 2. Effect of amount of (a) oleic acid; (b) PEG; (c) STPP and (d) PVP on sedimentation height.

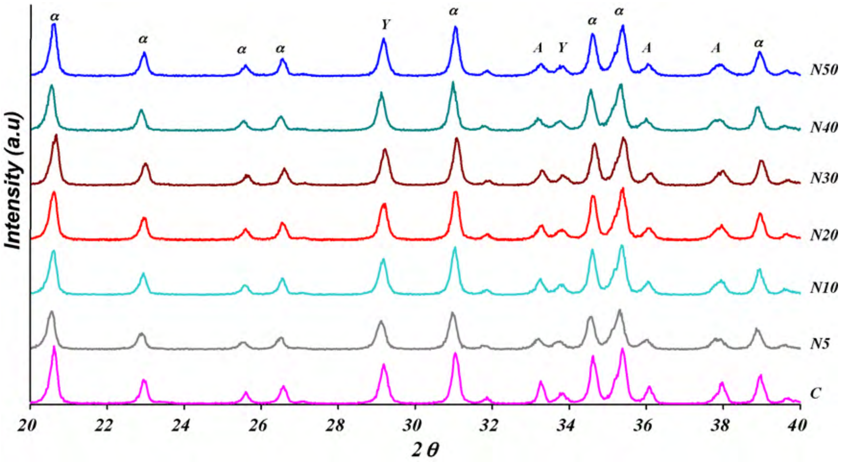

Fig. 3. XRD patterns of milled powders (α: α-Si_3N_4; A: AlN; Y: Y_2O_3).

Table 1
Average particle size of milled powders obtained by the dynamic light scattering method.

Sample code	Milling time (h)	Average particle size (nm)
C	1.5	530
N5	5	288
N10	10	286
N20	20	237
N30	30	230
N40	40	227
N50	50	224

ods shows that even though there was a decreasing particle size from sample *C* to *N50*, in the results a very high difference was observed. These differences can be explained by the formation of agglomerates which are difficult to deform, even using ultrasonic treatment in the dynamic light scattering method. However, in the BET method the diffusion of N_2 gas into agglomerates is possible, giving more realistic results than the dynamic light scattering method.

Additionally, even though a 70:30 volume ratio of ethanol–toluene suspension showed the most dispersed behavior, and is also used as a medium for dynamic light scattering measurements, it is insufficient in providing a perfect stabilization in the system without any dispersant addition. As a consequence, the dynamic light scattering results give the average particle size of the agglomerates. On the other hand, according to the BET results, a 20% increase in surface area between the *N30* and *N40* powders was observed; this value is about 8% for the *N5–N10*, *N10–N20*, *N20–N30* and *N40–N50* powders. These differences between the surface areas of powders can be explained by the storage of elastic energy produced by the balls and its release during the 40 h milling process. However, the oxidation of powders also has a role on surface area. Therefore, the oxidation behavior of powders was carried out using EDX analyze in scanning electron microscope. The oxygen content in *C* powder was calculated from starting composition as 10.80 wt.%. EDX analyze of this powder is in agreement with this result and it was found as 10.85 wt.%. EDX analyze of other samples was given in Table 2 and results showed that oxidation of powders increased by increasing milling time.

3.2. Sintering and mechanical properties

Sintering was carried out in a gas pressure sintering furnace at different temperatures for 1 h to find the relationship between the starting particle size and the densification temperature of the samples. It was observed that the *C* sample reached an almost theoretical density (99.4%) at 1825 °C whereas the samples, *NX*, had already densified at 1675 °C. The changing density of the samples (*C* and *NX*), related to the milling time and temperature, is given in Fig. 4. By decreasing the sintering temperature to 1625 °C all the samples which were produced from the nano-powders reached full density. However, when the sintering temperature was decreased to below 1675 °C (such as 1625 °C) the samples (*NX*) could not be fully densified. This result shows that merely decreasing the particle size is not the sole effect on densification for the *NX* samples produced from the nano-powders. Additionally, it is clear that the amount of oxidation on surface of non-oxide powders has not much effect on sintering of samples. Therefore, the *N5* powder was selected for further investigation in this study. Due to the oxygen content of *N5* powder is not much more than *C* powder sintering behavior can be explain related with lower powder size of *N5*.

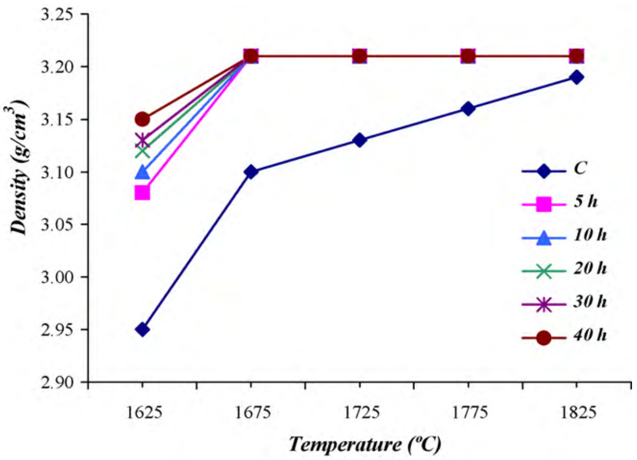

Fig. 4. Changing density of samples, produced by conventional (*C*) and high energy milling (*NX*) method.

In the second part of this study, the effect of the amount of additive (Y_2O_3) on the densification of the samples was explained related to the powder preparation process. In order that the amount of Y_2O_3 was decreased to less than 5 wt.%, two different compositions, doped with 3.5 and 2 wt.% Y_2O_3, were prepared. These samples were sintered at 1675 and 1725 °C. The results given in Table 3 indicate that by decreasing the amount of $Y_2O_{3,}$ the sample densification could not be successful at 1675 °C. However, the sample (*N5–3.5*), doped with 3.5 wt.% Y_2O_3, reached a theoretical density even at 1725 °C. Therefore, using the powder *N5*, it is possible to use a lesser amount of

Table 2
Specific surface area (SSA), equivalent grain size (D_{BET}) and oxygen content (wt.%) of the milled powders.

	Sample						
	C	*N5*	*N10*	*N20*	*N30*	*N40*	*N50*
SSA (m²/g)	8.9	14.7	15.1	15.7	16.4	19.5	20.9
D_{BET} (nm)	216	130	127	122	117	98	92
Oxygen content (wt.%)	10.85	12.60	12.65	12.70	–	–	14.50

Table 3
Effect of sintering temperature and amount of additive on the density of the *N5* sample.

Sample code	Sintering temperature (°C)	Additive (Y_2O_3%)	Density (g/cm^3)
N5–5	1675	5	3.21
N5–3.5		3.5	3.13
N5–2		2	3.08
N5–5	1725	5	3.21
N5–3.5		3.5	3.21
N5–2		2	3.14

additive (3.5 wt.% Y_2O_3) than the *C* sample (doped with 5 wt.% Y_2O_3), and to sinter it at 100 °C lower degree than that of the *C* sample of the same density.

3.3. Microstructure and mechanical properties

The SEM micrographs of the sintered samples are given in Fig. 5. In the sample *N5–5*, sintered at 1725 °C, grains have a lower aspect ratio and the grain boundary distribution is more homogenous than that of the *C* sample. On the other hand, the sample which was produced from the conventional powder has coarser and longer β-SiAlON grains (up to 6 μm) than that of the *N5–5*. This can be explained because of the smaller particle size of the starting powder and, as a result, the grain size decreases and the grain boundaries take up a substantial volume fraction of the material.[15] A change in the microstructure of the sample also was observed in the sample *N5–3.5*, sintered at 1725 °C. This sample has more equiaxed grains than that of the *N5–5* sample. As a consequence, an alteration in grain morphology has changed the mechanical properties (Table 4). As is well documented in the literature, β-SiAlON has a positive effect on the toughness of the samples because of its elongated grain shape. However, in the samples *N5–5* and *N5–3.5*, the grains have a lower aspect ratio and are in an equiaxed form. This morphology diminishes the toughness of these samples. However, a homogenous distribution of the grain boundary phase, with less than the *C* sample, improves the hardness of the *N5–5* and the *N5–3.5* samples.

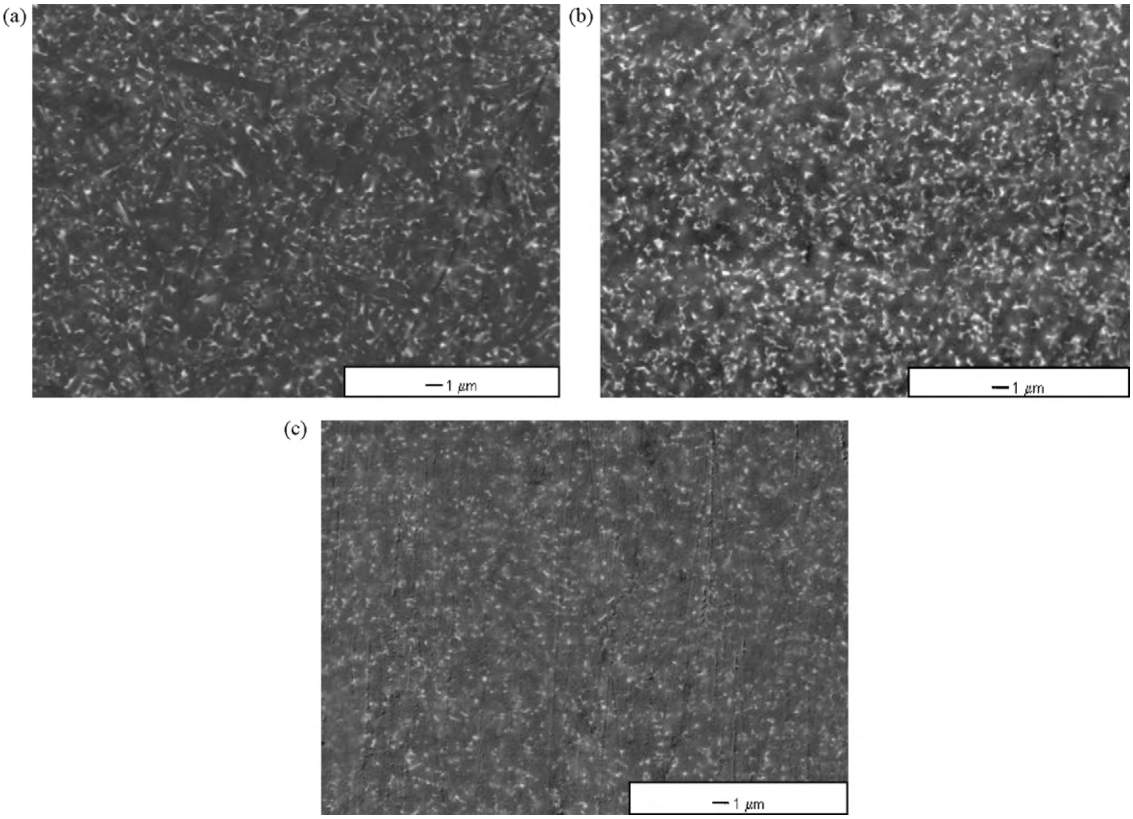

Fig. 5. SEM micrographs of (a) sample C sintered at 1825 °C: (b) sample *N5–5* sintered at 1725 °C and (c) sample *N5–3.5* sintered at 1725 °C.

Table 4
Relationship between density, mechanical properties and amount of additive.

Sample	Sintering temperature (°C)	Density (g/cm^3)	Weight loss (wt.%)	Hardness (HV10)	Fracture toughness (MPa m$^{1/2}$)
C	1825	3.19	1.70	14.2	6.4
N5–5	1725	3.21	1.45	16	4.8
N5–3.5	1725	3.21	0.90	16.5	4.4

4. Conclusion

The high energy milling in a wet medium system is an effective way to produce nano-sized β-SiAlON starting powders. The most efficient milling medium for the β-SiAlON suspensions is investigated as 70 vol.% ethanol–30 vol.% toluene with the addition of 3 wt.% PVP. The minimum β-SiAlON powder size was obtained as $\sim$92 nm after 50 h milling in this medium. However, a sintering behavior study of the powders (*NX*) shows that a longer milling time is insufficient in decreasing the sintering temperature for these powders. The *N5* powder, prepared by milling for 5 h and obtained as a 130 nm particle size, densified in the same density with the *N50* powder up to 1625 °C. Additionally, this sample is able to densify with a lower amount of Y_2O_3 addition (3.5 wt.%) and at 100 °C lower degree than that of the *C* sample. As a consequence of the smaller the particle size, a lower sintering temperature, a lesser amount of additive and a greater hardness are observed.

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