Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of the European Ceramic Society 24 (2004) 3303–3306

www.elsevier.com/locate/jeurceramsoc

Comparison of plasma-chemical synthesised SiAlON nano-powder and conventional prepared SiAlON powder

Friedrich Ivo Bulić[a,*], Ilmars Zalite[b], Natasha Zhilinska[b]

[a]*ARC Seibersdorf research GmbH/Division, Materials and Production Engineering, A-2444 Seibersdorf, Austria*
[b]*Institute of Inorganic Chemistry of the Riga Technical University, 34 Miera Str., Salaspils, LV-2 169, Latvia*

Abstract

Different mixtures of starting powders have been prepared to obtain a bulk material with an $\alpha+\beta$-SiAlON phase composition according to the general formula for α-SiAlON: $Me_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$; Me = Y; v = valency of the Me, where $m = 0.51$; $n = 1.0$; $x = m/v = 0.17$. This composition was derived from two different starting powders. One composition is based on powder mixture with a commercial available α-Si_3N_4 powder (Ube grade SN-E10) and additives (Y_2O_3, Al_2O_3 and AlN) produced by a conventional powder mixture process. The second powder was produced by a plasma-chemical synthesis. Both mixtures have the same ratio of oxides and nitrides. The compositions have been pressureless sintered under nitrogen atmosphere up to 1650 °C with a heating rate of 15 °C/min and a dwell time of 2 h. Data have been recorded and evaluated for the temperature range 1000–1650 °C. The relationship between density, phase composition, microstructure, and mechanical properties (hardness and fracture toughness) at different sintering temperatures were discussed.

Keywords: Powders-chemical preparation; Properties; Sialons; Si_3N_4; Sintering

1. Introduction

The majority of Si_3N_4-based ceramics (e.g. SiAlON) are made from powders and therefore depend to a large extent on the quality of the starting powders. The powder determines the processing, the sintering behaviour and the subsequent formation of the microstructure, which strongly influences many properties of the densified materials.[1]

SiAlON ceramics are still intensively studied and well reported. It is generally well known that the SiAlON, e.g. $\alpha+\beta$ composites possess excellent fracture toughness and strength due to the uniform microstructure of the elongated β-SiAlON grains formed in situ in the material. To obtain a fully dense ceramics with an uniformly distributed fine-grained microstructure with consistent properties, the use of a homogeneous, active nano-sized powder is required. Increasing interest in nano-sized powders has led to new preparation techniques, e.g. direct spray pyrolysis, laser-synthesis, sol-gel and a plasma chemical synthesis.

The latter technique enables production of nitride-based composites by evaporation and subsequent condensation of commercially available raw powders of chemical elements and their compounds in a radio frequency inductively coupled nitrogen plasma.[2]

2. Experimental

In investigations, a-nano sized starting powder based on the α-SiAlON with an equivalent composition of 85.8 wt.% Si_3N_4, 8.0 wt.% AlN, 2.0 wt.% Al_2O_3, 4.1 wt.% Y_2O_3 was used. This powder was prepared via plasma chemical synthesis in nitrogen plasma, using metallic (Si, Al) and oxide (Al_2O_3, Y_2O_3) powders as raw materials.[2] Specific surface area of this composite powder is 65 m^2/g, average particle size 35 nm (Table 1). The composite powders contain up to 10–20% of crystalline Si_3N_4 (ratio α/β is approximately 1:1).

The starting material for the conventional prepared “SiAlON” consists of a mixture of α-Si_3N_4 (UBE-SN-10E); AlN (H.C. Starck Grade C); Al_2O_3 (Alcoa Chemie GmbH, A16SG) and Y_2O_3 (Nanophase) powder. These powders were mixed with 2 wt.% of stearic acid, homogenised for 15 h in a rotating polyethylene bottle with

---

* Corresponding author.
E-mail address: friedrich.bulic@arcs.ac.at (F.I. Bulić).

0955-2219/$ - see front matter © 2003 Published by Elsevier Ltd.
doi:10.1016/j.jeurceramsoc.2003.10.031

Table 1
Chemical composition and size distribution of the starting powders

Sample designation	Type of starting powder	Chemical composition (wt.%)					SSA (m^2/g)	d_{50} (nm)
		Si_3N_4	Al_2O_3	Y_2O_3	AlN	Si_{free}		
N	Plasma-chemical synthesised "SiAlON"-nanopowder	83.70	2.00	4.10	8.0	1.30	65	35
C	Conventionally prepared SiAlON-powder	83.70	2.00	4.10	8.0	–	11	500

silicon nitride balls in hexane. Afterwards treated for 2 h in an ultrasonic bath. After subsequently drying at 80 °C the powder was sieved through a 200-μm mesh. Green bodies with a diameter of 15 mm and a height of 7–8 mm were produced by die pressing with a pressure of 200 MPa.

After removing the stearic acid at 600 °C, samples were pressureless sintered under nitrogen atmosphere up to 1650 °C with a heating rate of 15 °C/min and a dwell time of 2 h. For characterisation of the specimens sintering process was interrupted at 1000, 1200, 1300, 1400, 1450, 1500, 1550, 1600 and 1650 °C.

Chemical composition of the plasma-chemical synthesised "SiAlON"-powder (N, Si_{free}, Y, Al) was determined by chemical analysis. Phase composition of the fired specimens was performed via X-ray diffractometry (XRD). The microstructures were observed using scanning electron microscopy (SEM) on fracture surface.

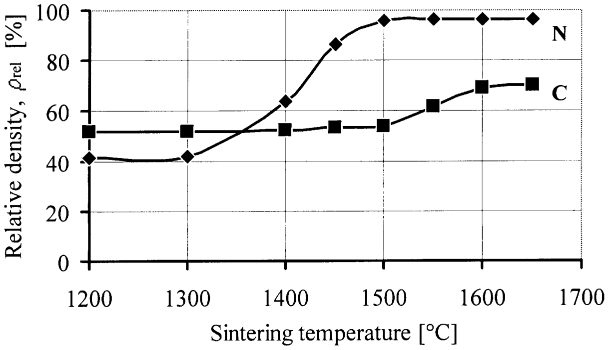

Fig. 1. Relative density of the sintered specimens made of "SiAlON" composite nano powder (N) and conventional "SiAlON" mixture (C). ◇ α-Si_3N_4 (1) □ β-phase (2a) △ α-Sialon (3) ■ β-Si_3N_4 (2b).

Densities of the sintered samples were determined by the Archimedes method. Hardness (load: 1 kg) and fracture toughness (load: 10 kg) were measured by the Vicker's indentation technique. Fracture toughness was calculated using the equation of Evans and Tanaky. The specimens and the compositions used are given in Table 1.

3. Results and discussion

Fig. 1 shows the variation of the relative density during the sintering process. Both materials showed nearly a constant relative density up to 1300 °C. The "green" relative density for sample "N" was 41.60% for sample prepared from conventional mixed powders "C" was 51.705. After 1300 °C the density of material "N" increased rapidly to a maximum of 96%. Even sample "C" increased its density up to 1650 °C and reached 72%.

The progression of the densification curve shows that the sintering of the nanopowder occures rapidly at 1400 °C, the density increased from 63.80% at 1400 °C to 96% at 1500 °C. With plasma-chemical synthesised nano-powder a faster densification at lower temperatures

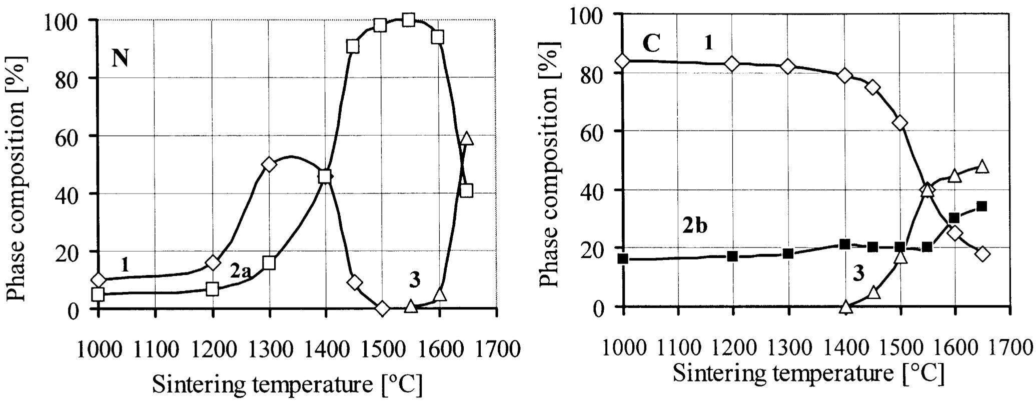

Fig. 2. Change of the phase composition of the material based on "SiAlON" composite nano powder (N) and conventional "SiAlON" mixture with industrial powders (C).

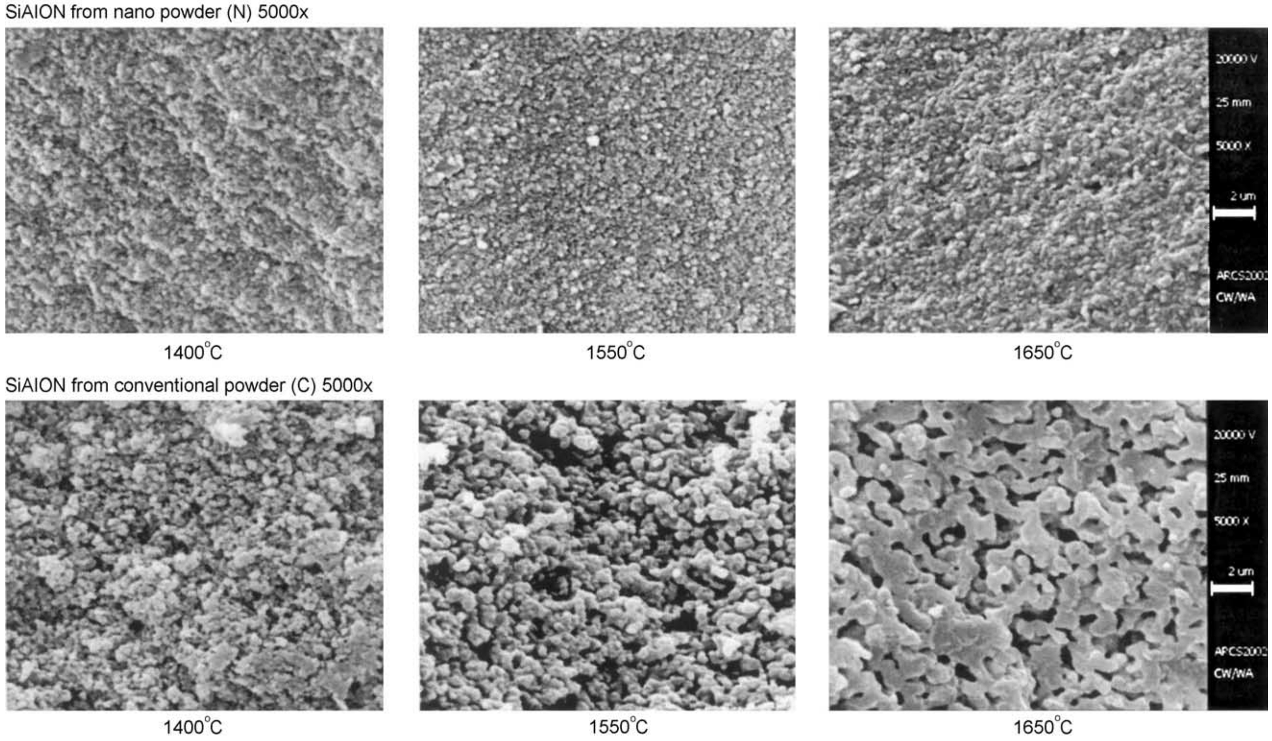

Fig. 3. Microstructure of the sintered specimens at different temperatures.

was achieved. In the same time the grain coarsening was reduced and preserved a finer microstructure in the sintered material (Fig. 3).

A relevant phase transition from α—to β—Si_3N_4 in the sample from commercial Si_3N_4 powder is being observed in the range of 1500–1600 °C (Fig. 2), but for nano-powder, it occurs from 1400 to 1450 °C.

The phase transformation during the sintering is shown in Fig. 2: The plasma-chemical synthesised powder is derivated from a complex powder composition, which consists of 10–20% of crystalline Si_3N_4 (ratio α/β is approximately 1:1) and probably of an in situ produced β-SiAlON precursor, which explains the observed sharp increase of the β-phase at 1400 °C and the observed slight grain growth at 1550 °C. Thus in situ produced "β-SiAlON nuclei" cannot be clearly differentiated from the other β-phase due to the XRD amorphous character. The point of intersection of the α- and β-Si_3N_4 line at 1400 °C of material "N" indicates that the XRD-amorphous part is almost fully tranformed into crystalline phase.

Dissolution of α-Si_3N_4 started at ~1350 °C. The formation of α-SiAlON in the material prepared from the industrial powders, designated with "C", starts at lower temperatures (1400 °C) than in sample "N" (1550 °C).

Particle size effect is a physical consideration independent of the composition. A smaller particle size generally enhances the kinetics of transformation.[5]

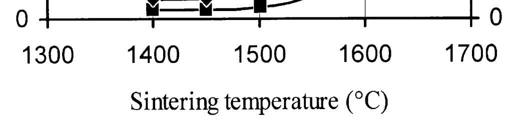

Fig. 4. Changes of material properties hardness (1, 3) and fracture toughness (2, 4) during the sintering process. 1, 2—nano powder (C); 3, 4—commercial powder (C). "SiAlON" from nano powder composite (N), "SiAlON" from conventional mixed powders (C). 1400 °C 1550 °C 1650 °C; 1400 °C 1550 °C 1650 °C.

In "C" the observed formation of αSiAlON starts approxmately 150 °C earlier (1400 °C) than in "N" (1550 °C) probably due to the slower dissolution rates of the "coarseh α-Si_3N_4" particles (0.5 μm). Thus the content of α-SiAlON in material "N" increased very rapidly with rising temperature.

The slow growth rate due to the low driving force in pressureless sintering results in very small microstructural changes.

SEM micrographs of fractured surfaces of “N” material prepared from plasma-chemical synthesised “SiAlON”-nanopowder shows at all temperatures a much finer grain sized microstructure in comparison with the obtained structure in the material based on a conventional powder mixture. The grain size of samples from nanopowders does not change even up to 1550 °C and is of 0.2–0.3 μm. According to Fig. 3, material “N”, the reaction is basically complete at 1650 °C, and it yields to a two phase α–β SiAlON composite, which is not distinguishable in the SEM micrograph. At 1550 °C some elongated β—Si_3N_4 grains are observed. The grain coarsing stage has not been adequates observed, but the microstruture at 1650 °C indicates a slight increase of grain growth in “N”. Some needle-shaped crystals with a diameter of approx. 0.2 μm and length up to 2 μm have been located.

The changes in grain dimensions are very slow due to the low driving force in gas pressure sintering and results in very small changes in the microstructural changes. It was observed in material “C” a change of the morphology of particles accompanied by neck growing, which takes place at 1650 °C (Fig. 3). The large grains grow at the expense of the smaller ones, which follows an Ostwald ripening mechanism. In the absence of any external driving forces, the only driving force for grain growth is the grain size difference, which causes different dissolution rates for grains.[6,7]

The hardness of material “N” is rising with the increase of the of α-content, the fracture thoughness increases with the increase of the needle-like grains within microstructure. Even a marginally decrease of fracture toughness is being observed shown in Fig. 4.

The Vicker’s hardness of the nanopowder was determined in a range of $HV_1 = 17.6–19$ GPa. These results are good corresponding with properties of materials prepared by hot pressing at 1850 °C.[3,4]

4. Conclusion

The results of this study show that the densification behaviour of the materials depends on the powder composition and the size of the particles used as starting powder. With a nano-sized powder it is possible to obtain a fully-dense material at relatively low temperatures (~1500 °C) with good mechanical RT properties in comparison with material made of a μm sized starting powder. Phase transition α→β Si_3N_4 in nanopowders occurs at lower temperatures (1550 °C), but the grain size of nanopowder materials is smaller that in the case of commercial Si_3N_4 powder.

References

1. Petzow, G. and Hermann, M., *Structure and Bonding,* Vol. 102. Springer-Verlag, Berlin, Heidelberg, 2002.
2. Preparation of nanodisperse transition metals carbonitrides by the plasmachemical method. In PM 2001 Congress in Nice, 22–24. October, Proceeding, Vol. 4. 2001, pp. 188–193. (CD).
3. Grabis, J., Zalite, I., Herrmann, M., Zhilinska, N. and Millers, T. In *Proceedings VIII-th International Baltic Conference, “Materials Engineering—99”.* Kaunas, Technologija, 1999, pp. 28–33.
4. Zhilinska, N., Zalite, I., Grabis, J. and Kladler, G. In Proceedings 2nd Tnt. Meeting on Space and Aerospace Materials Technology, Seibersdorf, 4th November 2002, Progress report of the AMTT users 2002 pp. 17–21.
5. Kato, A., Sarugaku, K. and Sameshima, S., Sinternility of silicon nitride powders. In *High-Tech Ceramic*, ed. P. Vincezini. Elsevier, Amsterdam, 1987, pp. 911–924.
6. Krämer, M., Hoffmann, M. J. and Petzow, G., Grain growth kinetics of Si_3N_4 during transformation. *Acta Metall. Mater.*, 1993, **41**(10), 293–947.
7. Krämer, M., Hoffmann, M. J. and Petzow, G. Grain growth studies of silicon nitride dispersed in an oxynitride glass. *J. Am. Ceram. Soc.* 1993, **76**(11), 2778–2784.