

α -sialon ceramics fabricated from nanopowders by sintering and hot pressing

Ilmars Zalite^a, Natalja Zhilinska^a, Aija Krumina^a and Gottfried Kladler^b

^a Institute of Inorganic Chemistry, Riga Technical University, 34 Miera Str., Salaspils, LV-2169, Latvia; ilmars@nki.lv

^b ARC Seibersdorf Research GmbH, A-2444, Seibersdorf, Austria

Received 2 June 2006, in revised form 25 September 2006

Abstract. Investigation of the fabrication of α -sialon ceramics from nanopowders by the method of ordinary sintering (1200–1650 °C) and hot pressing (1800 and 1910 °C) was carried out. Samples of sialons were made by using $\text{Si}_3\text{N}_4\text{-AlN-Al}_2\text{O}_3$ and $\text{Si}_3\text{N}_4\text{-AlN-Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ nanopowder composites, fabricated by the method of plasmachemical synthesis. Samples from nanopowders attain the density of 95–98% already at 1550–1600 °C, while industrial powders at the temperature of 1600–1650 °C reach the density of only 60–85%. The highest hardness of materials from nanopowders was attained after sintering at 1600–1650 °C and is $HV_5 = 21\text{--}23$ GPa depending on the composition. These results correspond well with properties of nanopowders obtained by hot pressing at 1800–1910 °C (at 1910 °C the hardness is $HV_1 = 20\text{--}21$ GPa, bending strength $\sigma_{3p} = 520\text{--}670$ MPa and fracture toughness $K_{Ic} = 4.0\text{--}7.0$ MPa.m^{1/2}, depending on the composition).

Key words: sialon ceramics, nanopowders, sintering, hot pressing.

1. INTRODUCTION

Special interest on sialon ceramics is related to their increased mechanical properties (hardness, fracture toughness and strength). Due to good corrosion resistance and mechanical characteristics, silicon nitride based ceramic materials, including sialons, are promising candidates for structural materials [¹] for application at increased temperatures up to 1200 °C.

A lot of investigations [^{2–4}] have been carried out during last years on the preparation of sialon ceramics, especially on the effect of microstructure of materials on their properties.

Sialon ceramics are being prepared from powders and therefore properties of ceramic materials 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 dense materials [5].

According to [6], there are two approaches to improve mechanical properties of ceramics. One is the control of the microstructure and another is the fabrication of the composite. The microstructure of the material can be significantly changed by using nanosized compounds and their composites for the preparation of materials. The distinctive properties of nanophase materials are low-temperature plasticity, high diffusion coefficient and high solubility. Investigations of the preparation of $\text{Si}_3\text{N}_4\text{-Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ and sialon ceramics from nanopowders [7-9] show that the application of nanopowders allows to decrease sintering temperature of powders and obtain ceramics with finer structure and changed properties.

The aim of this work was to investigate the compacting process of α -sialon nanopowders of several composition in the system $\text{Si}_3\text{N}_4\text{-AlN-Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ by sintering and hot pressing method as well as comparison of the ceramics with materials, obtained in similar conditions from industrial powders.

2. EXPERIMENTAL

Investigations were made on the preparation of α -sialon ceramic materials of different compositions from nanopowder composites. Three series of α -sialon were investigated with formulas $\text{Y}_{0.57}\text{Si}_{9.23}\text{Al}_{2.77}\text{O}_{1.05}\text{N}_{14.95}$, $\text{Y}_{0.45}\text{Si}_{9.69}\text{Al}_{2.31}\text{O}_{0.95}\text{N}_{15.05}$ and $\text{Y}_{0.48}\text{Si}_{9.39}\text{Al}_{2.61}\text{O}_{1.17}\text{N}_{14.83}$. Nanopowders ($\text{Si}_3\text{N}_4\text{-AlN-Al}_2\text{O}_3$ and $\text{Si}_3\text{N}_4\text{-AlN-Al}_2\text{O}_3\text{-Y}_2\text{O}_3$) (Table 1) were produced by the method of plasmachemical synthesis and have an average particle size of 30–50 nm [10]. Micrographs of some nanopowders are given in Fig. 1.

The composition of the starting mixtures was, in general, restricted to the concentration plane $\text{Si}_{12}\text{N}_{16} - \text{Al}_{12}\text{O}_{12}\text{N}_4 - \text{Y}_4\text{Al}_{12}\text{N}_{16}$, so the final compositions would be monolithic α -sialon, according to the phase diagram [11]. The specimen compositions used are plotted in Fig. 2 and given in Table 2.

Table 1. Chemical composition and size distribution of the starting powders

Powder	Chemical composition, wt%					SSA*, m ² /g	<i>d</i> ₅₀ , nm
	Si ₃ N ₄	AlN	Al ₂ O ₃	Y ₂ O ₃	Si _{free}		
Si ₃ N ₄ -AlN-Al ₂ O ₃	85.8	9.7	3.9	–	0.6	50	40
Si ₃ N ₄ -AlN-Al ₂ O ₃ -Y ₂ O ₃	83.7	8.0	2.6	4.1	1.3	70	30

* Specific surface area.

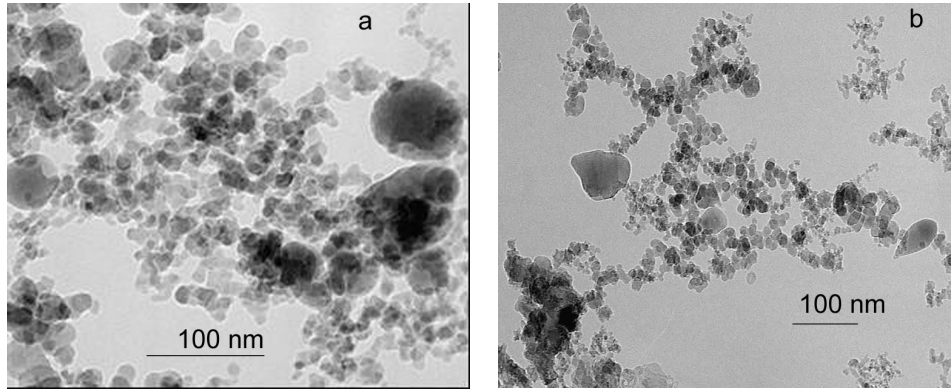


Fig. 1. Micrographs of $\text{Si}_3\text{N}_4\text{-Al}_2\text{O}_3\text{-AlN}$ (a) and $\text{Si}_3\text{N}_4\text{-AlN-Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ (b) nanopowders.

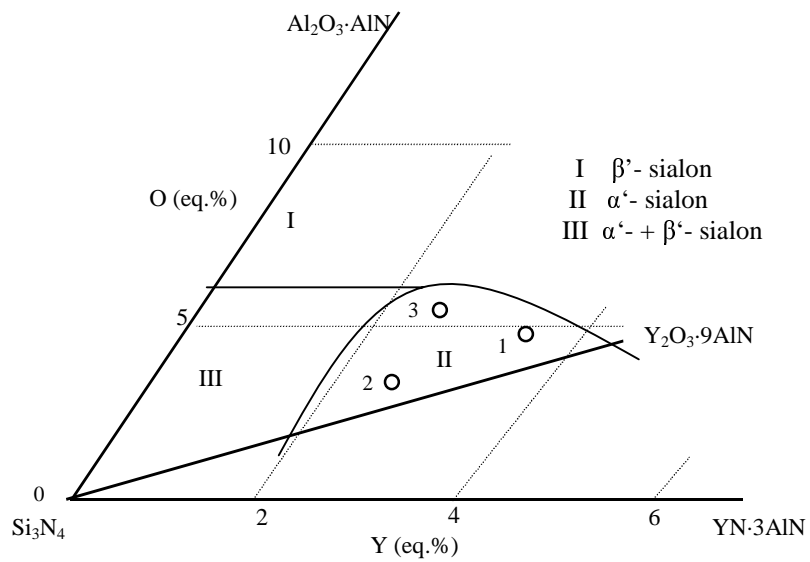


Fig. 2. Specimen composition spots in the phase diagram of the Y-Si-Al-O-N system.

Table 2. Composition of α -sialon specimens, wt%

No.	Si_3N_4	AlN	Al_2O_3	Y_2O_3	m^*	n^*
1	69.3	16.6	1.8	12.3	1.72	1.05
2	74.0	15.7	2.2	8.0	1.36	0.95
3	72.9	16.9	2.2	8.1	1.44	1.17

* "m" and "n" are independent composition parameters in the general formula $\text{Y}_{m/3}\text{Si}_{12-(m+n)}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n}$.

Table 3. Properties of α -sialon ceramics prepared by hot pressing (N₂, 2 h)

No.	Sintering temperature, °C	Density, g/cm ³	Open porosity, %	Bending strength, MPa	Hardness HV ₁ , GPa	Fracture toughness, MPa.m ^{1/2}
1A	1800	3.33	0.1	345 ± 20	21.9 ± 0.5	–
	1910	3.31	0	520 ± 15	20.8 ± 0.7	5.5 ± 0.3
2A	1800	3.26	0.2	535 ± 25	21.1 ± 0.8	–
	1910	3.26	0	620 ± 30	20.2 ± 0.5	4.0 ± 0.2
3A	1800	3.23	0.2	525 ± 30	20.4 ± 2.5	–
	1910	3.28	0	690 ± 40	20.9 ± 0.8	7.0 ± 0.3
3B	1910	3.30	0	700 ± 70	20.8 ± 0.7	7.2 ± 0.3

Samples of ceramics, obtained from nanopowders, were made by using Si₃N₄-AlN-Al₂O₃ (samples 1A and 2A) and Si₃N₄-AlN-Al₂O₃-Y₂O₃ (sample 3A) nanocomposites and small amount of AlN (H.C.Starck, grade B) and Y₂O₃ (H.C.Starck, grade C) powder additions for correcting of the composition (Table 3). Simultaneously, the sialon ceramics were obtained from commercial powders: α -Si₃N₄ (UBE, SN-10E), AlN (H.C.Starck, grade C), Al₂O₃ (Alcoa Chemie GmbH, A16SG) and Y₂O₃ (Nanophase) in the same conditions for comparison (marked 1B, 2B and 3B).

All powders were mixed with 2 wt% of stearic acid, homogenized in hexane for 15 h in a rotating polyethylene bottle with silicon nitride balls and afterwards treated for 2 h in an ultrasonic bath. After the following drying at 80 °C the powder was sieved through a 200 μ m mesh sieve. 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. Ordinary sintering (1200–1650 °C) and hot pressing (1800 and 1910 °C) were used for compacting the materials. The temperature was raised 10°/min; isothermal holding time was 2 h, sintering medium was nitrogen.

Chemical composition of the nanopowders (N, Si_{free}, Y, Al) was determined by the chemical analysis. Phase composition of the sintered specimens was performed via X-ray diffractometry. The form and size of particles were determined by the transmitting electron microscope. The microstructure of the fracture surface was observed using scanning electron microscopy. Density of the sintered samples was determined by the Archimedes' method. Hardness (load 1 and 5 kg) and fracture toughness (load 10 kg) were measured by the Vickers indentation technique.

3. RESULTS AND DISCUSSION

Figure 3 shows the variation of the relative density during the sintering process. All materials showed nearly a constant relative density up to 1300 °C for nano- and 1500 °C for industrial powders. The densification of all samples obtained from nanopowders occurs at the temperature range of 1550–1600 °C and

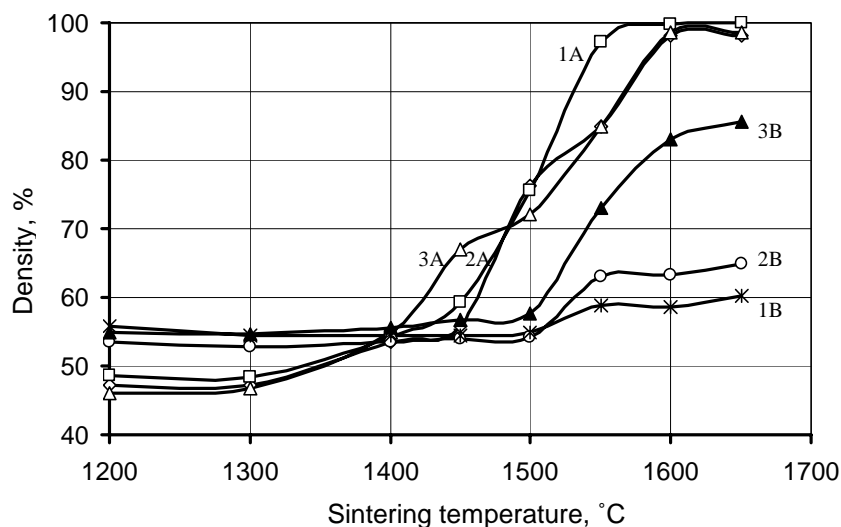


Fig. 3. Change of the relative density during sintering of the specimens.

at higher temperatures the increase of the density does not take place. Industrial powders almost do not sinter at the temperatures up to 1650 °C – the density is 60–85% at the temperature of 1650 °C.

The phase formation by sintering of industrial and nanopowders is different. In the case of nanopowders, amorphous Si_3N_4 first crystallizes into the α - and β - Si_3N_4 until 1400 °C, but over 1400–1450 °C β -sialon begins to form; at over 1500 °C also α -sialon forms and its amount increases with the increase of the temperature. If at 1650 °C sample 1A contains only α -sialon, then sample 2A contains also some β -sialon. The most characteristic is formation of β -sialon in sample 3A, where the formation of α -sialon begins only at 1600 °C. With the increase of compacting temperature (for example, hot pressing at 1800 or 1910 °C) the proportion of α -sialon phase increases. Incomplete phase transition in the samples of “A” series could occur due to increased oxygen content in nanopowders in comparison with the industrial powders.

In the samples of the “B” series, α -sialon forms directly from α - Si_3N_4 already starting from 1450 °C and at 1650 °C the transition of α - Si_3N_4 to the α -sialon has not been completely finished. Microstructure of the samples depends on their chemical composition. The grain size of samples from nanopowders at temperatures up to 1600 °C changes insignificantly and is in the range of 200–300 nm. Also at the temperature of 1650 °C the grain size of sintered samples does not change noticeably, except sample 2A, where the grain size increases a little bit (Fig. 4). The grain size increases in the samples of hot pressing: the average grain size is about 500 nm (Fig. 5).

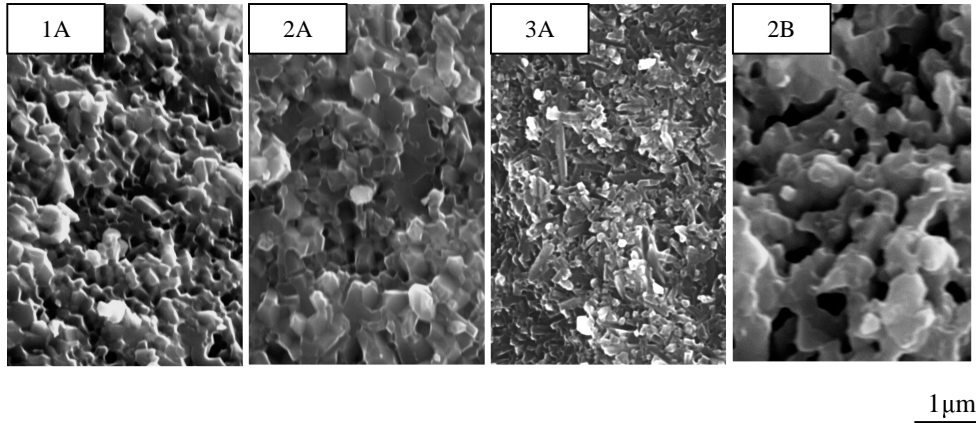


Fig. 4. Microstructure of the samples, sintered at 1650 °C.

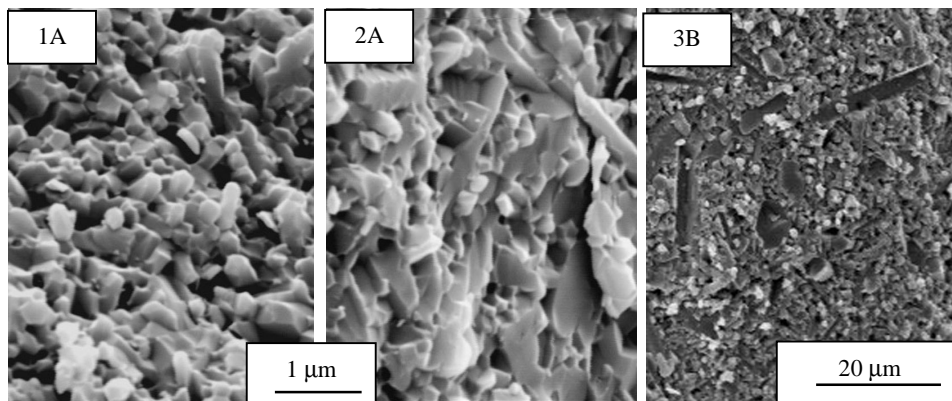


Fig. 5. Microstructure of the samples, hot pressed at 1800 °C.

Significant formation of needle-shaped crystals begins at the temperatures 1600–1650 °C. It was observed especially in the hot pressed samples. Moreover, there are no needle-shaped crystals in the sample 1A, but in the sample 2A the formation of such crystals is already characteristic, especially during hot pressing. In both cases the material consists only of the phase of α -sialon. More characteristic formation of needle-shaped crystals was observed in the sample 3A, where the β -sialon phase has been preserved. The average size of needle-shaped crystals is about 200 nm in crosscut and up to 2 μm in length, but in samples, fabricated by the method of hot pressing, up to 3–4 μm . The structure of samples, sintered at 1650 °C from industrial powders, is porous and the grain size is about 0.5–1.0 μm ; in the samples, prepared by hot pressing, grains are bigger

and the length of needle-shaped crystals reaches 20 μm (Fig. 5, 3B). Crystallite size (both for phases of α - and β -sialon) of samples, obtained from nanopowders at 1650 $^{\circ}\text{C}$, is about 100 nm, but in the samples of hot pressing the crystallite size is over 100 nm.

Properties of the materials change proportionally to the density, phase composition, grain size and shape of the material. As it is shown in Fig. 6, hardness of obtained materials is directly related to their density. Samples sintered at 1550–1600 $^{\circ}\text{C}$ possess maximum hardness ($HV_5 = 20\text{--}23$ GPa), which a little bit decreases with rising of the sintering temperature (Table 3). The bending strength increases with the sintering temperature, probably due to grain size and shape: samples with isoaxial grains have higher hardness, but with needle-shaped crystals – higher bending strength. With the increase of the amount of needle-shaped crystals also the fracture toughness increases. Materials sintered at 1650 $^{\circ}\text{C}$ from industrial powders are not fully dense; therefore their hardness is small (HV_5 varies from 2 to 3 GPa). Only the sample 3B is more dense with higher hardness.

As it is seen in the densification process of hot pressing (Fig. 7), kinetics of densification of nanopowders and industrial powders are significantly different: in the case of nanopowders more significant is the starting stadium of compacting (at 1430–1550 $^{\circ}\text{C}$), when the density grows due to the grain surface slipping.

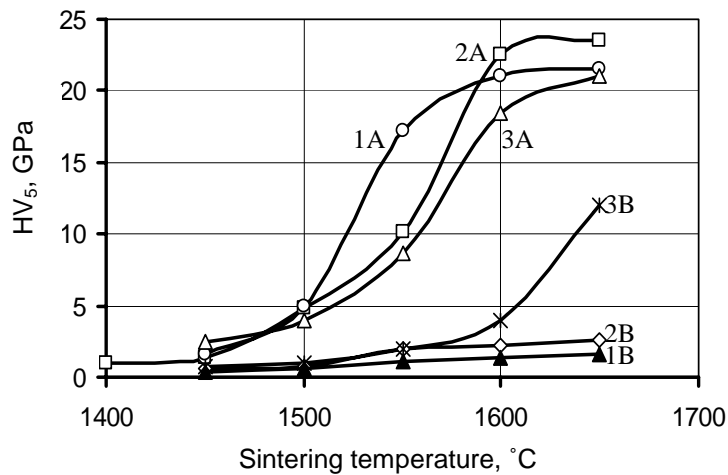


Fig. 6. Hardness of α -sialon samples depending on the sintering temperature.

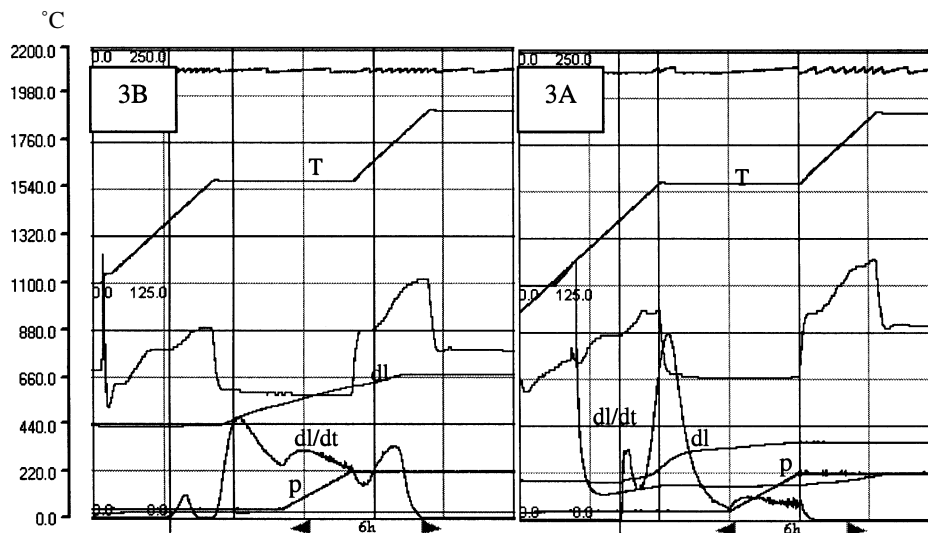


Fig. 7. Process of hot pressing of samples 3B and 3A.

4. CONCLUSIONS

The densification behaviour of investigated powders in the sintering process depends on the composition and particle size of the starting powder. It is possible to obtain dense materials from a nanosized powder at a relatively low temperature (1550–1600 °C) with good mechanical properties at room temperature in comparison with a material made of a μm -sized starting powder. The grain size of nanopowder materials is smaller (200–300 nm) than that of the commercial Si_3N_4 powder.

If industrial powders are applied, the formation of α -sialon takes place directly from α - Si_3N_4 , but for nanopowders the β -sialon forms first and transforms to the α -sialon at higher temperatures.

The hardness of obtained materials is directly related to their density and for samples from nanopowders at 1650 °C HV_5 was from 21 to 23 GPa. These results correspond well with properties of nanopowders obtained by hot pressing at 1800–1910 °C; for samples obtained at 1910 °C the hardness HV_1 is from 20 to 21 GPa, bending strength 520–670 MPa and fracture toughness 4.0–7.0 $\text{MPa}\cdot\text{m}^{1/2}$, depending on the composition.

REFERENCES

1. Gogotsi, Yu. G. Particulate silicon nitride-based composites. *J. Mater. Sci.*, 2000, **29**, 2541–2556.
2. Zhao, H., Wood, C. and Cheng, Y.-B. The effect of processing conditions on the microstructures of α -SiAlON ceramics. *Mater. Sci. Forum*, 2000, **325–326**, 213–218.

3. Young, W. T., Falk, L. K. L., Lemerrier, H. et al. The crystallisation of the yttrium-sialon glass: $Y_{15.2}Si_{14.7}Al_{18.7}O_{54.1}N_{7.4}$. *J. Non-Crystall. Solids*, 2000, **270**, 6–19.
4. Kim, J., Rosenflanz, A. and Chen, I.-W. Microstructure control of in-situ-toughened α -SiAlON ceramics. *J. Am. Ceram. Soc.*, 2000, **83**, 1819–1821.
5. Petzow, G. and Hermann, M. Silicon nitride ceramics. In *Structure and Bonding*. (Jansen, M., ed.). Springer, Berlin, 2002, **102**, 71–72.
6. Hojo, J., Eto, K., Umezu, M. et al. Microstructure and mechanical properties of sintered bodies of fine powders in Si_3N_4 -TiN system. *J. Ceram. Soc. Japan*, 1998, No 1, 25–30.
7. Bulic, F., Zalite, I. and Zhilinska, N. Comparison of plasma-chemical synthesised – SiAlON-nano-powder and conventional prepared SiAlON-powder. *J. Eur. Ceram. Soc.*, 2004, **24**, 3303–3306.
8. Zhilinska, N., Zalite, I., Krumina, A., Costin, W. and Mozdzen, G. Sintern der Materialien auf der Basis unterschiedlicher Si_3N_4 -Pulver. In *Verbundwerkstoffe, 14. Symposium Verbundwerkstoffe und Werkstoffverbunde*. Weinheim, 2003, 399–404.
9. Zalite, I., Zhilinska, N. and Krumina, A. Sintering of plasma-chemically synthesized SiAlON nanopowder. In *Nanomaterials and Nanotechnologies* (Zalite, I. and Krastins, J., eds.). Institute of Inorganic Chemistry, Riga Technical University, Riga, 2005, 98–103.
10. Zalite, I. Preparation of nanodisperse transition metals carbonitrides by the plasmachemical method. In *Proc. European Congress and Exhibition on Powder Metallurgy*. Nice, 2001, vol. 4, 188–193, CD.
11. Haviar, M. Influence of oxygen content on formation of yttrium α -SiAlON ceramics. *J. Am. Ceram. Soc.*, 1994, **77**, 2425–2428.

Nanopulbriitest paagutamise ja kuumpressimise teel valmistatud α -sialoonkeraamika

Ilmars Zalite, Natalja Zhilinska, Aija Krumina ja Gottfried Kladler

On uuritud α -sialoonkeraamika valmistamist nanopulbriitest tavalise paagutamise (1200–1650 °C) ja kuumpressimisega (1800 ja 1910 °C). Sialoonist katsekehad on valmistatud plasmakeemilise sünteesi teel saadud Si_3N_4 -AlN- Al_2O_3 ja Si_3N_4 -AlN- Al_2O_3 - Y_2O_3 nanopulbriitest. Nendest valmistatud katsekehade tihedus 95–98% saavutatakse juba 1550–1600 °C juures. Samas on tööstuslikest pulbriitest 1600–1650 °C juures paagutatud katsekehade tihedus ainult 60–85%. Suurim nanopulbriitest valmistatud keraamika kõvadus ($HV_5 = 21$ – 23 GPa – sõltuvalt koostisest) saadakse paagutamisel 1600–1650 °C juures. See on võrreldav kuumpressimisega temperatuuril 1800–1910 °C nanopulbriitest valmistatud materjalide omadustega (1910 °C juures on kõvadus $HV_1 = 20$ – 21 GPa (sõltuvalt koostisest), paindetugevus 520–670 MPa ja purunemissitkus 4–7 MPa·m^{1/2}).