ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 18, No. 3. 2012

Investigation of Production of Fine-grained SiAlON Ceramics from Nanopowders

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http://dx.doi.org/10.5755/j01.ms.18.3.2439

Received 07 June 2011; accepted 19 October 2011

Different sialons' compositions were used to find the effect of material starting components on sintering and properties of sialon materials. The nanopowders (Si_3N_4, AlN, Al_2O_3, Y_2O_3 and Si_3N_4-27 wt.% AlN nanocomposite) were produced by the plasmachemical synthesis. The composite materials were sintered by the method of pressure-less sintering. Sintering temperature decreased significantly, if Si_3N_4-AlN nanocomposite was used as one of the components. The increased amount of α- sialon phase and higher hardness are characteristic for materials obtained from separate Si_3N_4, AlN, Al_2O_3, Y_2O_3 nanocomponents.

Keywords: sialon, nanocomposite, pressure-less sintering, mechanical properties.

INTRODUCTION

SiAlONs is a general name for a large family of the silicon nitride based ceramics.

There are two main types of SiAlON ceramics used for engineering applications. α- SiAlON and β- SiAlON are solid solutions isostructural with α- and β- Si_3N_4, respectively. The common formula of β- sialon is $Si_{6-z}Al_zO_zN_{8-z}$, where „z" can change from 0 to 4.2. The formula of α- sialon is $M_xSi_{12-(m+n)}Al_{(m+n)}O_nN_{16-n}$, where M is the metal ion with the valence of p+ and $x = m/p$, but m characterizes the number of Si-N bonds in α- Si_3N_4, which are replaced by the Al–N bonds, and n characterizes the amount of Si-N bonds replaced by the Al–O bonds [1].

α- SiAlON ceramics are characterized by equiaxed grains with high hardness and good wear and oxidation resistance. β- SiAlONs are characterized by their elongated grains with good flexural strength and fracture toughness [2]. α/β SiAlON composites have been studied due to advantages in the physical properties of both SiAlONs [3].

The diffusion velocity and the distance of the diffusion way are of great importance for compacting of covalent compounds, for example, SiAlONs. The distance of the diffusion way can be decreased, if nanocomponents are used for production of compact material.

The aim of this investigation is to find the effect of material starting components on sinterability, structure, phase composition and properties of sialon materials on the example of 18 sialon compositions using the nanocomponents as raw materials.

EXPERIMENTAL

The sialon composites (18 compositions in the range of α- and α-/β- sialon existence (Fig. 1, Table 1)) obtained by the mechanical mixing of separate Si_3N_4, AlN, Al_2O_3, Y_2O_3 nanocomponents or previously prepared Si_3N_4-27 wt.% AlN nanocomposite with Si_3N_4, Al_2O_3 and Y_2O_3 additives were used for research. Starting nanocomponents were made by the plasma-chemical synthesis [4].

Four plasma-synthesized nanopowders were used: the Si_3N_4-AlN composite and separate Si_3N_4, Y_2O_3 and Al_2O_3 powders (Table 2).

Pure Si_3N_4 nanopowder and Si_3N_4-27 % AlN nanocomposite is typical of particles of irregular form with the average particle size of 30 nm – 40 nm and the specific surface area of powder (SSA) of 60 m^2/g – 80 m^2/g (dependent of obtaining regime) (Fig. 1). Powder consists of α- and β- Si_3N_4 (mainly in the ration 1 : 1) and the X-ray amorphous part. Depending of the SSA, the content of X-ray amorphous phase is in the range between 60 wt.% to 80 wt.%.

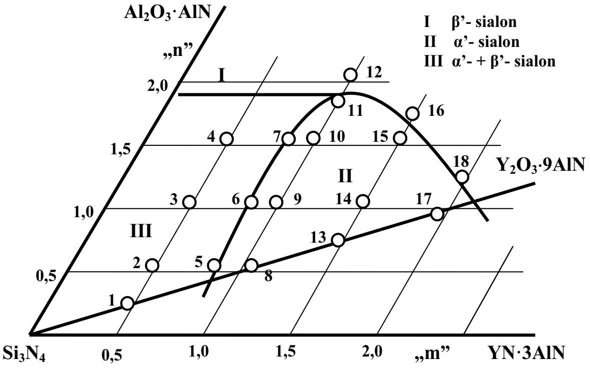

Fig. 1. The situation of investigated samples in the phase diagram of system Y-Si-Al-O-N [5]

Nanopowders of Al_2O_3 consist mainly of δ-, θ- Al_2O_3 phases, Y_2O_3 contains 30 wt.% of cubic and 70 wt.% of monoclinic phase.

All powders were mixed in isopropanol for 3 h in a planetary mill (400 rpm) in a silicon nitride vessel using silicon nitride balls. After drying at 80 °C the powders were sieved through a 200 µm mesh.

Green bodies with a diameter of 12 mm and a height of 7 mm – 8 mm were produced by die pressing with a pressure of 200 MPa. The density of samples ("green body") pressed from nanopowders was 31 % – 33 %.

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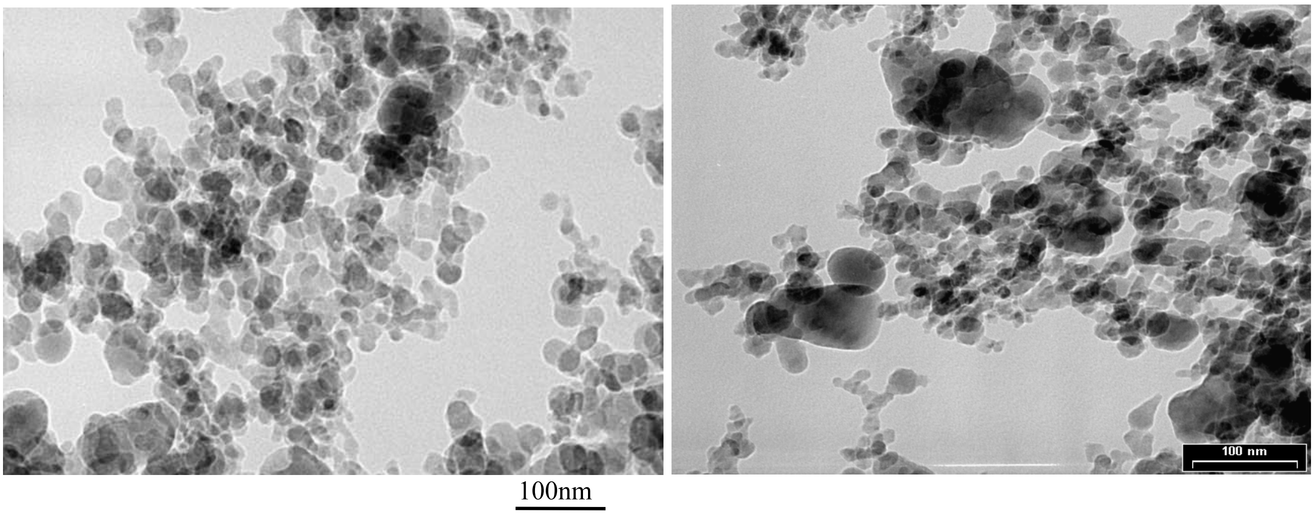
Table 1. Composition of SiAlON samples, wt.%

No. of sample	m*	n*	Si_3N_4	AlN	Al_2O_3	Y_2O_3
1	0.5	0.25	91.25	5.42	0	3.32
2		0.5	89.28	6.03	1.36	3.33
3		1.0	85.15	7.20	4.32	3.33
4		1.5	81.04	8.37	7.26	3.33
5	0.8	0.5	85.64	8.74	0.47	5.14
6		1.0	81.57	9.90	3.38	5.14
7		1.5	77.51	11.06	6.29	5.14
8	1.0	0.5	83.19	10.50	0	6.31
9		1.0	79.24	11.66	2.78	6.32
10		1.5	75.22	12.80	5.67	6.31
11		1.8	72.80	13.49	7.39	6.31
12		2.0	71.20	13.95	8.54	6.31
13	1.5	0.75	75.35	15.31	0	9.33
14		1.0	73.45	15.89	1.32	9.34
15		1.5	69.53	17.00	4.13	9.33
16		1.75	67.57	17.56	5.54	9.33
17	2.0	1.0	67.90	19.90	0	12.20
18		1.2	66.41	20.35	1.03	12.21

* – here "m" and "n" are parameters from the general formula $Y_{m/3}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$.



a b

Fig. 2. Micrographs of Si_3N_4 (a) and Si_3N_4-AlN (b) nanopowders

Table 2. Chemical composition and size distribution of the starting powders

Powder	Chemical composition [wt.%]					BET [m^2/g]	d_{50} [nm]
	Si_3N_4	AlN	Al_2O_3	Y_2O_3	Si_{free}		
Si_3N_4-AlN	71.1	27.1	–	–	0.4	75	30
Si_3N_4	98.1	–	–	–	0.7	65	40
Y_2O_3	–	–	–	100	–	25	65
Al_2O_3	–	–	100	–	–	50	40

Samples of sialon ceramics were made by the methods of pressure-less sintering. Samples were pressure-less sintered under nitrogen atmosphere up to 1750 °C with a heating rate of 10 °C/min and a dwell time of 2 hours.

Chemical composition of the plasma-synthesized sialon nanopowders (N, Si_{free}, Y, Al) was determined by the chemical analysis. Phase composition of the fired specimens was performed via X-ray diffractometry (XRD) (DRON-3 and Advance D8, Bruker AXS).

Density of sintered samples was determined by the Archimedes method. Microstructures were observed using scanning electron microscopy (SEM) (Hitachi, S4800) on fracture surface. Hardness (HV_5, load 49 N and HV_{10}, load 98 N*)* was measured by the Vickers indentation technique.

RESULTS AND DISCUSSION

As it follows from [6], sintering temperatures of materials obtained from nanopowders are significantly lower than those for materials from sub-micron industrial powders. Our research shows that essential for material formation is also the choice of starting nanocomponents. For example, replacing of separate Si_3N_4 and AlN nanopowders by the plasma-synthesized Si_3N_4-AlN nanocomposite of the same composition and dispersity, the sintering temperature of sialon decreases for approximately 100 °C (Fig. 3). The same fact has been observed in the case of sialons of other composition in the all range of existence of α- sialons and near it (Tables 3 and 4).

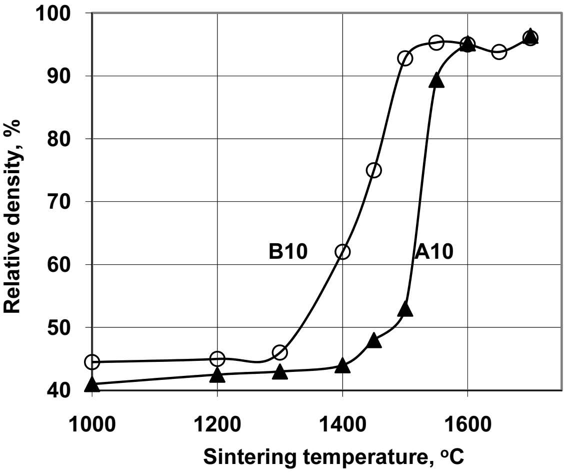


Fig. 3. Change of the relative density of samples A10 and B10 during sintering

Sialons of some compositions prepared from Si_3N_4-AlN nanocomposite sinter already starting from 1430 °C, but for most of composites at the region of α- sialons the temperature of approximately 1550 °C is necessary (Table 4) and only outside of the region of α- sialons higher sintering temperature is necessary. Samples obtained by the mechanical mixing of Si_3N_4 and AlN nanocomponents, which are located in α- sialons areas, predominantly start sintering from 1600 °C (Table 3). The common regularity has been observed: the sintering temperature of material decreases with the increase of coefficients „m” and „n” in the formula characterizing sialon composition.

With the increase of the density also the hardness of material raises. The sintered samples prepared from Si_3N_4-AlN nanocomposite have relatively high hardness at 1500 °C (Fig. 4, Table 4), but the maximum hardness value is achieved above 1650 °C temperature. Also, sintered samples of obtained by the mechanical mixing of separate Si_3N_4 and AlN nanocomponents the maximum hardness have at sintering temperature 1700 °C – 1750 °C (Table 3).

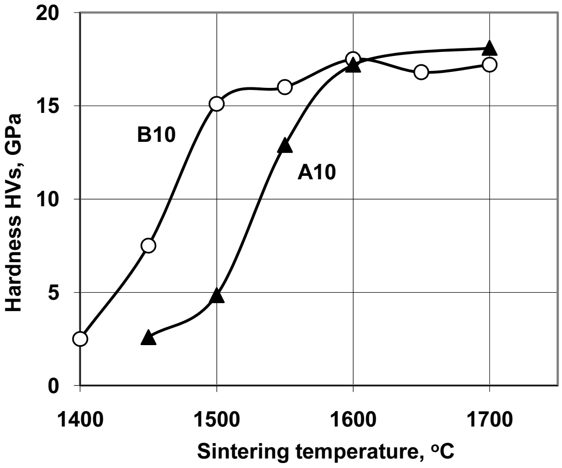


Fig. 4. The dependence of sialon samples A10 and B10 hardness on sintering temperature

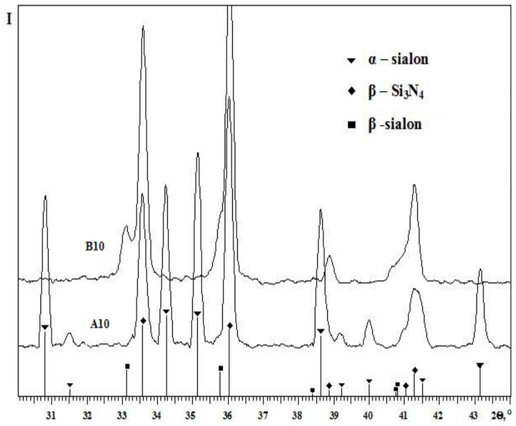


Fig. 5. Phase composition of sialons No. 10 sintered at 1600 °C

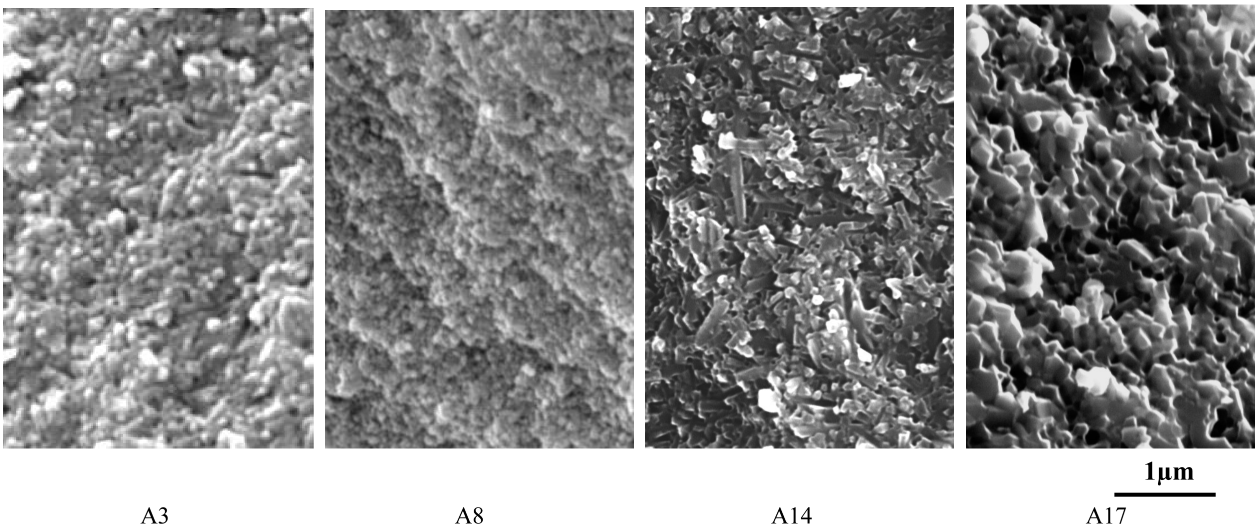
As it follows from the results of X-ray analysis, real samples contain more β- sialon phase, although most of composites are situated in the region of existence of α- sialon. Moreover, the content of α- sialon in the samples made from Si_3N_4-AlN nanocomposite is less than in the samples of same composition made from separate Si_3N_4 and AlN nanocomposites (Fig. 5). This can be explained with the fact that plasma-produced nanopowders are of high specific surface area and the oxygen from the air adsorbs on the surface of nanoparticles and it is complicated to get free from it also during sintering process. As a result, the sialon material contains more oxygen-containing compounds than it should be necessary according to the phase diagram. Due to this more glass phase forms during sintering stimulating the transition of α- sialon phase into the β- sialon [7]. Therefore also the hardness of material (Tab. 3 and 4) is lower than it could

Table 3. Density and hardness of samples obtained by the mechanical mixing of individual Si_3N_4, AlN, Al_2O_3, Y_2O_3 nanocomponents

No.	m	n	1550 °C		1600 °C		1700 °C		1750 °C	
			d, %	HV_{10}, GPa	*d* , %	HV_{10}, GPa	*d*, %	HV_{10}, GPa	*d*, %	HV_{10}, GPa
A1	0.5	0.25								
A2		0.5	58.8	1.6	68.2	3.1	76.3	11.7	95.2	18.2
A3		1.0	73.2	6.3	83.6	9.8	93.5	17.3	92.4	16.9
A4		1.5								
A5	0.8	0.5	74.4	6.1	84.2	9.7	94.2	19.0	93.6	18.4
A6		1.0	86.7	10.5	93.0	15.9	96.4	19.4	95.4	18.7
A7		1.5								
A8	1.0	0.5	84.2	8.7	92.7	14.5	97.0	18.2	94.7	17.9
A9		1.0	90.8	12.0	93.0	15.0	95.3	18.5	94.8	18.7
A10		1.5	89.4	12.9	95.2	17.2	96.4	18.1	98.7	18.5
A11		1.8	93.0	16.2	94.8	17.8	94.0	18.1	93.6	18.2
A12		2.0								
A13	1.5	0.75								
A14		1.0	55.2	2.7	89.3	15.6	97.3	18.3	96.5	18.6
A15		1.5	69.1	9.9	83.3	12.8	97.6	18.7	97.3	19.4
A16		1.75								
A17	2.0	1.0								
A18		1.2								

Table 4. Density and hardness of samples prepared from Si_3N_4-27 wt.% AlN nanocomposite with Si_3N_4, Al_2O_3 and Y_2O_3 additives

No.	m	n	1500 °C		1550 °C		1650 °C		1750 °C	
			d, %	HV_{10}, GPa	*d* ,%	HV_{10}, GPa	*d*, %	HV_{10}, GPa	*d*, %	HV_{10}, GPa
B1	0.5	0.25	52.0	–	68.9	9.6	80.1	11.2	90.3	15.2
B2		0.5	61.2	–	80.0	11.3	84.8	14.6	94.1	18.5
B3		1.0	78.5	–	88.4	15.1	92.8	16.4	95.7	17.6
B4		1.5	86.1	–	92.8	16.7	93.9	17.2	95.6	16.8
B5	0.8	0.5	78.6	–	89.4	15.4	97.1	16.6	97.8	18.5
B6		1.0	90.9	–	94.2	14.9	95.0	16.6	95.6	17.4
B7		1.5	92.0	14.2	94.0	14.7	90.8	15.7	89.8	16.5
B8	1.0	0.5	86.9	13.6	94.7	15.2	97.8	16.8	98.2	17.4
B9		1.0	92.2	14.5	95.1	15.6	96.4	17.8	95.6	17.5
B10		1.5	92.8	15.1	95.3	16.0	93.8	16.8	89.1	17.6
B11		1.8	93.9	14.3	94.4	15.8	89.2	16.5	81.9	17.2
B12		2.0	94.3	13.7	93.0	15.2	89.4	15.6	80.3	16.1
B13	1.5	0.75	96.0	14.2	98.2	14.1	97.9	15.5	99.9	16.2
B14		1.0	97.2	14.9	96.9	14.2	95.9	16.1	96.8	17.2
B15		1.5	98.0	15.3	97.6	14.5	95.6	15.7	91.0	16.4
B16		1.75	99.7	14.3	97.5	14.0	92.4	15.2	92.4	15.9
B17	2.0	1.0	99.6	14.1	98.7	15.2	95.6	16.3	95.4	15.7
B18		1.2	95.7	14.1	92.6	14.9	89.0	15.6	83.6	16.5



A3 A8 A14 A17

Fig. 6. Microstructure of sialons obtained by the mechanical mixing of individual Si_3N_4 and AlN nanocomponents sintered at 1650 °C

be expected in the case of pure α-sialon phase [8].

The decrease of α- sialon phase is especially explicit when Si_3N_4-AlN nanocomposite is used. The differences in material sintering process are related to the peculiarities of formation of used nanopowders: when Si_3N_4-AlN nanocomposite is produced in plasma, a lot of chemical interactions have been occurred already during producing of his composite: sialon phases possessing lower sintering temperature and less viscosity have been formed (for example, $Si_{1.8}Al_{0.2}O_{1.2}N_{1.8}$) [9]. Therefore the sintering of samples obtained from Si_3N_4-AlN nanocomposite occurs at lower temperature than for samples obtained from individual nanocomponents, but the product contains less α- sialon phase.

Microstructure of samples depends on their chemical composition (Fig. 6). Crystallite size of materials obtained from nanopowders at 1650 °C (both for α- and β- sialon) is ~100 nm, grain size is in the range of 200 nm – 300 nm. Considerable formation of needle-shaped crystals (especially for sample A14) begins at 1600 °C – 1650 °C. The average diameter of needle-shaped crystals is of approximately 200 nm and length – up to 2 µm.

CONCLUSION

The sintering temperature of ceramics samples made from Si_3N_4-AlN nanocomposite is lower than that for samples from separate nanocomponents. It has been found that sialons of some compositions sinter already starting from 1430 °C, but for most of composites at the region of α- sialons the temperature of approximately 1550 °C is necessary and only outside of the region of α- sialons higher sintering temperature is necessary. The common regularity has been observed: the sintering temperature of material decrease with the increase of coefficients „m” and „n” in the formula characterizing sialon composition.

Due to the peculiarities of used nanopowders (increased amount of oxygen adsorbed from the air on the surface of nanoparticles) obtained sialon ceramics contains more β- sialon phase resulting in a slightly decreased hardness of ceramics than it was expected for the α- sialon phase.

Acknowledgments

The research was made due to financial support of the European Structural Funds (Project No. 2009/0215/1DP/ /1.1.1.2.0/09/APIA/VIAA/082).

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Presented at the 20th International Baltic Conference
"Materials Engineering 2011"
(Kaunas, Lithuania, October 27–28, 2011)