The Effect of Raw Components on the Densification and Properties of Nanostructured Sialon Materials

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Abstract — **Two sialon compositions ($Y_{0,33}Si_{10,5}Al_{1,5}O_{0,5}N_{15,5}$ and $Y_{0,5}Si_{9,5}Al_{2,5}O_{1,0}N_{15,0}$) were used to determine the effect of starting components on densification and properties of sialon materials. Plasma synthesized nanopowders (Si_3N_4, AlN, Al_2O_3, Y_2O_3 and 73 wt% Si_3N_4-27 wt% AlN nanocomposite) were used for the investigation. Materials were sintered using traditional or spark plasma sintering methods. Sintering temperature was reduced significantly, if Si_3N_4-AlN nanocomposite was used as one of the components. The increased amount of α-sialon phase and higher hardness were characteristic to materials obtained from individual Si_3N_4, AlN, Al_2O_3, Y_2O_3 components.**

Keywords — **Nanocomposite, properties, sialon, traditional and spark plasma sintering.**

I. INTRODUCTION

Ceramic materials based on Si_3N_4 (including sialons) are characterized by outstanding mechanical properties (hardness, bending strength, etc.) at temperatures up to 1400 °C, and good wear and corrosion resistance [1]. These materials are promising candidates for application as structural materials at elevated temperatures [2].

The powder determines processing, sintering behaviour and subsequent formation of microstructure; microstructure has a strong effect on many properties of dense materials [3]. Diffusion velocity and diffusion distance are of great importance in compaction of compounds with covalent bonds, for example, sialons. The diffusion distance can be decreased by using nanosized raw powders for production of compact materials. As it is obvious from many investigations of compaction [4]–[6], the application of Si_3N_4 nanopowders enables to decrease the sintering temperature and to accelerate the sintering process. This results in material with more fine-grained structure and modified properties.

This investigation is based on previous research [7]–[8] and is a continuation of it. The aim of this paper was to show the effect of different nanosized starting components on densification, structure, phase composition and properties of sialon materials for two compositions.

II. EXPERIMENTAL

Two sialon composites — $Y_{0,33}Si_{10,5}Al_{1,5}O_{0,5}N_{15,5}$ (composition 1) and $Y_{0,5}Si_{9,5}Al_{2,5}O_{1,0}N_{15,0}$ (composition 2) — were prepared for research. Individual Si_3N_4, AlN, Al_2O_3, Y_2O_3 nanopowders (series A) and previously synthesized Si_3N_4-27 wt% AlN nanocomposite with Al_2O_3 and Y_2O_3 additives (series B) were used to prepare sialon compositions. These nanopowders and Si_3N_4-27 wt% AlN nanocomposite were prepared via plasma-chemical synthesis in nitrogen

plasma, using metallic (Si, Al) and oxide (Y_2O_3, Al_2O_3) powders as raw materials [9]. Their characteristics are given in Table I. Si_3N_4 nanopowder (both as pure nitride nanopowder and in nanocomposite Si_3N_4-AlN) contains up to 20 % crystalline Si_3N_4 (ratio α-/β- is approximately 1:1), the rest is X-ray amorphous Si_3N_4. Particles of pure Si_3N_4 nanopowders and Si_3N_4-AlN nanocomposite are irregular. Micrographs of these nanopowders are given in Fig. 1. Nanopowder of Al_2O_3 consists mainly of δ-Al_2O_3 and θ-Al_2O_3 phases. Y_2O_3 contains 30 wt % cubic phase and 70 wt% monoclinic phase.

TABLE I
CHARACTERISTICS OF THE STARTING POWDERS

Powder	Chemical composition, wt.%*					SSA, m^2/g	Average particle size, nm
	Si_3N_4	AlN	Al_2O_3	Y_2O_3	Si_{free}		
Si_3N_4	98.1	—	—	—	0.7	65	35
AlN	—	98.0	—	—	—	40	50
Y_2O_3	—	—	—	100	—	25	65
Al_2O_3	—	—	100	—	—	50	40
Si_3N_4-AlN	71.1	27.1	—	—	0.4	75	30

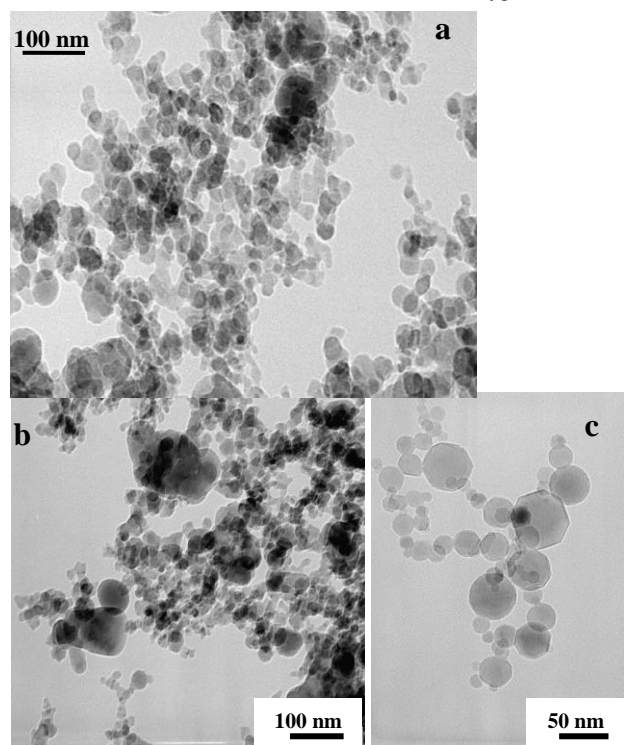* — shortfall in the mass balance is due to adsorbed oxygen from air.

Fig. 1. Micrographs of Si_3N_4 (a), Si_3N_4-AlN (b) and Al_2O_3 (c) nanopowders.

Samples of sialon ceramics were sintered using traditional or spark plasma sintering (SPS) methods. Traditional sintering was performed under nitrogen atmosphere at temperatures up to 1750 °C with heating rate 10 °C/min and an isothermal dwelling time of 2 h. Sialon nanopowders where prepared for traditional sintering as follows: 3 wt% stearic acid was mixed mechanically with sialon nanopowder for 1 h in planetary mill (400 rpm, vessel material — Si_3N_4, milling ball material — Si_3N_4) using isopropanol as dispersing environment. After mixing samples were dried in an oven at 80 °C and sieved. Samples where pressed (200 MPa) in pellets with 12 mm diameter and 4-6 mm height. Stearic acid was burned out at 600 °C.

SPS compacting was performed using *Toshiba* equipment (*Dr. SINTER*, *SPS-825.CE*): at 100 °/min up to 1600 °C, 50 °/min from 1600 °C to 1700 °C, isothermal dwelling time at 1700 °C was 5 min, samples were cooled with furnace. The load on sample was 30 MPa. Sintering was done in vacuum. Current pulsation rate was of 14 impulses per second.

Phase composition and crystallite size of specimens was determined using X-ray diffractometry (XRD) (*Advance D8*, *Bruker AXS*).

Particle size and morphology of powders was examined using transmitting electron microscope (TEM) (*Philips CM20*). The average particle size was evaluated from the data of specific surface area (SSA).

Density of sintered samples was determined using Archimedes method. Microstructure was observed by the scanning electron microscopy (SEM) (*Hitachi*, *S4800* and *Supra 40VP*, *Zeiss*, HR-SEM) on fracture surface. Hardness (HV_5, load 49 N) was measured using Vickers indentation technique.

III. RESULTS AND DISCUSSION

As it follows from [10], the sintering temperature of materials obtained from nanopowders was significantly lower than sintering temperature of materials obtained from sub-micron industrial powders. Our research showed that the choice of starting components also is significant in formation of materials. For example, if individual Si_3N_4 and AlN nanopowders were replaced by plasma-synthesized Si_3N_4-AlN nanocomposite with the same composition and dispersity, the sintering temperature of sialon decreased by approximately 100 °C (Fig. 2).

The differences in sintering process are due to the peculiarities of formation of nanopowders. A lot of chemical interactions in plasma synthesized Si_3N_4-AlN nanocomposite occur already during production of this composite. Some sialon phases (for example, $Si_{1.8}Al_{0.2}O_{1.2}N_{1.8}$) possess lower sintering temperature and have been less viscosity formed [11]. Therefore the samples obtained from Si_3N_4-AlN nanocomposite (B series) sinter at lower temperature than samples obtained from individual nanopowders, but the product contains less of α-sialon phase.

Also the hardness of B series samples reaches the maximum value at lower temperatures (Fig. 3). Such regularity has been observed also for composition 2.
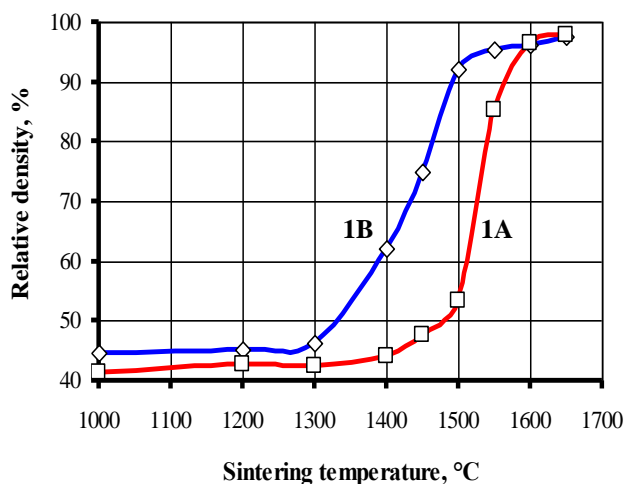

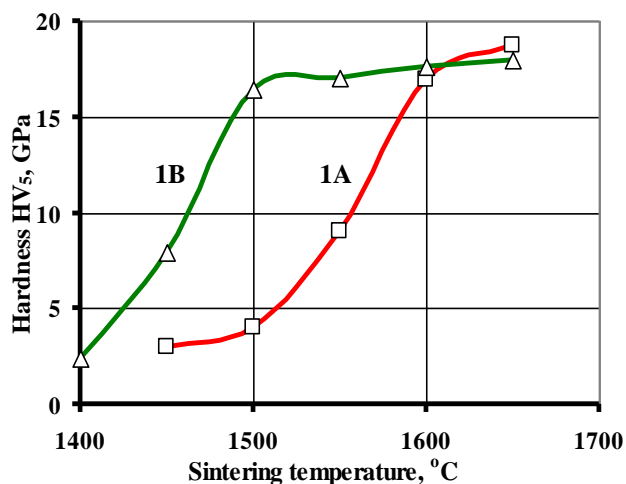**Fig. 2.** Change of relative density of samples with composition 1 during sintering.

Fig. 3. The dependence of sialon hardness on sintering temperature for samples with composition 1.

Microstructure of samples depended on their chemical composition (Fig. 4). Considerable formation of needle-shaped crystals (especially for sample with composition 2) began at 1600–1650 °C. The crystallite size of materials obtained at 1650 °C (for both α- and β-sialon) was approximately 100 nm, but the grain size is in the range of 200–300 nm (the average diameter of needle-shaped crystals) and length — up to 2 μm.

As shown by X-ray phase analysis, the content of α-sialon phase was about 50 % in the sample 1A and about 100 % in the sample 2A. The content of α-sialon in B series samples I was significantly lower (Fig. 5) for both compositions; this also determines the properties of materials, respectively hardness. Obviously the formation of α-sialon phases is more difficult for B series.
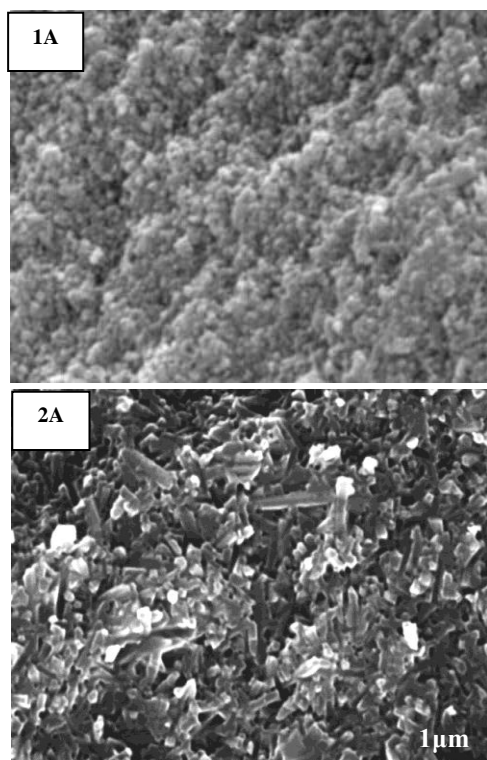
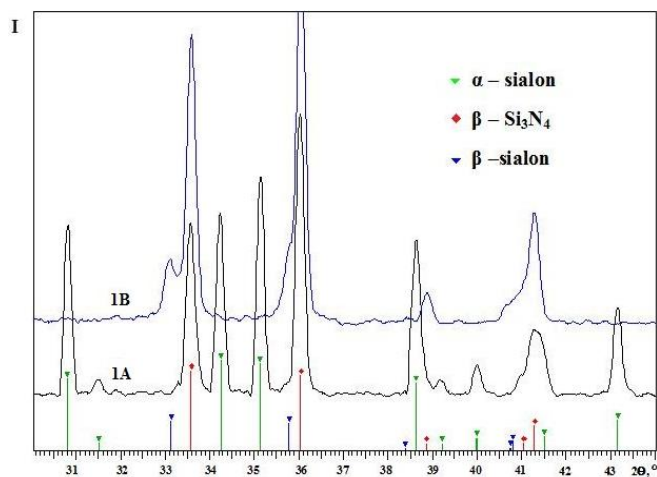**Fig. 4.** Microstructure of series A sialons sintered at 1650 °C.

Fig. 5. Phase composition of sialon of composition 1 sintered at 1600 °C.

Similar regularities have been observed using SPS sintering: series B samples stop shrinkage at the temperature, which is of about 100 °C lower than for series A samples (Table II).

TABLE II

CHARACTERISTICS OF SAMPLES SINTERED BY THE SPS METHOD (1700 °C)

No.	Temperature, °C		Relative density, %	Open porosity, %	HV$_5$, GPa	Crystallite size, nm
	beginning of shrinkage	end of shrinkage				
1A	1210	1600	97.8	0	16.8 ± 0.9	65–75
1B	1020	1500	96.4	0.3	15.7 ± 0.6	80–90
2A	1170	1550	97.8	0.2	17.1 ± 0.5	70–75
2B	1000	1450	96.0	0.3	15.5 ± 0.7	80–90

All characteristics of samples obtained using SPS method are almost the same as in the case of traditional sintering. An exception is the phase composition of samples sintered using SPS process: they consist of almost pure β-sialon phase. This partially explains lesser hardness of these samples in comparison to those produced by traditional sintering. This shows that the rapid increase of temperature and the short sintering time of SPS process results in a high density material, but is not sufficient to transition completely from β- to α-sialon.

Such a peculiarity of the SPS process can be explained by the formation of a specific phase during the thermal treatment of nanopowders. Contrary to the case of industrial powders (Si$_3$N$_4$ Ube), where α-sialon forms directly from α-Si$_3$N$_4$, in the case of nanopowders α- and β-Si$_3$N$_4$ phases first crystallize from amorphous Si$_3$N$_4$ until 1400 °C. Then with the rise of temperature (above 1400–1450 °C) silicon nitride transforms into β-sialon, which becomes the main phase at temperatures around 1500 °C [4]. Over 1500-1550 °C α-sialon begins to form and its amount increases together with temperature (Fig. 6.). At 1650 °C both sialon phases (α- and β-) exist, as well as a small amount of Y$_2$Si$_3$O$_3$N$_4$. It is obvious that at these experimental conditions short sintering time is too low for the formation of α- or α-/β- sialon phases corresponding to the phase diagram [12].
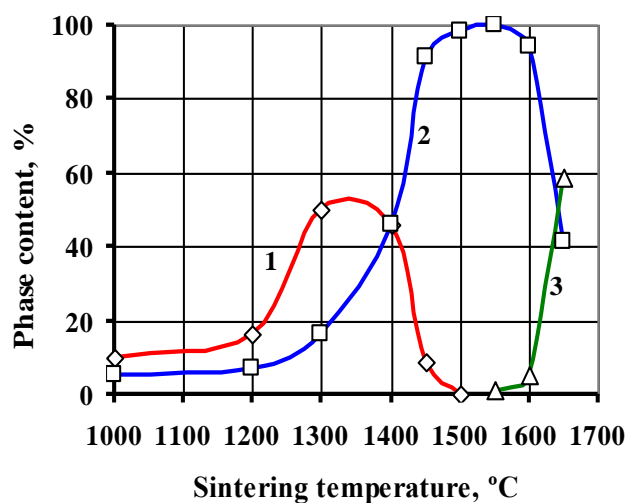

Fig. 6. Changes of phase composition of sialon 1A: 1 - α-Si$_3$N$_4$, 2 - β- Si$_3$N$_4$ and β- sialon, 3 - α-sialon.

IV. CONCLUSION

Two sialon compositions (Y$_{0.33}$Si$_{10.5}$Al$_{1.5}$O$_{0.5}$N$_{15.5}$ and Y$_{0.5}$Si$_{9.5}$Al$_{2.5}$O$_{1.0}$N$_{15.0}$) were prepared from plasma synthesized nanopowders (Si$_3$N$_4$, AlN, Al$_2$O$_3$ and Y$_2$O$_3$) and Si$_3$N$_4$— 27 wt% AlN nanocomposite. Materials were sintered by traditional and spark plasma sintering.

It was shown that in the case of spark plasma sintering short sintering time was not sufficient to form α-/β-sialon phases.

It was found that in the tradicional and SPS sintering process the sintering temperature decreased significantly, if Si$_3$N$_4$-AlN nanocomposite was used as one of the components. However, the increased amount of α- sialon phase and higher

hardness are characteristic for materials obtained from individual Si_3N_4, AlN, Al_2O_3 and Y_2O_3 nanopowders.

REFERENCES

1. **Schulz, I., Herrmann, M., Endler, I., Zalite, I., Speisser, B., Kreusser, J.** Nano Si_3N_4 composites with improved tribological properties. *Lubrication Science,* 2009, vol. 21, pp. 69–81. http://dx.doi.org/10.1002/ls.72
2. **Gogotsi, Yu. G.** Particulate silicon nitride-based composites. *J. Mater. Sci.*, 2000, vol. 29, pp. 2541–2556. http://dx.doi.org/10.1007/BF00356803
3. **Petzow, G., Hermann, M.** Silicon nitride ceramics. *Structure and Bonding*. Springer, Berlin, 2002, vol. 102, pp. 71–72.
4. **Bulic, F., Zalite, I., Zhilinska, N.** Comparison of plasma-chemical synthesised – SiAlON nano-powder and conventional prepared SiAlON-powder. *J. Eur. Ceram. Soc.*, 2004, vol. 24, pp. 3303–3306. http://dx.doi.org/10.1016/j.jeurceramsoc.2003.10.031
5. **Zhilinska, N., Zalite, I., Krumina, A., Costin, W., Mozdzen, G.** Sintern der Materialien auf der Basis unterschiedlicher Si_3N_4-Pulver. In *Verbundwerkstoffe, 14. Symposium Verbundwerkstoffe und Werkstoffverbunde*. (Degischer, H.P., DGM). WILEY-VCH, 2003, pp. 399–404. http://dx.doi.org/10.1002/9783527609017.ch64
6. **Zalite, I., Zhilinska, N., Krumina, A.** Sintering of plasma-chemically synthesized SiAlON nanopowder. In: *Nanomaterials and Nanotechnologies* (Zalite, I. and Krastins, J., eds.). Institute of Inorganic Chemistry of the Riga Technical University, Riga, 2005, pp. 98–103.
7. **Žilinska, N., Zālīte, I., Krastiņš, J.** Investigation of Production of Fine-grained SiAlON Ceramics from Nanopowders, Materials Science (Medžigotyra), vol. 18, No. 3, 2012, pp. 275–279. http://dx.doi.org/10.5755/j01.ms.18.3.2439
8. **Zalite, I., Zilinska, N., Steins, I.** The role of the raw components on compacting and properties of nanostructured sialon materials. Riga Technical University 55th International Scientific Conference, Section "Material Science and Applied Chemistry", Book of abstracts, RTU Press, October 14–17, Riga, 2014, p. 41.
9. **Zalite, I., Grabis, J.** Nanosize Powders of Refractory Compounds for Obtaining of Fine-Grained Ceramic Materials. *Materials Science Forum,* 2007, vol. 555, pp. 267–272. http://dx.doi.org/10.4028/www.scientific.net/MSF.555.267
10. **Zalite, I., Zhilinska, N., Kladler, G.** α-SiAlON Ceramic from Nanopowders. *Powder Metallurgy Progress,* 2006, vol. 6, no. 2, pp. 88–93.
11. **Shveikin, G.P., Lukin, N.V., Khoroshavin, L. B.** SiAlONs – Promising Refractory and Ceramic Materials. *Refractories and Industrial Ceramics,* 2003, vol. 44, pp. 52–58. http://dx.doi.org/10.1023/A:1023923929851
12. **Kurama, S., Herrmann, M., Mandal, H.** The Effect of Processing Conditions, Amount of Additives and Composition on the Microstructure and Mechanical Properties of -SiAlON Ceramics. *J. Eur. Ceram. Soc.*, 2002, vol. 22, pp. 109–119. http://dx.doi.org/10.1016/S0955-2219(01)00237-0

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Ilmārs Zālīte, Ints Šteins, Natalja Žilinska. Izejas materiālu ietekme uz nanostrukturētu sialona materiālu saķepšanu un īpašībām.
Darbs veltīts dažādu izejas komponentu lomas noskaidrošanai sialonu kompozīcijas izveidē, kompakta materiāla ieguvē un ietekmē uz iegūtā materiāla īpašībām. Izgatavotas divas atšķirīgas α-sialona ($Y_{0,33}Si_{10,5}Al_{1,5}O_{0,5}N_{15,5}$ un $Y_{0,5}Si_{9,5}Al_{2,5}O_{1,0}N_{15,0}$) kompozīcijas kā izejvielas izmantojot augstfrekvences plazmā sintezētas Si_3N_4, AlN, Al_2O_3 un Y_2O_3 nanokomponentes (A sērija) un Si_3N_4–27 masas % AlN nanokompozītu (B sērija) ar Al_2O_3 un Y_2O_3 piedevām sastāva koriģēšanai. Kompaktu materiālu ieguvei izmantota klasiskā bezspiediena saķepināšana slāpekļa vidē (temperatūras celšanas ātrums 10 °C/min.; izturēšanas laiks 2 h) vai dzirksteļizlādes plazmas saķepināšana (temperatūras celšanas ātrums 100 °C/min.; izturēšanas laiks 5 min.) temperatūrās līdz 1700 °C. Kā ir pierādīts iepriekš, no nanopulveriem iegūto materiālu saķepināšanas temperatūra ir ievērojami zemāka nekā no submikrona izmēra rūpnieciski ražotiem pulveriem. Mūsu pētījumi liecina, ka būtiska loma sialona materiāla saķepšanā ir arī nanoizmēra izejas komponentu izvēlei. Piemēram, aizstājot atsevišķu Si_3N_4 un AlN nanopulveru maisījumu ar plazmā sintezētu tāda paša sastāva un dispersitātes Si_3N_4-AlN nanokompozītu, sialona saķepšanas temperatūra samazinās par aptuveni 100 °C. Turpretim, materiāliem, kas iegūti no atsevišķām Si_3N_4, AlN, Al_2O_3 un Y_2O_3 nanokomponentēm, ir raksturīgs palielināts α-sialona fāzes saturs un augstāka cietība. Tas varētu būt saistīts ar izmantoto nanopulveru veidošanās īpatnībām: iegūstot Si_3N_4-AlN nanokompozītu plazmā daudzas ķīmiskās mijiedarbības ir notikušas jau iegūšanas laikā — veidojas sialonu saturošas fāzes ar zemāku saķepšanas temperatūru un mazāku viskozitāti (piemēram, $Si_{1,8}Al_{0,2}O_{1,2}N_{1,8}$). Tāpēc paraugu, kas iegūti no Si_3N_4-AlN nanokompozīta, saķepšana notiek zemākā temperatūrā nekā paraugiem, kas iegūti no atsevišķām nanokomponentēm. Paraugu fāžu sastāvs ir atkarīgs no to ķīmiskā sastāva: rentgenstruktūras analīze parāda, ka α-sialonu fāzes saturs 1A paraugā ir aptuveni 50 % un paraugā 2A — aptuveni 100 %. B sērijas paraugos α-sialonu saturs ir ievērojami zemāks; tas arī nosaka materiālu īpašības, piemēram, cietību.
Paraugu mikrostruktūru lielā mērā nosaka gan to ķīmiskais sastāvs, gan kompaktēšanas temperatūra. Materiālu, kas iegūti no nanopulveriem 1600 °C temperatūrā gan α-, gan β-sialonu fāžu kristalītu izmērs ir ∼ 100 nm, graudu lielums ir 200–300 nm. Ievērojama adatveida kristālu veidošanās (īpaši 2A paraugam) sākas 1600–1650 °C. Vidējais adatveida kristālu diametrs ir aptuveni 200 nm un to garums ir līdz 2 µm.