



# Synthesis of $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$ powder by SHS method

WIKTORIA WIERZBA, KAROL OSTALECKI, ZBIGNIEW PĘDZICH, MIROSLAW M. BUĆKO\*

AGH University of Science and Technology, Faculty of Materials Science and Ceramics  
al. Mickiewicza 30, 30-059 Kraków  
\*e-mail: bucko@agh.edu.pl

## Abstract

The self-propagating high temperature synthesis, SHS, was used to prepare sialon with the assumed stoichiometry of  $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$  ( $z = 4$ ). Powders of elemental Al, elemental Si,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  were chosen to prepare starting mixtures. Molar proportions between elemental silicon and elemental aluminium were changed, and the amounts of aluminium and silicon oxides resulted from the assumed stoichiometry. The mixtures of powders in the form of a loose bed were placed within a high-pressure reactor in a graphite container. The SHS reaction was initialized by a flow of current through the container. The reaction was carried out in the nitrogen atmosphere under a pressure of 0.1 MPa, 1 MPa, or 3 MPa. The influence of composition, grain size distribution of the starting powders and nitrogen pressure on SHS synthesis products was checked by the XRD and SEM methods.

**Keywords:** Sialon, SHS, Phase composition, Powder, Morphology

## SYNTEZA PROSZKU $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$ METODĄ SHS

Samorozwijająca się synteza wysokotemperaturowa (SHS) została użyta do wytworzenia proszku  $\beta$ -sialonu o założonej stechiometrii  $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$  ( $z = 4$ ). Jako surowce wyjściowe wybrano proszki pierwiastkowego Al, pierwiastkowego Si,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ . Zmieniało proporcje molowe pomiędzy pierwiastkowym krzemem i pierwiastkowym glinem, a ilość użytych tlenków glinu i krzemu wynikała z założonej stechiometrii. Mieszanki proszków w formie luźnego złoża były umieszczane w komorze wysokociśnieniowej w grafitowym pojemniku. Reakcja SHS była inicjowana przepływem prądu przez pojemnik. Atmosfera azotu dla przeprowadzenia reakcji była ustalana na poziomie 0,1 MPa, 1 MPa i 3 MPa. Badano wpływ składu chemicznego mieszanki wyjściowej, rozkładu wielkości ziaren surowców oraz ciśnienia azotu na powstające proszki sialonowe. W tym celu wykorzystano metodę dyfrakcji rentgenowskiej (XRD), mikroskopii skaningowej (SEM) oraz piknometrii helowej.

**Słowa kluczowe:** sialon, SHS, skład fazowy, proszek, morfologia

## 1. Introduction

Ceramic materials are very interesting because of their possibility of wide applications in various technical fields. Recently a significant care has been taken on oxy-nitride materials due to their unique high-temperature properties, which make them to be refractory products. The development of the areas in which refractory materials are used entails the production of new materials with improved functional properties. One of them are sialon materials with the general formula  $\text{Si}_{6-z}\text{Al}_2\text{O}_z\text{N}_{8-z}$ , where  $z$  ranges from 0 to 4.2. It is based on the atomic arrangement existing in the  $\text{Si}_3\text{N}_4$  polymorphs, where a part of Si is replaced by Al with a corresponding atomic replacement of N by O [1–4]. The most interesting characteristics of sialons is constituted by very good high temperature properties, such as excellent thermal shock resistance, low thermal expansion, good oxidation resistance, and stability up to 1800 °C. Moreover, they have good mechanical properties, for example high strength and good fracture toughness [1–3, 5, 6]. As a result sialons are great for metal casting applications [1, 3, 7, 8], wear components [9], cutting tools [1, 4, 8], gas turbines, and engine components [1, 8, 10].

One of the most popular conventional method of producing sialons is carbothermal reduction nitridation (CRN) [8, 9, 11–13]. Unfortunately, this technology is considered to be time-consuming. The self-propagating high-temperature synthesis (SHS) is the technology, which solves this problem. This method is also called a combustion synthesis (CS) and consists in using heat released during the exothermal reaction to self-heating a set of reagents to high temperature which creates specific conditions for chemical synthesis. The reaction is initialized by a current flow through the powder mixture in the form of a loose bed, and can be carried out in an inert atmosphere or in gas which is one of the reagent, for example in nitrogen. The reaction is highly exothermic and as a result it is self-propagating. This leads to a cost-effective and rapid preparation of sialon ceramics [14–16], and that is why it was used in the presented work.

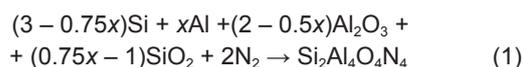
The aim of the presented study was to investigate the effect of change in the ratio of two components, elemental aluminium and elemental silicon on the possibility of forming sialon of the  $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$  stoichiometry by the SHS. In the proposed system the temperature increase as a basis of the SHS process was carried out by the nitridation reaction of elemental silicon and elemental aluminium due to its highly

exothermic nature. In the study definite ratios of elemental silicon to elemental aluminium ( $Si_{el.}/Al_{el.}$ ) were assumed, and relevant proportions of other substrates calculated.

## 2. Experimental

The starting mixture of powders were prepared of appropriate amounts of elemental Al (P.Ch. Stanchem, Poland, 68.61  $\mu\text{m}$ ), elemental Si (waste product from monocrystals production, 6.45  $\mu\text{m}$ ),  $Al_2O_3$  (EA1200, P.P.U.H. KOS, Poland, 5.18  $\mu\text{m}$ ) and  $SiO_2$  (Aerosil® OX 50, Evonik Industries AG, Germany, 0.52  $\mu\text{m}$ ) powders. The proportions between substrates were established to obtain a sequence of mixtures starting from a mixture containing elemental silicon, elemental aluminium and aluminium oxide with no  $SiO_2$ , and finishing on one containing elemental aluminium, both oxides and no elemental silicon. The phase contents of the starting powder mixtures are presented in Table 1. It indicates that elemental silicon replaced  $SiO_2$  in the precursor mixture in an amount ranging from 0 mol.% to 100 mol.%, simultaneously the replacement of  $Al_2O_3$  by elemental Al ranged from 100 mol.% to 33 mol.%.

The formal chemical reaction of the synthesis of the assumed stoichiometry of sialon can be represented as follows:



where  $x = 1.33 - 4.00$ .

Preparation of powder mixtures started from homogenization in a rotatory-vibratory mill in isopropyl alcohol for 2 h using  $Si_3N_4$  grinding media. After homogenization, the slurry was subsequently dried in a laboratory dryer at 40°C for at least 8 h until the powder mixtures were completely free of alcohol. Then the mixtures were placed in a high-pressure reactor in a graphite container in the form of a loose bed in batches of about 30 g. The reactor chamber was filled up with nitrogen to a pressure 0.1 MPa, 1 MPa, or 3 MPa. The reaction was initialized by passing a current of 200 A for 5 minutes through the graphite container. The obtained products were crushed in a jaw-crusher and milled in a rotatory-vibratory mill in isopropyl alcohol for 6 h using the  $Si_3N_4$  grinding media. After milling, the resultant slurries were dried in the laboratory dryer in 40°C for at least 8 h.

Based on obtained results influence of aluminium grain size on sialon formation was also investigated. In such case

three different aluminium powders (APS 7/99.7 – 8.05  $\mu\text{m}$ , AG 45/99.8 – 15.79  $\mu\text{m}$ , AG 63/99.7 – 35.53  $\mu\text{m}$ , Benda-Lutz, Austria) were used as a precursor. The phase content of the starting powder mixtures corresponds to 2 mole of Si and 1.33 mole of Al and  $Al_2O_3$ . A pressure of nitrogen was equal 3 MPa.

The phase composition of synthesized powders was analyzed using the X-ray diffraction method (XRD) (Empyrean, Panalytical). The morphology of the reaction products was examined by means of scanning electron microscopy (SEM) (Nova NanoSEM™, FEI Company).

## 3. Results and discussion

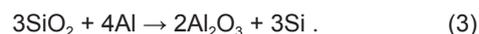
Fig. 1 summarizes the phase compositions of the powders synthesized under different pressures of nitrogen as a function of the elemental Si content; product phases and the residue of substrates are shown separately. As it can be seen, the final products consisted of a few phases according to the composition of the reagents and pressure of nitrogen.

For the samples with higher amounts of elemental aluminium, containing simultaneously up to 1 mole of the elemental Si in the powder mixture, the primary reaction is the formation of aluminium nitride, and then its reaction with  $Al_2O_3$  according to a formal equation:



which product is aluminium oxynitride with the spinel structure,  $\gamma$ -alon.

The mentioned samples show high contents of silicon, even higher than the elemental silicon content in the substrate powder mixtures (Fig. 2), accompanied by a lack of silicon oxide. It reveals that  $SiO_2$  is reduced by elemental aluminium as follows:



In this range of phase composition the synthesis of sialon is limited; an increase in sialon content is observed for the samples with higher amounts of silicon. It is worth noting that any form of silicon nitride was detected in the SHS-derived powders. This suggests that the sialon phase can be formed in the following reaction:

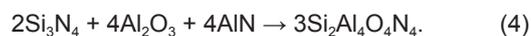


Table 1. Compositions of starting powder mixtures.  
Tabela 1. Skład wyjściowych mieszanek proszkowych.

Content [mole]				$Si_{el.}/Al_{el.}$
Elemental Si	Elemental Al	$Al_2O_3$	$SiO_2$	
0.000	4.000	0.000	2.000	0
0.333	3.556	0.222	1.667	10.68
0.667	3.111	0.444	1.333	4.66
1.000	2.667	0.667	1.000	2.67
1.333	2.222	0.889	0.667	1.67
1.667	1.778	1.111	0.333	1.07
2.000	1.333	1.333	0.000	0.67

The reaction between  $\gamma$ -alon and silicon leading to the formation of sialon should also be taken into account:



The indicated reactions responsible for the sialon synthesis are in good agreement with literature suggestions [17].

It can be stated that the increase of nitrogen pressure led to an increase in sialon content in the SHS-derived powders, and this effect was stronger the higher was the nitrogen pressure (Fig. 3). The increase of nitrogen pressure promoted volatilization of silicon and the formation of Si-N phases during combustion [18] due to higher temperatures of the SHS process.

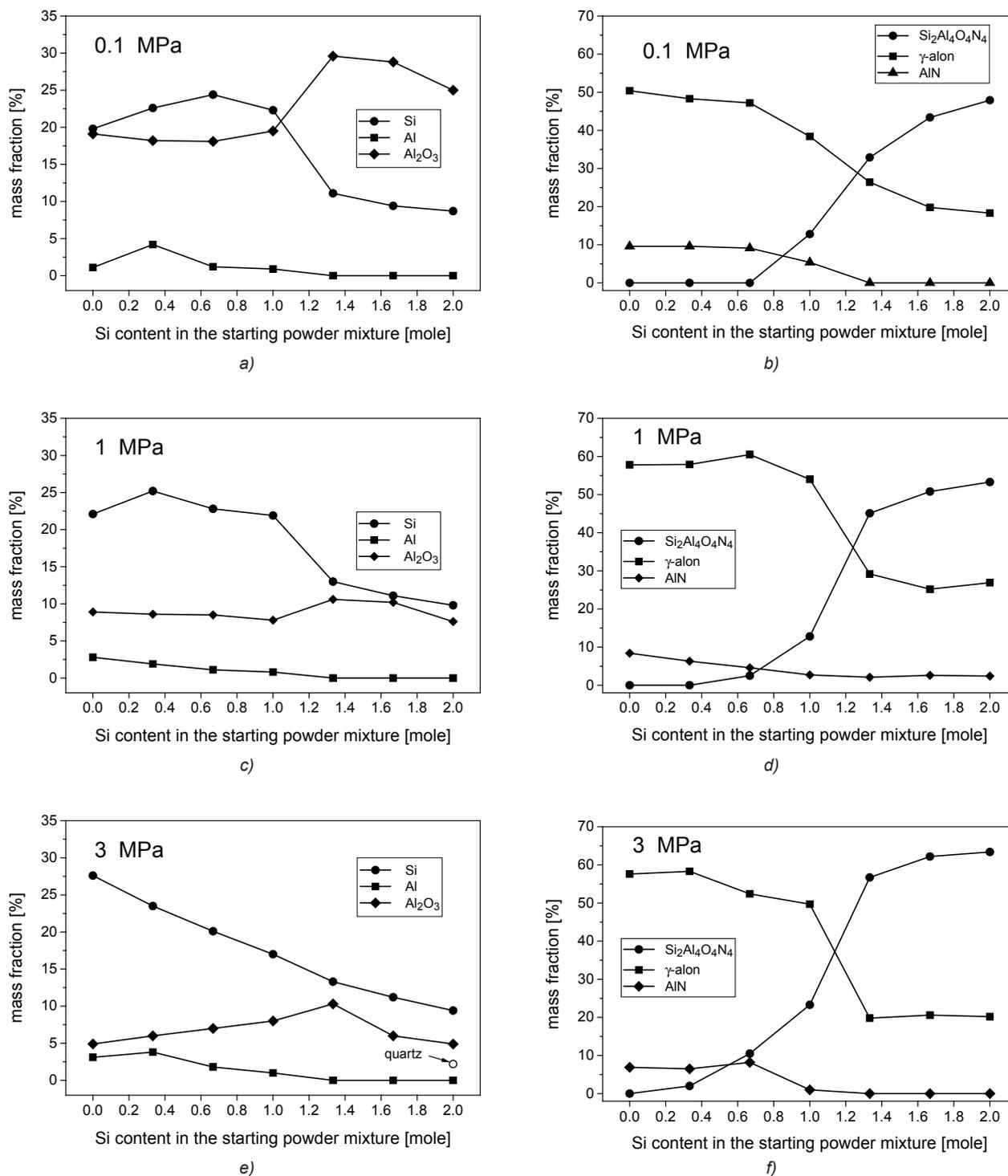


Fig. 1. Phase composition of SHS-derived powders as a function of elemental silicon (Si) content and nitrogen pressure: a), c), e) product phases, and b), d), f) substrate phases.

Rys. 1. Skład fazowy proszków otrzymanych metodą SHS jako funkcja zawartości pierwiastkowego krzemu i ciśnienia azotu: a), c), e) produkty i b), d), f) substraty.

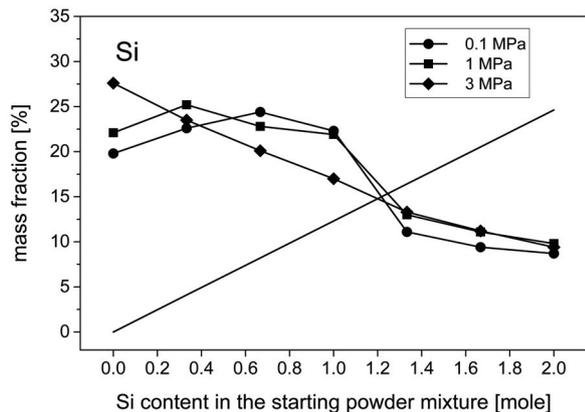


Fig. 2. Content of silicon in the SHS-derived powders as a function of elemental silicon (Si) content in the starting mixtures. A straight line illustrates the elemental silicon content in the corresponding mixtures.

Rys. 2. Zawartość krzemu w proszkach otrzymanych metodą SHS w funkcji zawartości krzemu pierwiastkowego w mieszance wyjściowej. Linia ciągła ilustruje zawartość krzemu pierwiastkowego w odpowiednich mieszankach.

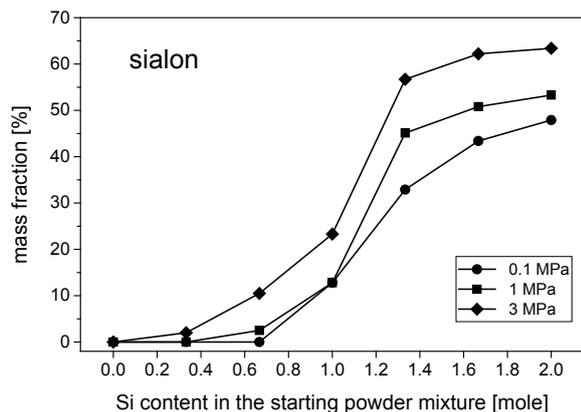


Fig. 3. Sialon content in the SHS-derived powders in relation to elemental silicon content and nitrogen pressure.

Rys. 3. Zawartość sialonu w proszkach otrzymanych SHS w zależności od udziału krzemu pierwiastkowego i ciśnienia azotu.

Fig. 4 shows the influence of aluminium powder morphology on formation of the sialon phase. The analysis of the phase composition of powders after the SHS synthesis led to the conclusion that there was a strict dependence between the grain size of aluminium and the amount of  $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$  phase. As shown in Fig. 4, the amount of sialon grows with decreasing the size of aluminium powder. What is more, the SHS-derived powders were composed only with four phases:  $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$  as the majority, and  $\gamma$ -alon, Si and  $\text{Al}_2\text{O}_3$  as minor phases. Aluminium, AlN and quartz were not observed. In that case the results indicated that the decrease in grain size of the substrates significantly increased efficiency of the synthesis which resulted in an increased degree of conversion to  $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$ .

The SHS-derived powders exhibited complex morphologies, as it can be seen in Fig. 5. Sialon and AlN could be observed as hexagonal, elongated grains. Moreover, long thin fibers, which could be the remnants of a liquid phase, were probably also AlN. The grains of  $\gamma$ -alon existed as cubic ones. Large, homogeneous areas could be recognized as molten silicon and aluminium. The observed diversity in the morphology of particles could be attributed to the complex run of the SHS process.

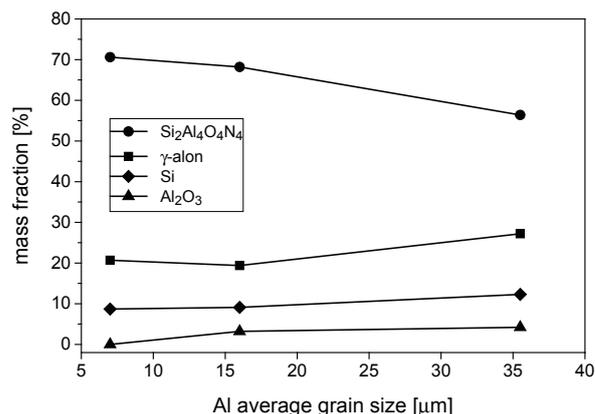


Fig. 4. Effect of the average grain size of elemental aluminium on the phase composition of the final product.

Rys. 4. Wpływ średniej wielkości ziaren aluminium na skład fazowy końcowego produktu.

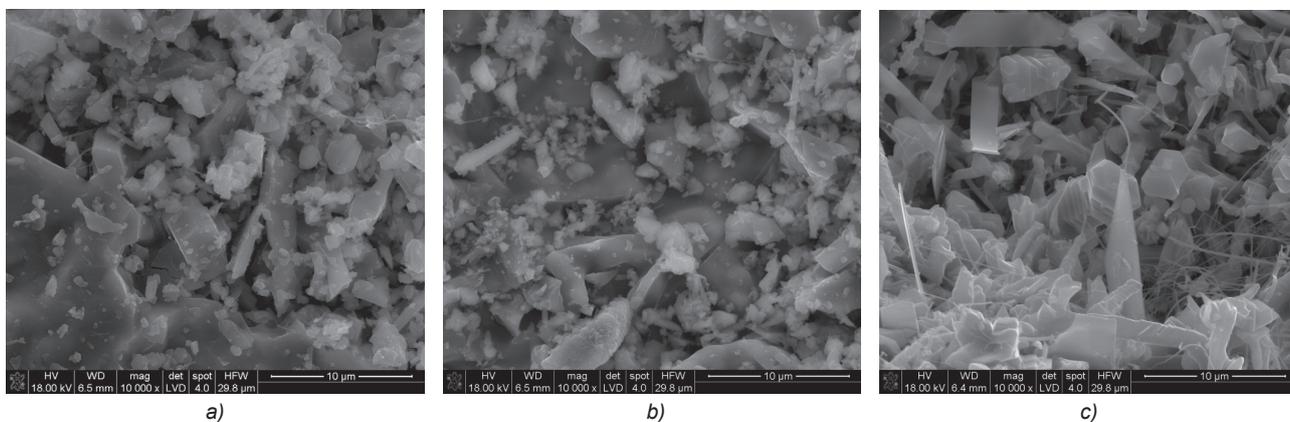


Fig. 5. SEM images of the SHS powders derived from mixtures with the highest (2 moles) (a), middle (1 mole) (b), and the least (0 moles) (c) amount of elemental silicon. Pressure of nitrogen atmosphere was 3 MPa.

Rys. 5. Obrazy SEM proszków otrzymanych metodą SHS z mieszanin o najwyższej (2 mole) (a), średniej (1 mol) (b) i bez zawartości (0 moli) (c) krzemu w próbkach. Ciśnienie azotu wynosiło 3 MPa.

## 4. Conclusions

The performed experiments proved that the SHS technique could be used for producing low-cost sialon powders with reasonable efficiency using elemental silicon and elemental aluminium added to  $\text{Al}_2\text{O}_3/\text{SiO}_2$  substrate mixtures. The obtained sialon products were multi-phase, and their phase composition strongly depended on the starting mixture composition. The most promising phase composition of the sialon product was achieved when the starting mixture contained the highest amount of elemental silicon. The resulting powder was characterized by the highest degree of conversion of precursors to sialon. Moreover, the amounts of non-oxide remnants in this powder remained at the lowest level. The experiment indicated that the amount of sialon in the product powder increased with the nitrogen pressure increase. In that case the pressure of 3 MPa was recognized as optimal. What is more, the amount of  $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$  increased up to 80% with decreasing the average grain size of substrates. Measured densities of the SHS-derived powders showed a strict dependence upon the phase composition. The conducted experiments indicated the substrates ratio, the grain size, and the nitrogen pressure as the most important factors influencing the final phase composition of the sialon powders. However, they did not result in a ready recipe for pure  $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$  powder manufacturing. Due to the complex run of the SHS synthesis, optimization of  $\text{Si}_2\text{Al}_4\text{O}_4\text{N}_4$  synthesis process should be performed, using the results of the presented work.

## Acknowledgement

The present work was supported by the AGH University of Science and Technology, Faculty of Materials Science and Ceramics under the grant nr 11.11.160.617.

## References

- [1] Jack, K. H.: Review: Sialons and related nitrogen ceramics, *J. Mater. Sci.*, 11, (1976), 1135–1158.
- [2] Ekstrom, T., Nygren, M.: Sialon Ceramics., *J. Am. Ceram. Soc.*, 75, 2, (1992), 259–276.
- [3] Jack, K. H., Wilson, W. I.: Ceramics Based on the Si-Al-O-N and Related Systems, *Nat. Physic. Sci.*, 238, (1972), 28–29.
- [4] Riley, F. L.: Silicon Nitride and Related Materials, *J. Am. Ceram. Soc.*, 83, 2, (2000), 245–265.
- [5] Dutta, S.: State-of-the-Art of Sialon Materials, in *Proceedings of 49<sup>th</sup> Meeting of the Structures and Materials Panel Including a Specialist Meeting on Ceramics for Turbine Engine Applications*, 7–12 Oct. 1979, Cologne, Germany.
- [6] Pawlik, T., Sopicka-Lizer, M., Mikruskiewicz, M., Gwizdź, M.: Corrosion resistant sialon-based refractories for applications in the aluminium industry, *Mater. Ceram. / Ceram. Mater.*, 61, 4, (2009), 250–252.
- [7] Ekström, T., Kall, P. O., Nygren, M., Olsen, P. O.: Dense single-phase  $\beta$ -Sialon ceramics by glass-encapsulated hot isostatic pressure, *J. Mater. Sci.*, 24, (1989), 1853–1861.
- [8] Gilbert, J. E., Mosset, A.: Preparation of  $\beta$ -Sialon from coalmine schists, *Mater. Res. Bull.*, 10, 32, (1997), 1441–1448.
- [9] Uludag, A., Turan, D.: SiAlON Ceramics for the High Temperature Applications: High Temperature Creep Behavior, *Int. J. Mater., Mech. Manuf.*, 2, (2015), 105–109.
- [10] Yang, G., Yin, L., Fang, X., Fang, M., Liu, Y., Huang, Z., Liu, B.: Fabrication and liquid-solid, two-phase erosion wear behaviour of  $\beta$ -Sialon ceramic from pyrophyllite by carbothermal reduction and nitridation, *Ceram. Int.*, 40, (2014), 10737–41.

- [11] Mackenzie, K. J. D., Meinhold, R. H., White, G. V., Sheppard, C.M., Sherriff, B. L.: Carbothermal formation of  $\beta$ -sialon from kaolinite and halloysite studied by  $^{29}\text{Si}$  and  $^{27}\text{Al}$  solid state MAS NMR, *J. Mater. Sci.*, 29, (1994), 2611–2619.
- [12] Zheng, J., Forslund, B.: Carbothermal Preparation of  $\beta$ -SiAlON Powder at Elevated Nitrogen Pressures, *J. Eur. Ceram. Soc.*, 19, (1999), 175–185.
- [13] Liu, X. J., Sun, X. W., Zhang, J. J., Pu, X. P., Ge, O. M., Huang, L. P.: Fabrication of  $\beta$ -Sialon powder from kaolin, *Mater. Res. Bull.*, 38, (2003), 1939–1948.
- [14] Lis, J.: Sinterable powders of covalent compounds produced by self-propagating high temperature synthesis (SHS) (in Polish), *Ceramika/Ceramics*, 44, (1994), 91–108.
- [15] Puszynski, J. A., Dargar, S. R., Liebig, B. E.: Combustion Synthesis of Ceramics Composites and Solid Solutions from Nanoreactants in Innovative Processing and Synthesis of Ceramics, Glasses and Composites VIII, Proceedings of the 106<sup>th</sup> Annual Meeting of The American Ceramic Society, Indianapolis, Indiana, USA, 2004, Bansal, N. P., Singh, J. P., Schneider, H. (Eds), *Ceramic Transactions*, 166, (2005), 11–21.
- [16] Niu, J., Nakamura, T., Nakatsugawa, I., Akiyama, T.: Reaction characteristics of combustion synthesis of  $\beta$ -Sialon using different additives, *Chem. Eng. J.*, 241, (2014), 235–242.
- [17] Xuemei, Y., Niu, J., Nakamura, T., Akiyama, T.: Reaction mechanism for combustion synthesis of  $\beta$ -Sialon using Si, Al and  $\text{SiO}_2$  as raw materials, *J. Alloys. Compd.*, 561, (2013), 1–4.
- [18] Wang, H., Han, J.-C., Du, S.: Effect of nitrogen pressure and oxygen-containing impurities on self-propagating high temperature synthesis of  $\text{Si}_3\text{N}_4$ , *J. Eur. Ceram. Soc.*, 21, (2001), 297–302.



Received 5 October 2016, accepted 27 November 2016.