21R-Sialon ceramics, obtained by hot pressing

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Abstract. The formation, densification behaviour and mechanical properties of 21R polytype were studied. Self-propagating high-temperature synthesis obtained the starting powder of 21R-sialon. Sealing was carried out by hot pressing in the temperature range 1650-1800°C. With increasing temperature, there is an increase in density and mechanical properties.

1. Introduction
Silicon nitride is one of the most promising high-temperature materials. Silicon nitride and materials based on it have a high operating temperature up to 1400-1750°C, wear resistance, chemical inertness, high (especially silicon nitride) strength and crack resistance [1, 2]. Therefore, the appearance of these materials made it possible to raise the issue of replacing metal products with ceramic ones for operation in extreme thermomechanical conditions, for example, in the hot zone of gas turbine and piston engines. The replacement of carbide and other types of cutting tools with a more efficient ceramic tool continues, ceramics favourably differs from them, for example, in the field of processing of cast iron or superalloys. Currently, research is being conducted to use nitride and silicon carbide products in virtually all industries in developed countries. They have already found wide application in aerospace, metallurgy, chemical, electronic and other industries [3, 4].

There are several Sialon types: α; β; X; O1; H; R [1-8]. Sialons are Si-Al-O-N phase and related systems. They consist of tetrahedra (Si, Al)(O, N)₄. Double compounds are distributed in the edges of the tetrahedron. All of existed combinations that contain four elements are distributed in the plane of Si₃N₄-SiO₂-Al₂O₃-AlN. It is possible to separate the areal to two isosceles triangles, they consist of two systems Si₃N₄-Al₂O₃-SiO₂ and Si₃N₄-Al₂O₃-AlN [9-11].

R-sialons - one of the types of sialons - are poorly studied materials, and are practically not mentioned in the literature. There are three modifications of R-Sialons: 15R (Si₁₆₋ₓAl₁₄₋ₓOₓN₂₋ₓ), 21R (Si₁₆₋ₓAl₁₈₋ₓOₓN₁₆₋ₓ) and 27R (Si₁₆₋ₓAl₂₀₋ₓOₓN₂₀₋ₓ) [12]. Literary sources describe very scarce information on the synthesis of each polytype and the results of studying the properties of these materials are practically absent. Basically, R-Sialons are mentioned as side phases in the synthesis of α- and β-sialons [13-15].

In the last two years, a number of articles by the Indian scientist Mita Biswas from the Central Research Institute of Glass and Ceramics of India have been published. Mita Biswas actively studies the properties of R-Sialons and states in its works that this material is underestimated, as it has high mechanical properties that are almost identical to α- and β-sialons [16]. Ceramics based on the R-
modification of sialon mainly contain elongated or prismatic grains - this contributes to the emergence of the so-called self-reinforcing effect, which makes it possible to use sialon ceramics to create wear-resistant products. The researcher also notes the lack of generalized information on R-sialons [16-18].

The work aimed to obtain, by hot pressing, 21R-Sialon ceramics based on powders synthesised by the method of self-propagating high-temperature synthesis (SHS). SHS technology is based on the initiation of an exothermic chemical reaction of silicon with nitrogen and the further spontaneous propagation of the combustion front in powder mixtures with the formation of silicon nitride. The significant thermal effect of the SHS reaction of the interaction of nitrogen with silicon makes it possible to obtain powders with high yield without supplying heat from external sources [19].

2. Materials and Method

Commercial 21R-Sialon powders obtained by the SHS method (PLATINA LLC) were used as the initial ones. The 21R-Sialon powder is represented by well-crystallized particles with an average of 0.1-2 microns (Figure 1). The specific surface of the powder is 12 m²/g. The phase composition of the powders is shown in Figure 2.

The powder was subjected to mechanical activation in a planetary mill for 60 min in isopropyl alcohol. Balls made of zirconium dioxide with a diameter of 5 mm were used as grinding bodies. The dried mixture was forced through a sieve № 0063.

![Figure 1. SEM image 21R- Sialon powder.](image)

Before firing, dilatometric studies of the studied powder were performed. Figure 3 shows the curve of continuous shrinkage of 21R-Sialon in the temperature range 20-1800°C. The sintering temperature of the 21R-Sialon is 1689°C. Based on this temperature, subsequent hot pressed in the temperature range 1650-1800°C in increments of 50°C. Before firing samples were prepared in the form of disks (25 mm diameter) charge by the semi-dry pressing method from the received.
Figure 2. XRD patterns 21R- Sialon powder

Figure 3. The curve of continuous shrinkage of 21R-Sialon in the temperature range of 20-1800°C.

For dense ceramics used hot pressing furnace Thermal Technology Inc. high temperature experts, model HP20-3560-20. To identify the phase and chemical composition were used X-ray diffraction analysis was used (XRD 6000 SHIMADZU diffractometer, CuKα radiation, λ = 1.5406 Å, scanning speed 2θ = 2 deg/min). The phase composition of the samples was identified using the PDF-2 database, JCPDS-ICDD (Set 1-2002). Morphology and structural features of the samples were studied by scanning electron microscopy (electron microscope NVision 40, Carl Zeiss). Density and open porosity were measured by the Archimedes method using water. The flexural strength three bending test were studied by Instron 5581. The microhardness test was studied by Micro-hardness Tester 401/402 MVD.

3. Results and discussion
The structure and ceramic properties of these samples were studied after sintering. With an increase in the sintering temperature, 21R-Sialon crystals grow (Figure 4). If at a firing temperature of 1650°C there is a large number of crystals of 1-2 μm with single crystals of 5 μm (Figure 4a), then at a firing temperature of 1800°C the size of crystals is 5-6 μm (Figure 4d).
Figure 4. SEM images of 21R-SiAlON ceramic HP processed at (a) 1650, (b) 1700, (c) 1750 and (d) 1800 °C for 60 min under 30 MPa in nitrogen.

The properties of 21R-Sialon ceramic samples are presented in Table 1. An increase occurs with increasing temperature. Density from 2.47 g/cm$^3$ to 2.86 g/cm$^3$, open porosity from 24.4% to 8.6% and flexural strength from 98 MPa to 195 MPa. Due to the high porosity, Sample 1 and Sample 2 microhardness could not be measured. Microhardness of Sample 3 and Sample 4 was 10.1 GPa and 13.5 GPa, respectively.

The maximum density of the samples is not large and amounts to 2.86 g/cm$^3$, but it is higher than in [7], where under the same sintering conditions a density of 2.605 g/cm$^3$ was achieved. To maximize compaction of this material, it is necessary to either raise the calcination temperature or use sintering additives in a small amount such as Sm$_2$O$_3$, Nd$_2$O$_3$, and YAG [7].
Table 1. The sintering parameters, density, open porosity, flexural strength and microhardness of the 21R-SiAlON ceramics.

| Sample | Sintering parameters (°C/min) | Density (g/cm³) | Open porosity (%) | Flexural strength (MPa) | Microhardness (GPa) |
|--------|-------------------------------|----------------|-------------------|-------------------------|---------------------|
| 1      | 1650/60                       | 2.47           | 24.4              | 98±15                   | -                   |
| 2      | 1700/60                       | 2.61           | 18.1              | 115±17                  | -                   |
| 3      | 1750/60                       | 2.68           | 14.2              | 151±17                  | 10.1±1.2            |
| 4      | 1800/60                       | 2.86           | 8.6               | 195±18                  | 11.5±1.1            |

4. Conclusion
As a result, 21R-Sialon ceramics were obtained by hot pressing in the temperature range 1650-1800°C. The phase composition, strength, hardness and microstructure of the obtained ceramic samples were studied. The mechanical properties of 21R vary with firing temperatures. They are in the range of 2.47-2.86 g/cm³ for density, 24.4-8.6% for open porosity, 98-195 MPa flexural strength for and 10.1-11.5 GPa for microhardness. To maximize the compaction of this material, it is necessary either to raise the firing temperature or to use sintering additives.

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References
[1] Izhevskiy V A 2000 Journal of the European Ceramic Society 13 2275
[2] Rosenflanz A 1999 Current Opinion in solid state and materials science 5 453
[3] Li Q, Yang Z, Zhong J, Sun Y, Jia D, Duan X and Zhou Y 2019 Journal of the European Ceramic Society 4 934
[4] Kargin Y P, Lysenkov A S, Ivicheva S N, Zakharov A I, Popova N A and Solntsev K A 2010 Inorganic Materials 7 799
[5] Li H X, Sun W Y, Yan D S 1995 Journal of the European Ceramic Society 7 697
[6] Jack K H 1976 Journal of materials science 6 1135
[7] Wang P L, Sun W Y, Yan D S 2000 Journal of the European Ceramic Society 1 23
[8] S Ivicheva et al 2019 IOP Conf. Ser.: Mater. Sci. Eng. 525 012084
[9] Kovziridze Z, Nijaradze N, Tabatadze G, Cheishvili T, Mshvildadze M, Mestvirishvili Z and Daraxvelidze N 2017 Journal of Electronics Cooling and Thermal Control 4 103
[10] Ekström T, Nygren 1992 Journal of the American Ceramic Society 2 259
[11] Jack K H 1978 Materials Research Bulletin 12 1327
[12] Huang Z, Wu L 2018 Phase Equilibria Diagrams of High-Temperature Non-oxide Ceramics (Springer: Singapore) p 181
[13] Falk L K, Shen Z J and Ekström T 1997 Journal of the European Ceramic Society 9 1099
[14] Bandyopadhyay S 1997 Journal of the European Ceramic Society 7 929
[15] Calloch P, Brown I W, MacKenzie K J, Hanna J V and Rees G J 2016 Ceramics International 2 2330-2338
[16] Biswas M, Sarkar S and Bandyopadhyay S 2018 Ceramics International 15 18703-18710
[17] Biswas M, Sarkar S and Bandyopadhyay S 2019 Metallurgical and Materials Transactions A 5 2381-2390
[18] Biswas M, Sarkar S and Bandyopadhyay S 2019 Materials Chemistry and Physics 222 75-80
[19] Amosov A P, Borovinskaya I P and Merzhanov A G 2007 Poroshkovaya tekhnotologiya samorasprostranyayushchegosya vysokotemperaturnogo sinteza materialov (Moscow: Mashinostroyeniye-1) 471 p