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Study of the structure of SiAlON obtained by synthesis with low-temperature plasma energy

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Abstract. This article presents the results of studies of the effect of low-temperature plasma on a sample prepared from powders Si_3N, AlN, urea solution and liquid glass. X-ray phase analysis established, that the use of plasma chemical synthesis produced the phase β-SiAlON compositions Si_5AlON_7 with hexagonal system (Pearson symbol hP14, space group $P6_3/m$**.** The diffractograms also show an X-ray amorphous phase and traces of initial compounds. A diagram showing the physical and chemical processes occurring during the interaction of the plasma flux with components in plasma chemical synthesis is presented.
Keywords: SiAlON, plasma, plasma chemical method, refractories.

1. Introduction

Silicon nitride and compounds based on it are popular materials that have physical and chemical properties. These silicon nitride-based materials include β-SiAlON, which is a solid solution of variable composition based on β-Si_3N_4, where silicon atoms are replaced by aluminum atoms, and nitrogen atoms are oxygen atoms [1]. β-SiAlON ($Si_{6-z}Al_zO_zN_{8-z}$, z = 0–4.2) is a phase in the refractory system Al_2O_3-C because of its high thermal and mechanical properties, as well as significant chemical inertness [2, 3]. β-SiAlON – low temperature phase, having a reinforced microstructure of elongated grains with high fracture toughness (7–8 MPa·$m^{0.5}$) [4, 5], with excellent durability (700–1100 MPa), and good thermal conductivity (13.5–19.7 W/mK), relatively low Vickers hardness (1500–1700 kg/mm^2) [6].

At the present time, about 10 methods of obtaining SiAlON [7]: reaction sintering of nitrides and oxides of silicon aluminum; self-propagating high-temperature synthesis (SPS), spark plasma sintering, carbothermic process; heat treatment of aluminosilicates in ammonia (NH_3) et al. In our work, we have proposed a new method for the synthesis of SiAlON using the energy of low-temperature plasma [8]. This method has unique properties, which cannot be obtained by other methods. Specifically, the use of thermal plasma, created in a plasma generator at atmospheric pressure and higher pressures, allows to create a high average mass temperature of the plasma jet. This average mass plasma temperature can reach values of 4000–6000 K for diatomic and polyatomic gases with their enthalpy values ~$2\cdot10^2$ kcal/mol [9]. It is possible to significantly increase the temperature of the plasma jet to the value 20 000 K through the use of single-atom gases. In this case, the efficiency of plasmatrons depends on their designs and varies over a very wide range 50–95 %.

Chemical reactions occurring during the synthesis of high-temperature materials at temperatures in excess of 2800 K, occur with high speed (contact time is 10^{-3}–10^{-5} s) and intensity [10]. As a result, a wide range of raw materials can be used in plasma-chemical synthesis: liquid, gas, refractory, solid materials.

The aim of the work was to study the structural-phase composition of SiAlON obtained by plasma-chemical synthesis using the energy of low-temperature plasma in a nitrogen atmosphere.

2.Materials and methods

Before plasma treatment, the following components were used as starting materials: powders: β-Si_3N_4, AlN, H_4N_2CO (urea solution) and liquid glass – Na_2SiO_3.

All powders were preliminarily sifted through a sieve with a fraction 0.315 mm. Using a hydraulic press, the briquette was formed into a rectangular parallelepiped, square base, sized 45×45×15 mm^3.

Then the briquette was annealed at a temperature of 400°C for 30 min. The briquette was placed in a plasma reactor, and heating was carried out in a low-temperature plasma jet in a nitrogen medium. When the plasma jet interacts with the briquette, its surface and internal heating is carried out. Fig.1 shows a schematic of the plasmachemical reactor.

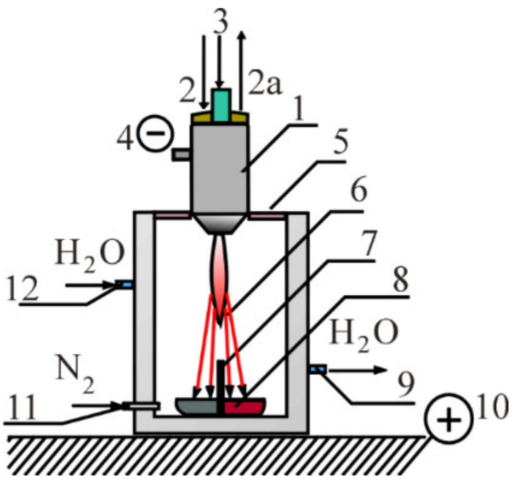

Fig.1. Schematic representation of the reactor 1 –plasmatron; 2 – water cooling channels; 3 – gas channel (nitrogen); 4 – electrical polarity (-); 5 – asbestos plate; 6 – Plasma jet; 7 – graphite electrode; 8 – source briquette; 9 – water cooling channels; 10 – electrical polarity (+); 11 – nitrogen channel.

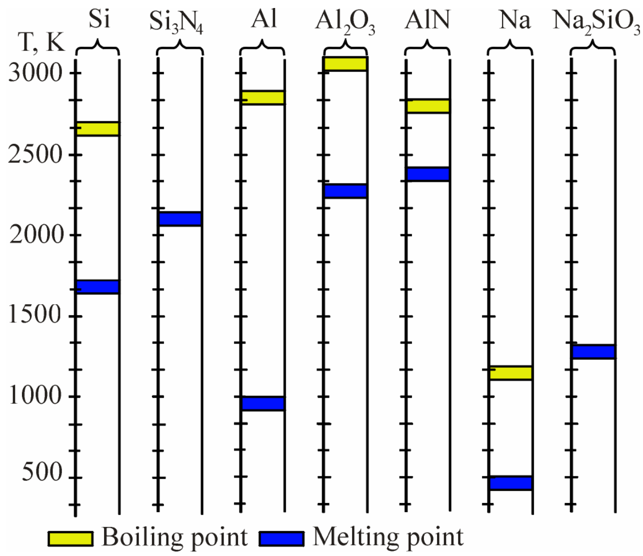

Fig.2. Diagram of melting and boiling points for components used in synthesis SIAlON.

Exposure of the plasma beam to the sample was carried out for three minutes. After plasma exposure, the sample was cooled in air to room temperature. As a result of plasma-chemical synthesis, an inhomogeneous material was obtained. Three areas were identified on the sample. The first area that directly interacted with the plasma beam. The second area is a transitional area between the material processed directly by the plasma jet and the area that did not interact directly with the plasma. These areas were separated and powders were prepared from them for X-ray diffraction studies. The average size of the powders is 150 µm. X-ray structural study was carried out on diffractometers DRON-3 using $Co_{K\alpha}$. The diffractograms analyzed using the Match Crystal Impact software package. Electron microscopic studies were performed by scanning electron microscopy on an electron microscope QUANTA 200 3D.

3. Results and discussion

3.1. Comparative characteristics of the components used in plasma-chemical synthesis

Fig.2 shows a diagram with melting and boiling points for the components used for synthesis SiAlON. It can be seen that among the components, materials involved in the synthesis are both low, and high melting and evaporation temperatures. Such a wide range of values melting and boiling points of the components leads to a complex multi-stage process of chemical reactions. The study of chemical reactions for such a set of components is possible only through the laws of thermodynamics of irreversible processes. To understand chemical processes and create a physicochemical model of formation SiAlON, of plasma chemical synthesisit is necessary to establish the relationship of physical and chemical processes, occurring during the interaction of a plasma jet with components in the process of plasma-chemical synthesis and to determine the structural-phase states of the synthesis products. This relationship has been established and presented in the diagram (Fig.3).

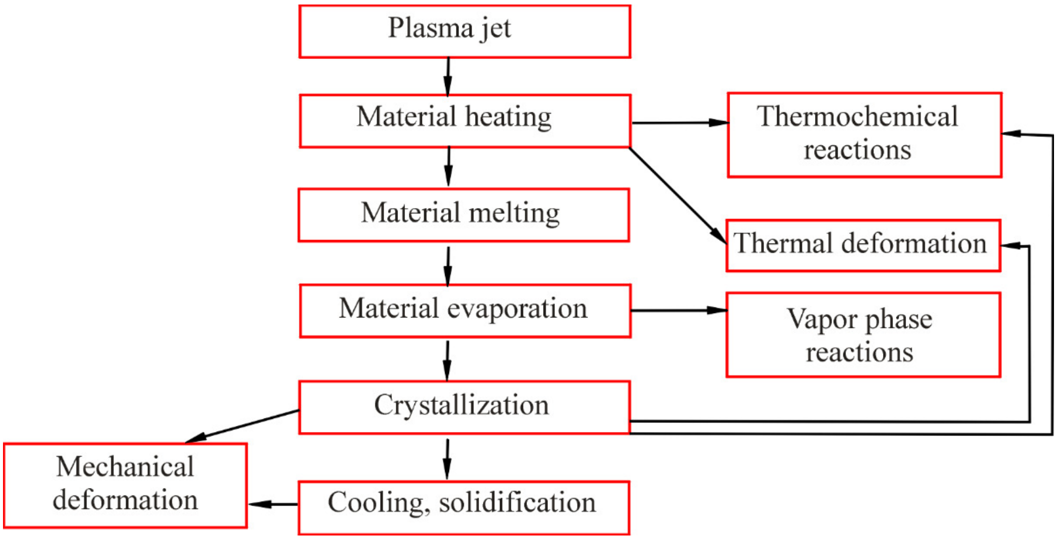

Fig.3. Relationship between physical and chemical processes occurring during the interaction of a plasma jet with components during plasma-chemical synthesis.

3.2. Electron-microscopic studies of products of plasma-chemical synthesis of material

As a result of exposure to high temperature of the plasma-beam chemical reactions of the sample components occurred with changes in its geometric dimensions and shape. Part of the sample material evaporated and condensed on the reactor walls.

Fig.3 shows a micrograph of the sample surface after treatment with a plasma beam. Three areas can be distinguished in this microphotograph.

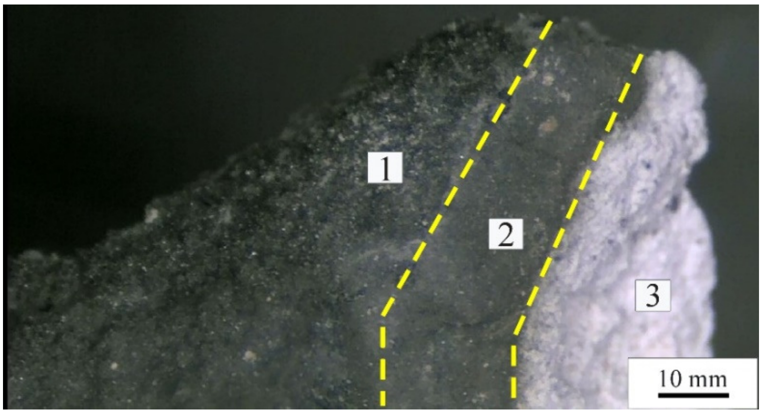

Fig.4. Optical micrograph of a sample cleavage with the boundary of the plasma-chemical synthesis front after the interaction of the material with a low-temperature plasma flow.

The first area of the gray material – this is the part of the sample that interacted with the plasma beam and was heated to 3000 K (Fig.4, area 1).The second area – this is the transition region between the plasma irradiated material and the area not interacting significant with the plasma (Fig. 4, area 2). The third area is light gray. Material from this area was not directly exposed to the plasma beam and was briefly heated to a temperature of 1000–1500 K (Fig.4, area 3).

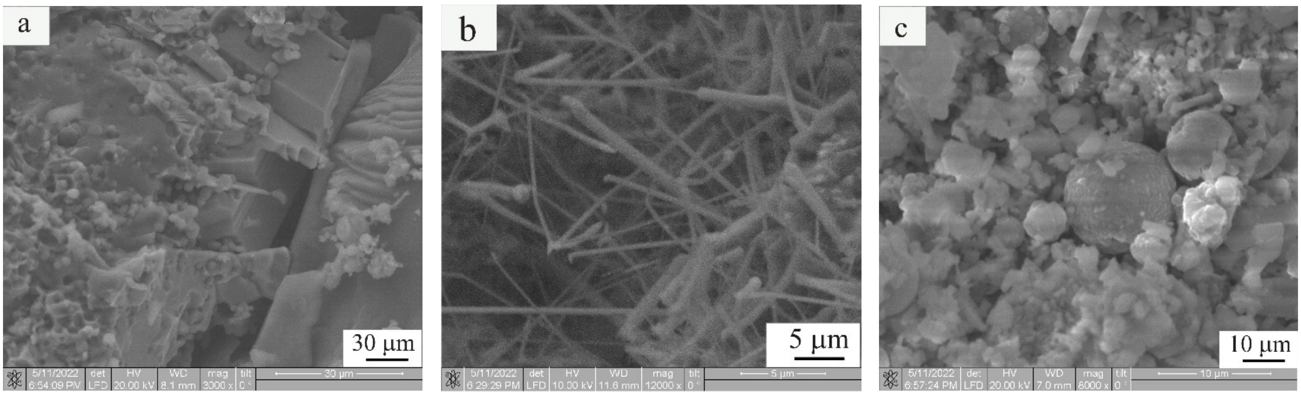

Fig.5. SEM surface micrographs from different regions of the sample after plasma chemical synthesis in the micrographs of Fig. 4: a) area 1; b) area 2; c) area 3.

The electron microscopic images show, that in that part of the sample, which did not interact directly with the plasma beam, observe sintered material, consisting of particles of different morphology and sizes (Fig.4c). On the transition area 2 (Fig.4b) SEM fibrous structure is visible, composed of whiskers. The microphotograph of the surface (Fig.4a), which directly interacted with the plasma flow (area 1) the porous nature of the surface is visible. Particles of various shapes and sizes are observed on this surface: in the form of small individual rounded particles; in the form of larger sintered from small rounded particles; in the form of prismatic blocks.

3.3. X-ray studies of the products of plasma chemical synthesis of the material

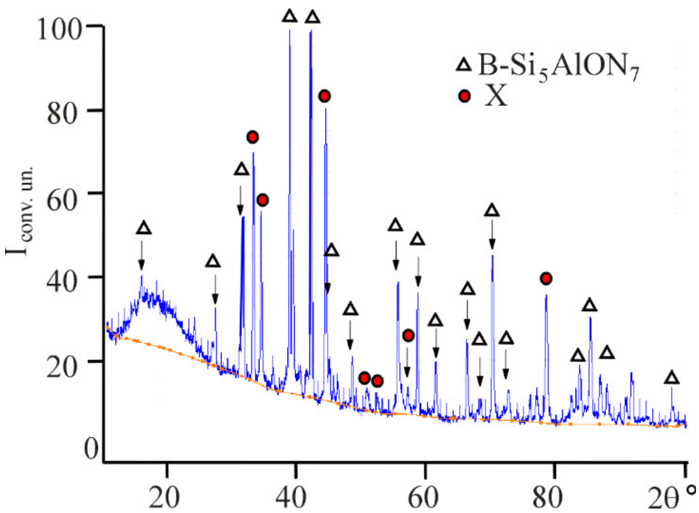

Fig.5. Diffractogram of the sample from area 1 in Fig. 4, obtained by the plasma-chemical method, using $Co_{K\alpha}$ radiation.

Based on a qualitative X-ray phase analysis, it was established, that main phase is β-SiAlON $Si_{6-Z}Al_ZO_ZN_{8-Z}$, z = 1 (AlN_7OSi_5) with hexagonal system (Pearson symbol hP14, space group *$P6_3/m$*. X-ray reflexes from the phases of the initial components involved in the plasma chemical synthesis were also detected in the diffractogram. In the diffraction patterns, in addition to the crystalline phases, there is a diffuse maximum in the region of small angles.

4. Conclusion

It was found that the effect of low-temperature plasma on the sample, prepared from powders Si_3N, AlN, urea solution and liquid glass leads to the formation of a material with a heterogeneous structural-phase composition, containing β-SIALON. Three areas are highlighted: area of material exposed directly to the plasma beam; area that has not been directly exposed to the plasma beam; the transition area between these two areas.

Electron microscopic studies have established, that a fibrous structure is formed in the transition region, consisting of filamentous crystals.

X-ray phase analysis established, that the use of plasma chemical synthesis produced the phase β-SiAlON compositions Si_5AlON_7 with hexagonal system (Pearson symbol hP14, space group $P6_3/m$.

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