Features of the phase composition and morphology of the particles of sialon synthesized from silicon and aluminum nitrides

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Abstract. The phase composition and morphological features of sialons were studied under the same conditions of firing (duration, temperature) using different initial components, silicon nitride, aluminum nitride, and a mixture of silicon nitrides and aluminum with the application of nitrides of the corresponding oxide (aluminum or silicon) sol-gel method. The effect of the initial reagents composition on the phase composition of the final product and the morphological features of the sialon powders obtained in a single firing step in a nitrogen atmosphere is shown.

1. Introduction

The development of reliable methods for the synthesis of ceramic and composite materials based on oxonitrides of silicon and aluminum, capable of withstanding high temperatures and operating in corrosive environments is an urgent task of modern materials science. Sialons or oxonitrides of silicon-aluminum (which are oxonitridoaluminosilicates and in literature mostly called oxynitrides) are sufficiently widely studied ceramic materials [1-6], which combines high thermomechanical properties and the ability to work under aggressive conditions of metallurgical processes [5]. In the four-component Si3N4-SiO2-AlN-Al2O3 system in addition to the \( \beta \)-sialon \( \text{Si}_{6-x}\text{Al}_x\text{O}_x\text{N}_{8-x} \) \( (0 \leq x \leq 4.2) \), the solid solution of isomorphic \( \beta \)-Si3N4, the space group \( P6_3/m \), O’-sialon \( \text{Si}_{2-x}\text{Al}_x\text{O}_{1+x}\text{N}_{2-x} \) \( (0 \leq x \leq 0.3) \), X-phase of \( \text{Si}_{12}\text{Al}_{18}\text{O}_{39}\text{N}_8 \) composition, and a number of ordered polytypes based on AlIN (8H, 15R, 12H, 21R, 27R, 2H) with wurtzite -type structure are formed. The so-called \( \alpha \)-sialons have the formula \( M_n\text{Si}_{12-(pm+n)}\text{Al}_{(pm+n)}\text{O}_{6+n} \text{N}_{16-n} \) realized for \( M^{p+} = \text{Li, Mg, Ca, Sr, Y and rare-earth metals} \).

Because of its high strength, chemical stability and heat resistance sialon-based products are used in conditions of high-speed mechanical loading, thermal shock, exposure to aggressive chemical agents and abrasive. Depending on the additives sialon-based materials are used not only as high-temperature structural ceramics and corrosion-resistant materials [6], but when doping sialons with rare-earth elements as luminophores [7-9].

The main difficulty in obtaining sialons is the need for high temperatures to form a liquid phase that facilitates the sintering of sialonic ceramics and the tendency of sialonic materials to decompose at high temperatures. Therefore, it is important to carry out research to develop effective and reproducible methods for the synthesis of sialon from the initial components of various chemical nature (nitrides, oxides, hydroxides, salts) in order to obtain the target powder or ceramic product and reduce the temperature of obtaining composite materials based on it. In this respect, it is of interest to
use methods that make it possible to obtain substances that are initial for synthesis with an increased reactivity and high dispersity by applying to the crystal nitrides of silicon or aluminum the hydrolysis products of silicon and aluminum alkoxides based on the stoichiometry of the required sialon composition.

2. Results and discussion
A comparative analysis of structural and morphological features of sialons obtained under identical conditions from different starting components was carried out using three different initial reaction mixtures, the calculated composition of which corresponded to the phase of $\text{Si}_3\text{Al}_2\text{O}_6\text{N}_4$; 1 - 3$\text{AlN} + 3\text{SiO}_2$ (reference designation $\text{SiAlON-I}$); 2 - 2$\text{Si}_3\text{N}_4 + 3\text{Al}_2\text{O}_3$ (reference designation $\text{SiAlON-II}$); 3 - $\text{Si}_3\text{N}_4 + \text{AlN} + \text{Al}_2\text{O}_3$ (reference designation $\text{SiAlON-III}$). Calculated amounts of silicon or aluminum oxides were introduced into the reaction mixtures as neutral or acid sols prepared from alkoxides of silicon or aluminum (tetaethoxysilane or aluminum sec-butoxide), simple or polyhydric alcohols with the addition of mineral acids.

Interest in aluminum and silicon alkoxides during the synthesis of sialons is primarily due to the use of their hydrolysis products to obtain pure (in terms of chemical and phase composition) and active highly dispersed oxides of silicon and aluminum and more uniform distribution of the initial nitride materials over the grain surface. The alumina and silicon oxides obtained with the use of alkox technologies differ in structural and texture characteristics from traditional crystalline varieties and amorphous hydroxides obtained by coprecipitation, and varying the conditions of hydrolysis can affect the main characteristics of the final product, including its phase composition.

Powders of silicon nitride and aluminum nitride synthesized by the self-propagating high-temperature synthesis (SHS) at the Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences (ISMAN, Chernogolovka) were used as the starting nitrides. $\text{Si}_3\text{N}_4$ powder ($\text{N} = 37.2\%$, basic impurities: $\text{O} \leq 1.64\%$, $\text{Fe} \leq 0.023\%$) was represented by particles of silicon nitride with an $\alpha$-$\text{Si}_3\text{N}_4 > 95\%$ content of predominantly a fibrous structure with a length of about 2 μm and a thickness of up to 200 nm, the specific surface area of the powder - 8.2 m$^2$/g. $\text{AlN}$ aluminum nitride at $\geq 96\%$ consisted of the main substance (the content of N-33.0 wt.%) contained some amounts of impurities ($\text{O} \leq 1.2\%$, $\text{Fe} \leq 0.1\%$, $\text{C} \leq 0.05\%$), specific surface of the powder - 5.0 m$^2$/g. According to the microscopy data aluminum nitride powder is represented by bulk particles of detrital form with particle sizes from 200 nm to 2 μm. For preparing the solids, silicon and aluminum alkoxides were used: tetaethoxysilane (TEOS), aluminum sec-butoxide, ethyl and isopropyl alcohols, 30% hydrochloric acid or nitric acid.

Gelation of the sol containing amorphous hydrated $\text{SiO}_2 \cdot \text{nH}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot \text{nH}_2\text{O}$ particles on $\text{AlN}$ and $\text{Si}_3\text{N}_4$ powders, respectively, was carried out in air, aging of the solids in the resulting mixtures occurred at room temperature. Preheating and heat treatment to remove water, alcohols, acids and products of hydrolysis of tetaethoxysilane and aluminum sec-butoxide were not carried out. The firing of the powders of the obtained composites from nitrides and xerogels or alumogels was carried out without preliminary pressing in corundum crucibles in a furnace with a graphite heater under a nitrogen atmosphere at 1600-1650°C for 2-3 hours.

To identify the phase and chemical composition of the initial nitride powders of $\text{Si}_3\text{N}_4$ and $\text{AlN}$ and the firing products after the application of silicasols and aluminosols X-ray diffraction analysis was used (XRD 6000 SHIMADZU diffractometer, CuKα radiation, $\lambda = 1.5406$ Å, scanning speed $20 = 2$ 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).
**Figure 1.** Change in the phase composition of SiAlON-I powders prepared using acidic silica sols from the calcination temperature.

**Figure 2.** Change in the phase composition of SiAlON-II powders prepared using acidic silica sols from the calcination temperature.
Figure 3. Change in the phase composition of SiAlON-III powders prepared using neutral and acidic silica sols from the calcination temperature.

According to X-ray diffraction analysis, all samples obtained as a result of firing are mainly β-SiAlON powders (Card No. 36-1333 for the composition Si₃Al₃O₉N₅) with a hexagonal crystal structure (figures 1-3). It should be noted that the samples of powders are not always single-phase, and can consist of a mixture of sialons of various compositions or contain a certain amount of impurities of the initial components. The phase composition of sialon can vary not only depending on the composition of the initial mixture, but also on the conditions of preparation and heat treatment of the samples.

For example, in samples of SiAlON-I (prepared using neutral silica sols at pH 7) an increase in the duration of heat treatment at 1600°C for 1 to 3 hours results in the appearance of a phase of X-sialon, which is belongs to the structural type of mullite and have an elongated form of crystallites. In the case SiAlON-I (prepared with the use of acid silica sols at pH 1÷2) along with β-SiAlON γ-phase (Si₆Al₁₀O₂₁N₄, PDF no. 36-0832) isostructural AlN is formed (figure 1). In samples of SiAlON-II (prepared from silicon nitride powders and neutral and acid aluminosols) after firing for 2 hours at 1600°C traces of the initial nitrides are present, but with increasing duration of heat treatment the samples of Si₃Al₃O₉N₅ obtained are single-phase. With an increase in the firing temperature of SiAlON-II samples to 1650°C is observed the formation a polytype 15R isostructural AlN (figure 2). In SiAlON-III samples, as the firing time increases, traces of the initial nitrides also disappear and the composition of β-SiAlON changes (figure 3).

Figure 4 shows micrographs of SiAlON-II powders obtained on the basis of silicon nitride and aluminosol, which illustrating the morphological features of crystalline particles at different processing temperatures of 1600°C and 1650°C. A change in the morphology of the crystallites of SiAlON-III samples with an increase in the firing time is illustrated in figure 5.
Figure 4. SEM micrographs of SiAlON-II powders illustrating the morphological features of crystallites at different processing temperatures of 1600°C (a) and 1650°C (b) samples obtained by depositing neutral (pH 7) and acidic (pH 2) aluminosols on Si₃N₄.

Figure 5. SEM micrographs of crystallites of SiAlON-III samples with increasing firing time (a-1 hour, b-3 hours).

The obtained samples of the phase Si₃Al₃O₅N₅ with the structure of β-SiAlON were used to study thermoexoelectronic emission (TEE) [10]. The choice of the composition of the samples was not accidental and is due to the effective atomic number $Z_{ef} = 11.7$, which is close to the effective atomic number of bone tissue, which is important for individual dosimetry. The positions of the peaks of the TEE peaks at 190, 225, 282 (the main peak of the TEE) and at 359 and 416°C were determined by decomposition of the experimental TEE curves into components. Studies have shown that sialons (in particular Si₃Al₃O₅N₅) may be of interest as sensors for thermoexoelectronic dosimetry of electron radiation.

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