Formation of Si₃Al₃O₃N₅ oxonitride from mixtures of xerogels and silicon and aluminum nitrides in the nitrogen atmosphere

S N Ivicheva, A A Klimashin, N A Ovsyannikov, A S Lysenkov and Yu F Kargin

A.A. Baykov Institute of Metallurgy & Material Science RAS, Moscow, Russia

E-mail: ivitcheva@mail.ru

Abstract. To obtain silicon and aluminium oxonitrides, the transformations of xerogels and nitrides during firing in a nitrogen atmosphere were studied by thermal and x-ray phase analysis. It was established that the interaction between nitrides and xerogels in a nitrogen atmosphere with the formation of oxonitrides is due to reduction-nitriding reactions. The CO and hydrogen which are formed during the pyrolysis of adsorbed and chemisorbed alcohols (which are the products of the hydrolytic decomposition of silicon and aluminium alkoxides in xerogels) is a reducing agent for the finely disperse oxides. The effect of the composition of the initial mixtures on the phase composition of the final product (SiAlON) and the morphological features of the powders obtained in one stage of firing in a nitrogen atmosphere is shown.

1. Introduction

The interest in aluminium and silicon alkoxides as components for the synthesis of sialons is associated primarily with the use of products of their hydrolysis to obtain pure (in chemical and phase composition) and active highly dispersed silicon and aluminium oxides and the possibility of their uniform distribution over the grain surface of the initial nitride powders. The oxides of aluminium and silicon obtained using alkoxotechnology differ in structural and textural characteristics from traditional crystalline and amorphous hydroxides species collected by coprecipitation, and by varying the hydrolysis conditions (pH, concentration, etc.) the main characteristics of the final product can be affected, including on its phase composition, distribution in the volume of the reaction mixture and dispersion. The use of freshly prepared sols makes it possible to evenly distribute the oxide component over the surface of nitride grains and introduce various dopants (for example, sintering or luminescent [1-4]) into the composition of ceramics. The result of hydrolysis and polycondensation of alcoholates on the surface of nitrides is the formation of highly dispersed active hydrated oxides (hydroxides). The polycondensation of intermediates can be controlled by adjusting the pH of the medium, concentration, solvent, and temperature. The phase transition temperatures of sol-gel technology products usually have different values compared to crystalline oxide mixtures and can contribute to the sintering of ceramic samples at lower temperatures, and themselves act as sintering additives. These and a number of other considerations led to the use of the products of the hydrolysis of silicon and aluminium alkoxides as an oxide component for the synthesis of sialons from silicon nitrides and aluminium and oxides and to study the possibility of synthesizing oxonitride aluminium silicates by nitriding with highly dispersed mixed xerogels of silicon and aluminium.

2. Materials and Method
A comparative analysis of the effect of the composition of the initial mixture on the phase composition of the final product and the morphological features of the sialons obtained under the same conditions (calcination temperature, nitrogen atmosphere) was carried out using reaction mixtures 1 (SiAlON-I): AlN + SiO₂ (sol); 2 (SiAlON-II): 2Si₃N₄ + 3Al₂O₃ (sol); 3 (SiAlON-III): Si₃N₄ + AlN + Al₂O₃ (sol) and when using mixed sol 4 (SiAlON-IV): 2SiO₂ (sol) + Al₂O₃ (sol), calculated on the same composition of the final product Si₃Al₃O₃N₅. The reaction mixtures were prepared by adding Si₃N₄ and AlN powders to neutral or acid sols based on silicon or aluminium alkoxides (tetraethoxysilane or aluminium sec-butoxide), simple or polyhydric alcohols, and organic and mineral acids.

It is known that a nitrogen molecule is powerful [5] and the dissociation of nitrogen molecules under experimental conditions (1600–1700°C) for nitriding the resulting xerogels is practically impossible. However, according to XRD data, for all reaction mixtures 1–4, phases of oxonitrides with a hexagonal crystal structure corresponding to β-Si₃Al₃O₃N₅ were obtained.

Figure 1 shows the X-ray diffraction pattern of SiAlON-IV samples obtained by nitriding at 1650°C a mixed Si-Al sol (not containing the initial nitrides), the phase composition of which is represented by β-Si₃Al₃O₃N₅ and Al₂O₃ (corundum). Thus, it is obvious that during the heat treatment of SiAlON-I - SiAlON-IV mixtures, the nitriding reaction of highly dispersed oxides proceeds.

![Figure 1](image_url)

**Figure 1.** X-ray diffraction pattern of SiAlON-IV after firing at 1650°C in a nitrogen atmosphere

The micrograph (SEM) (Figure 2) shows the change in the morphology of the particles of the mixed sol of SiAlON-IV before and after firing at 1650°C in a nitrogen atmosphere. It can be seen that (Figure 2a) round-shaped nanoparticles ranging in size from 20 to 50 nm of the initial sol form agglomerates (Ssp. ~ 200 m²/g) and, after firing at 1650°C, transform into strong intergrowths of faceted β-Si₃Al₃O₃N₅ crystals up to 15–20 μm long (Figure 2b).

The interaction of nitrides and xerogels in the synthesis of sialons from mixtures 1-3 (initial nitride powders with sols deposited on them) and nitriding conditions for mixed Si-Al xerogels were studied by thermogravimetric (DTA-TG) analysis of samples in a nitrogen atmosphere. To create the same synthesis conditions, nitrogen was supplied in a substantial excess with the same purge rate. The features of phase formation were studied taking into account thermal analysis data of the initial nitride powders with sols deposited on them after various processing steps: 1 - after polymerization and ageing of sols on crystalline nitrides at room temperature; 2 - after heat treatment (drying) at 300°C in air to reduce the amount of adsorbed reagents (water and hydrolysis products of Al and Si alkoxides) in the sintering reaction mixture; 3 - after heat treatment of the initial mixtures at 550°C in a nitrogen atmosphere. It has been established that different conditions of heat treatment of the initial mixtures after deposition of
nitride particles and ageing of Si and Al xerogels on the particles can lead to the formation of the phases of different compositions. In particular, according to the XRD data, after preliminary drying in air at 300°C and subsequent firing of samples at 1650°C aluminosilicates (mullite, etc.) are formed, and not sialons, i.e., the nitriding process is not implemented. It can be assumed that preliminary heat treatment at 300°C in the air of initial mixtures of nitrides with deposited sols and mixed sols containing products of the hydrolysis of Si and Al alkoxides leads to hydrolytic oxidation and the removal of “active” adsorbed or chemisorbed radicals that activate the nitriding process.

According to DTA-TG analysis, it was found that the formation of β–Si₃Al₃O₅N₅ from mixtures 1–4 includes several stages: gel dehydration, pyrolysis in a nitrogen atmosphere of chemisorbed products of the hydrolysis of Si and Al alkoxides with the release of decomposition products of organic compounds, and the interaction of intermediate products in the process of nitriding with the formation of crystalline phases. Depending on the composition of the initial mixture an exothermic effect and a noticeable increase in mass are observed on the DTA and TG curves at 1100–1300°C indicating the initiation of the nitriding process and the formation of silicon-aluminium oxonitride. They are most pronounced in mixtures of SiAlON-I and SiAlON-III (in which used aluminium nitride). As an illustration in figure 3 DTA and TG curves of analysis of the initial SiAlON-I mixture in a nitrogen atmosphere are presented.

**Figure 2.** SEM micrographs of the initial X-ray: (a) - amorphous mixed sol and (b) - SiAlON-IV after firing at 1650°C

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**Figure 3.** DTA and TG curves of the analysis of the initial AlN + SiO₂ mixture for SiAlON-I in a nitrogen atmosphere: 1 - mass change curve, 2 - DTA curve.
3. Results and discussion

For SiAlON-IV samples, there was no mass gain due to nitriding under TG experiment conditions (up to 1450°C), which may indicate that the nitriding process occurs at higher temperatures.

Changes that occur during heating of samples of mixtures 1–4 were studied using complex thermal analysis on an STA 409 Luxx Netzsch thermal analyzer, combined with a quadrupole mass spectrometer. Mass spectral (MS) analysis of the mixed Si-Al sol for SiAlON-IV was carried out in a nitrogen atmosphere.

During the MS analysis, a fairly high ionic current of hydrogen (H2+) and carbon evolution (C+) are recorded. Obviously, this is due to the dehydrogenation of the organic products of hydrolysis of Si and Al alkoxides that make up the gel. For example, alcohols (sec-butyl, isopropyl, ethyl, etc.) due to the catalytic action of the finely dispersed Al and (or) Si compounds in the gel upon heating. In [6], a hypothesis was put forward on the catalytic effect of alumina in relation to the high-temperature decomposition of alcohols, and hydrogen and aldehyde (which subsequently decomposes into simpler gases: ethylene, methane, CO (carbon monoxide) and hydrogen) are indicated as reaction products for ethanol.

According to TGA/MS in air and nitrogen, powder samples of all initial mixtures contain sorbed and chemically bound water, which are removed at 50–200°C and 200–300°C, respectively, as well as chemisorbed nitrate ions (when using acid sols), which are removed mainly at 200-300°C. It should be noted that the MS contains a high content of the organic component (C+, CH4+, C3H8+ and other organic radicals with masses from 42 to 46), there remains a high ion current of hydrogen (H2+), apparently associated with the catalytic dehydrogenation of organic alcohols and contributing to the reduction of a certain amount of SiO2 to SiO. This assumption confirms that when the firing temperature is increased to 1700°C for SiAlON-IV according to XRD, in the samples, in addition to Si3Al3O3N5, there are other sialons - Si2Al2O5N (35-0023) and Si6Al10O21N4 (36-0832) [JCPDS-International Center for Diffraction Data. All rights reserved by PCPDFWIN v.2.4, 2003]. Their composition corresponds to a lower (relatively to Si3Al3O3N5) Si content, probably due to the volatility of SiO, which can be formed in the reducing environment of the experiment. There is a gas liberation (radicals with a mass of 28, which does not exclude the formation of carbon monoxide (CO+)), which is also characterized by reducing properties, according to the TGA/MS of the initial mixture for SiAlON-IV in the air at ~ 300°C and above.

4. Conclusion

Thus the sequence of chemical transformations for all the initial mixtures of SiAlON-I, II, III, IV is caused not only by the decomposition of hydrated oxides deposited on nitride particles but also by reduction processes involving radicals formed during the thermolysis of hydrated gels (obtained based on alkoxides aluminium and silicon) activating the nitriding process in the synthesis of sialons.

Acknowledgments

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