Sintering parameters effect on phase composition of aluminum oxinitride ceramics

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Abstract. Samples of a ceramic material based on aluminum oxynitride were obtained and the efficiency of the sintering methods was evaluated at temperatures of 1750-1950 °C and a holding time of two to ten hours. The heating parameters, the influence of the sintering atmosphere and the quality of the initial powders on the formation of the aluminum oxynitride phase are considered. Next, the phase composition of the powders was determined by the XRF method. Conclusions are drawn about the effect of heating methods for ceramic materials and the nitrogen gas phase (N2) on the formation of the aluminum oxynitride phase.

1. Introduction

In the manufacture of protective structures and dual-use products, an acute need has arisen for the use of new materials of low weight, rather high strength, while having transparency in the optical, ultraviolet and infrared ranges [1, 2]. This complex of properties is particularly relevant for the protection of digital electronic equipment, in particular: infrared sensors, lenses, aerometric instruments and systems, etc., used in “hard” conditions. Ceramic material based on aluminum oxynitride meets these requirements.

Aluminum oxynitride (ALON) is a solid solution in the pseudo-binary system Al₂O₃ - AlN. The composition of AlON is consistent with the formula Alₙ(64 + x) / 3 O₃₂₋ₓ Nₓ, where the composition with x = 5 is the main stable phase in the γ-AlON region. Thus, its stoichiometric formula is Al₂₃O₂₇N₅.

For the first time, the possibility of the existence of a spinel-type phase in the Al₂O₃-AlN system was announced by Japanese scientists Yamaguchi and Yanagida in 1959 [3]. Later, other independent research teams confirmed the existence of such a phase. In 1973, the phase diagram of this system was first introduced [4]. This was the beginning of active research and development in the field of obtaining a dense material based on the phase of cubic spinel Al-O-N in the system of aluminum oxide - aluminum nitride. In 1976, it was reported about obtaining the first samples with optical transparency (Figure 1) [5]. In 1979, a refined state diagram for the γ phase of aluminum oxynitride was presented (Figure 2), but it was noted that the technology for producing transparent ceramics is not completely clear [5].

Although the methods for producing ceramic materials, including materials based on aluminum oxynitride, are known, it turned out to be not so easy to get this material into practice with the required physical properties and the volume of the desired phase tending to 100% The main difficulties lie in the high requirements for the equipment used and the raw materials used. The initial powders are subject to particularly stringent requirements for purity and dispersion of particles. According to [6],...
Al₂O₃ powder should have a purity of at least the second decimal place, and a particle size of less than 1 micron (table 1), including the almost complete absence of particle size variation.

| Initial powder | Chemical purity, % | Main phase     | Average particle size, μm |
|----------------|--------------------|----------------|---------------------------|
| Al₂O₃          | 98,0               | α-Al₂O₃        | 0.1                       |
| AlN            | 98,0               | AlN            | 10.0                      |

Special requirements are also placed on molds, sintering furnaces and their technologies of work. Since the temperature of the beginning of the formation of the required type of ceramics starts from 1700 °C (and under certain conditions it is required to heat up to temperatures above 2000 °C), the sintering process should be carried out in a nitrogen atmosphere of nitrogen. When the density is lower than 97% of the theoretical density, the optical properties of transparent ceramics sharply decrease [1], including the mechanical properties (table 2).

| Density, g/cm³ | Young's modulus, GPa | Flexure Strength, MPa | Hardness (Knoop Indent, 200g), Kg/mm² |
|---------------|----------------------|-----------------------|---------------------------------------|
| 3.7           | 317                  | 379-700               | 1850                                  |

To improve the process of sintering, reduce porosity and reduce the sintering temperature, special additives are used, namely, yttrium and lanthanum oxides. Y₂O₃ and La₂O₃ are used together, since they contribute to the formation of a liquid phase, which in turn reduces the number of pores and defects, which is especially important at the grain boundaries. Yttrium ions promote grain growth and mobility of boundaries, and lanthanum ions - on the contrary, have inverse properties, due to which it is possible to obtain a minimum of defects at grain boundaries and average the sizes of all grains [7]. The combination of all these factors will allow to achieve greater transparency, but subject to the addition of 0.05-0.15 mass percent of such additives.
To obtain the properties of optical transparency, after sintering, the products are polished and polished to remove a micro defective layer from the surface that hides the transparent ceramics.

To check (confirm) the literature data in this work, samples of a ceramic material based on aluminum oxynitride were obtained and taking into account the previously obtained results [8], the effectiveness of sintering methods was evaluated at temperatures of 1750-1950 °C and exposure time from two to ten hours. The influence of the heating parameters, the sintering atmosphere and the quality of the initial powders on the formation of the aluminum oxynitride phase is considered.

2. Materials and techniques
As starting materials, powders of aluminum oxide and nitride, Al2O3 and AlN obtained by plasma chemical synthesis (table 3.) [9, 10].

| Table 3. Characteristics of the starting powders |
|-----------------------------------------------|
| Initial powder | Chemical purity, % | Average particle size, μm |
|----------------|-------------------|--------------------------|
| Al2O3          | 98.0              | 0.1                      |
| AlN            | 98.0              | 10.0                     |

In a vacuum shaft furnace of resistance, the process was carried out at the In vacuum shaft furnace of resistance, the process was carried out at a temperature of 1800-1850 °C in vacuum with a residual pressure of 10⁻² ... 10⁻³ mm. Hg Art., within 10 hours. The sample was mounted on a boron nitride pad. This sintering regime was chosen to estimate the degree of influence of the atmosphere of gases (N2) on the concentration of the target phase of aluminum oxynitride. temperature 1800-1850 °C in vacuum with a residual pressure of 10⁻² ... 10⁻³ mm. Hg Art., within 10 hours. The sample was mounted on a boron nitride pad. This sintering regime was chosen to estimate the degree of influence of the atmosphere of gases (N2) on the concentration of the target phase of aluminum oxynitride.

Sintering in an induction vacuum furnace was carried out at 1750–1950 °C with an exposure from 2 to 8 hours, the residual pressure was 0.1–0.05 mm Hg. st. The sample was placed in a crucible on a substrate of boron nitride. To saturate the sample with nitrogen, the crucible was filled with aluminum nitride in powder form.

The obtained compacts and initial powders were studied using a Tescan Vega scanning microscope. The XRPA method was used to analyze the phase composition on a Bruker D8 ADVANCE diffractometer.

3. Results and its discussion
Samples, sintered in a vacuum resistance furnace, partially retained their geometric cylinder shape, but in the center of the sample there was a strong shrinkage and cracking (Figure 3a). In turn, the samples sintered in an induction vacuum furnace, at a temperature of 1750–1950 °C, lost a significant part of their mass, namely, 70% of the original (Figure 3b). Sample a), dark gray, sample b) turned out to be a light gray shade and is optically transparent to the lumen (Figure 4).

To quantify the volume of the target phase, x-ray phase analysis of the samples was performed. Sample a) does not have a target phase, only 2 modifications of alumina and a small admixture of silicon oxide (Figure 5). Such results are probably related to the fact that the amount of nitrogen in the mixture was not sufficient even for the minimum formation of the aluminum oxynitride phase. In the process of heating and holding the billet in the furnace, there was a complete release of nitrogen from the mixture, which explains the strong shrinkage and porosity of the sample, resulting in its destruction.
Figure 3. Type of samples: (a) a sample copered in a shaft furnace; (b) a sample sintered in an induction furnace.

Figure 4. Translucence of sample (b) (a sheet with a painted cross was placed under the sample and a flashlight shines from below).

Other samples were sintered in an induction furnace, at a temperature of 1750–1950 °C, with a shutter speed of 2 hours. With such parameters, after sintering, the samples have three phases Al₂O₃, AlN and a phase of oxynitride (Al₅O₆N in our case) (Figure 6). At the same time, the sample lost about 70% of its mass. The effect of sample mass loss at these temperatures remains to be seen. Perhaps this is due to the formation of the gas phase of AlO₂ at temperatures close to 2000 °C, as noted in [11].
Figure 5. Diffractogram of a sample obtained in a vacuum resistance furnace

Figure 6. Diffractogram of a sample obtained in an induction vacuum furnace at 1900 °C

Sintering was also carried out with temperature parameters of 1750 °C and holding for 10 hours. Under such conditions, it was possible to achieve about 80% of the target phase of oxynitride, and the remaining part was aluminum oxide (Figure 7).

We attribute these results to the fact that under such conditions the composition point fell into the homogeneous zone (Figure 2), while no complete transition of alumina to the oxynitride phase occurred. This sample is presented in Figure 4. The highest density, which managed to achieve 84% of theoretical. Unfortunately, due to the size of the samples, it was not possible to carry out physical and mechanical tests.
In further studies, it is planned to pay attention to the parameter of grain size and compaction, in order to achieve the required physical, mechanical and optical properties of the resulting ceramic material. It is also necessary to examine and experimentally test the possibility of adding sintering additives to the composition and, as a result, their influence on the structure and properties of aluminum ceramics nitinitride [12].

**Figure 7.** Diffractogram of a sample obtained in an induction vacuum furnace at 1750 °C

**4. Conclusions**

Was obtain the phase of aluminum oxynitride in the amount of 80-90%, however, it was not possible to achieve a homogeneous composition of the sample, which directly affects the optical, mechanical and physical properties.

A holding time of about 10 hours at 1750 °C in an induction furnace is sufficient to form the aluminum oxynitride phase, but the optimal composition should be selected for entering the homogeneity zone, according to the $\text{Al}_2\text{O}_3-\text{AlN}$ system diagram.

The sintering gas atmosphere, namely the nitrogen environment, directly affects diffusion during the formation of oxynitride. The concentration of nitrogen in the mixture is not sufficient for the diffusion from aluminum nitride to oxynitride to flow through; nitrogen escapes from the volume of the workpiece, which leads to the destruction of the sample.

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