Effect of sintering methods and temperatures on porosity of the ceramics from aluminum oxinitride

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Abstract. The paper presents the results of studies of the effect of temperature regimes and time on porosity in ceramic samples made of aluminum oxinitride. Getting rid of the porous structure allows reducing the scattering of rays and, as a result, achieving the required optical characteristics.

1. Introduction
Ceramic materials have a wide range of applications from the construction industry to the aviation industry. However, not many ceramic materials have optical properties. Optimum combination of optical and high strength properties is possessed by ceramics based on aluminum oxinitride Al₂₃O₂₇N₅ [1]. The preparation of such ceramics consists of several stages. The first stage is synthesis of powder materials [2]. The second stage is compacting (pressing), specifies the form of future samples. Next, the compacted preform is sintered. The final stage is mechanical processing, grinding and polishing. However, in each stage, precise technological parameters must be observed to obtain the required qualities of the finished ceramic product. Requirements are given for the chemical purity of the powders, as well as for the particle size, of 1-10 μm. Sintering of the powder is required to be carried out in a vacuum, at temperatures about 2000-2100 °C, for 10-12 hours [3,4].

To reduce the sintering temperature and porosity, a variety of sintering additives, such as yttrium oxide Y₂O₃ [6], are used. Also, hot isostatic pressing (HIP) method is used to combine two processes, sintering and pressing. This technology also reduces the porosity and thus increases the optical and mechanical properties [7].

In this paper, tests of samples from a ceramic material, aluminum oxinitride Al₂₃O₂₇N₅ are presented and an analysis of the data is presented.

2. Materials and techniques
The material for creating ceramic samples was powdered materials Al₂O₃ and AlN, obtained by the method of plasma-chemical synthesis. The parameters of powders are given in Table. 1.
Table 1. Characteristics of the starting powders

| Initial powder | Chemical purity, % | Average particle size, μm |
|----------------|-------------------|--------------------------|
| Al₂O₃          | 98.0              | 0.1                      |
| AlN            | 98.0              | 10.0                     |

The powders were mixed in planetary micro furniture in a ratio of 40:60 for 50-60 minutes. The process was carried out in isopropyl alcohol to prevent the agglomeration of the powder particles and the abrasion of the drum walls by grinding bodies made of zirconia. The resulting mixture was subjected to uniaxial pressing to obtain blanks for further sintering.

The sintering process was carried out according to two schemes. Samples of type I were obtained by uniaxial pressing of a mixture of powders followed by reaction sintering. The pressing was carried out in a mold at a pressure of 50 MPa. Sintering was carried out in a vacuum chamber for 30-120 minutes at temperatures of 1700-1800 °C. In this case, the chamber was subjected to two consecutive cycles of "nitrogen purge" - evacuation to a residual pressure of $10^{-2} \ldots 10^{-3}$ mm of mercury. The pressed billets were placed in a boron nitride crucible.

Samples of type II were obtained by hot pressing a mixture of powders at temperatures of 1700-1900 °C and pressure of 50 MPa for 12 minutes. The mixture of powders was placed in a graphite form, whose walls were covered with a coating of boron nitride on an alcohol base to prevent the effect of carbon. The obtained samples of both types were subjected to grinding and polishing.

Tescan Vega scanning microscope was used for testing and research of compacts and powders. The XRD method was used to analyze the phase composition on a Bruker D8 ADVANCE diffractometer. The microhardness test was carried out on a Wolpert Wilson instruments 402mvd device at a load of 500 g and a test time of 10 seconds. Strength characteristics were determined on a universal test machine INSTRON 3382 in a three-point bending scheme. Measurements of the velocity of longitudinal ultrasonic waves were carried out according to standard procedure using an ultrasonic flaw detector from Panametrics, EPOCH-4, at frequency of 10 MHz using a scheme of combined transducers. The velocity of the longitudinal ultrasonic waves $V$ was calculated from the formula $V = \frac{2d}{t}$, where $d$ is thickness of the sample, $t$ is propagation time of ultrasonic signal at the measurement point, and the attenuation coefficient of longitudinal ultrasonic waves was calculated from the relation (i.e., (1)), where $A_1$ and $A_2$ are the amplitudes of two consecutive ultrasonic pulses.

$$\alpha = \left[ \frac{1}{2d} \right] \ln \left( \frac{A_1}{A_2} \right)$$

3. Results and its discussion

The results of the described technological operations are samples of ceramics measuring 65 mm in diameter and 10-15 mm in height (Figure 1).

Figures 1b and 1c show images of samples obtained by hot pressing technology. The sample has light spots of 1-3 mm in size. To eliminate the identified shortcomings, a number of additional sinterings were carried out at elevated temperatures.

Unfortunately, the samples did not show the expected optical properties. Such results are associated with insufficient sintering time and low temperature. These factors did not allow to get rid of porosity.

The surface of the broken sample shows the presence of pores and the size difference of some crystals, 1-5 μm (Figure 2).

It was suggested that this result is related to the sintering temperature. At temperature of 1900 °C, only the homogeneity region is achieved, while for the healing of pores, a liquid phase is required, which correlates with the phase diagram of this system (Figure 3).
A possible solution to this problem is addition of yttrium oxide $Y_2O_3$, of the order of 1.5% by weight or increase in the sintering temperature and holding time.

X-ray phase analysis of samples after sintering of mixture of aluminum oxide and aluminum nitride powders by hot pressing technology at temperatures 1700°-1900°C (samples type II) showed the presence of aluminum oxynitride and alumina in the samples (Figure 4).

The analysis showed the presence of the $Al_{23}O_{27}N_5$ phase and not a large number of $Al_2O_3$ phases, as well as aluminum oxycarbide and aluminum carbonitride. These data indicate that the conversion process of oxynitride phase was not completed. The effect of carbon impurities from the coating was also affected.
Ultrasonic method was used to study the speed of sound in the samples. Measurements of the velocity of longitudinal ultrasonic waves were carried out according to a standard procedure using an ultrasonic flaw detector from Panametrics, EPOCH-4, at a frequency of 10 MHz using a scheme of combined transducers. The velocity of the longitudinal ultrasonic waves $V$ was calculated from the formula $V = \frac{2d}{t}$, where $d$ is thickness of the sample, $t$ is propagation time of the ultrasonic signal at the measurement point, and the attenuation coefficient of the longitudinal ultrasonic waves was calculated from the relation (i.e., (1)), where $A_1$ and $A_2$ are the amplitudes of the two consecutive ultrasonic pulses. The results are shown in Table 2.

Because of that, the higher attenuation coefficient and low sound propagation velocity in the sample, it can be assumed that in samples of type I there is larger number of inhomogeneous regions.
The values of the sound velocity and the attenuation coefficient obtained for Type II samples are close to those given in the literature. 

**Table 2. Physical and mechanical characteristics of samples**

|        | \( V_{\text{average}}, \text{m/s} \) | \( \alpha_{\text{average}}, \text{dB/mm} \) | \( \text{HV}_{0.3} \), MPa | \( \sigma_i \), MPa | \( K_{\text{IC}} \), MPa/m² |
|--------|-------------------|-----------------|-----------------|----------------|-----------------|
| Type I: | 9304±46           | 0,6±0,03        | 958±98,5        | 122,13±13,37   | 4,02±0,37       |
| Type II:| 10127±506         | 0,18±0,01       | 1335,8±144,4   | 138,52±11,17   | 4,51±0,21       |

The obtained samples showed characteristics similar to those given in the literature, such as hardness and fracture toughness, but the flexural strength showed lower values. Such indicators are associated with structural heterogeneity and defects in the sample [9].

4. Conclusions
The influence of sintering additives and temperature regimes on the formation of mechanical and optical properties of ceramics should be studied to achieve transparency. These data will help reduce the porosity in the preparation of the following samples and, accordingly, achieve optical properties.

Obtained samples by the methods of reaction sintering (I) and hot pressing (II) showed presence of the \( \text{Al}_2\text{O}_2\text{N}_5 \) phase, a small amount of phases of \( \text{Al}_2\text{O}_3 \), aluminum oxycarbide and aluminum carbonitride. The presence of these phases shows that the process of conversion of the oxynitride phase was not completed and as a result did not lead to the expected optical properties. Obtained microstructure and strength data indicate the presence of an inhomogeneous structure and structural defects and is possibly associated with an insufficient sintering temperature of 1700 - 1900 ° C. An increase in temperature would lead to the appearance of a liquid phase and the healing of pores.

The way to achieve the required characteristics can be a method of liquid-phase sintering. The sintering is carried out in two stages, heating up to the temperature of existence of the liquid phase and sintering with a temperature of 50-100 °C below the liquid phase existence temperature, in the homogeneity region.

Hot pressing technology is more efficient, as fewer defects are achieved in the sample (pores, defects, impurities).

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