Technologies of obtaining aluminum oxynitride by HIP and reactive sintering methods and their influence on the phase composition and density of ceramics

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Abstract. In this paper, methods for sintering ceramics from aluminum oxynitride are considered. In particular, the effect of reaction sintering and hot isostatic pressing methods is investigated. The influence of these methods on the structure and phase analysis of the obtained ceramic samples was determined.

1. Introduction

Aerospace, automotive, manufacturing, laboratory equipment, and more industries need new materials with combination of properties not specific to one material. Aluminum oxynitride have combination of high strength characteristics, low density and optical transparency, therefore technology of obtaining this material very interesting for many researchers. First mention of existence of spinel aluminum oxynitride phase in Al2O3 – AlN system was in 1959 by Yamaguchi and Yanagida [1]. Today research is aimed at make obtaining technology more cheap and effective. The production technology of this material implies the exact execution of each production stage, since any deviation from the technology leads to a decrease in transparency. To obtain ceramics of the required quality, it is necessary to observe high purity of the raw materials at all stages prior to sintering, as well as to choose the optimal sintering technique and composition.

Aluminum oxynitride (ALON) is a solid solution in the pseudo-binary system Al2O3 - AlN. The composition of ALON is consistent with the formula Al(64 + x)/3 O 32-xNx, where the composition with x = 5 is the main stable phase in the γ-ALON region. Thus, its stoichiometric formula is Al23O27N5. The physical and mechanical properties of aluminum oxynitride ceramic given by Surmet [2] are presented in table 1. We accept these characteristics as a standard for aluminum ceramic.

| Material | Flexural strength, MPa | Hardness according to Knoop, kg / mm² | Young's modulus, GPa | Density, g / cm³ | Temperature Melting, °C | Lattice parameter, Å |
|----------|------------------------|----------------------------------------|----------------------|------------------|-------------------------|----------------------|
| ALON     | 379 -700               | 1850                                   | 380                  | 3.69             | 2140                    | 7.946                |

2. Materials and techniques

Oxynitride was obtained by sintering of Al2O3 and AlN powders. Al2O3 and AlN was synthesized by plasma synthesis technology with a grain size of 155nm and 1µm and a chemical purity of 99.5% .
Sintering compositions were selected according to the state diagram of the Al₂O₃ - AlN system (figure 1a). Four compositions were chosen (figure 1b) for sintering ceramics (table 2) with the addition of a sintering additive Y₂O₃. The addition of yttrium oxide promotes compaction of ceramics and increases the intensity of grain growth [3]. The mixing of the powders was carried out in a planetary micro mill for thirty minutes. Sintering was carried out using two techniques. Reactive sintering in an atmosphere of gaseous nitrogen at a temperature of 1880 °C with a holding time of 4.5 hours. Hot isostatic pressing (HIP) was carried out in a nitrogen atmosphere at a temperature of 1650 °C and holding for 2 hours. Density was measured by hydrostatic weighing in distilled water. The structure was studied using an optical microscope. Phase analysis was determined by x-ray phase analysis (XRD).

Figure 1. a - system Al₂O₃ – AlN; b – part of diagram with composition of ceramic specimen

| Specimen № | AlN, mol % | Al₂O₃, mol % | Y₂O₃, mas % |
|------------|------------|--------------|-------------|
| 1          | 30         | 70           | 0,5         |
| 2          | 28         | 72           | 0,5         |
| 3          | 33,5       | 67,5         | 0,5         |
| 4          | 24         | 76           | 0,5         |

3. Results and its discussion
Samples of the obtained ceramics have translucency and have a degree of compaction close to 100%. Thus, samples obtained by the reaction sintering method have an average density of ~ 99.6% of theoretical density and has the following structure (figure 2).
Samples obtained by the HIP method also have a density close to 99.6 theoretical and have a similar structure (figure 3). But the samples obtained by this method have in their volume a large amount of carbon embedded from graphite molds.

Samples obtained by reaction sintering have the following phase composition (figure 4).

Figure 4 shows that the main intensity peaks are in the Al$_5$O$_6$N phase, but there are reflections of the Al$_9$O$_3$N$_7$ phase. What caused the appearance of the second phase of aluminum oxynitride remains to be seen, it is assumed that such a result may be due to the heterogeneity of the nitrogen supply process during sintering. It should also be noted that the lattice parameter is not the same (Table 2) for different compositions. According to Figure 5, one can clearly see that the lattice parameter increases with the content of AlN in the mixture.
Table 3. Lattice parameters of aluminum oxynitride ceramic

| Specimen № | 1    | 2    | 3    | 4    |
|------------|------|------|------|------|
| Lattice parameter, Å | 7,949 | 7,945 | 7,950 | 7,939 |

Figure 5. The dependence of the lattice parameter on the AlN content in the obtained ceramic samples

Ceramic compositions are selected correctly, but sintering technology requires testing. Ceramic samples sintered using the HIP method have a high degree of carbon contamination due to the reaction of the powder mixture and the sintering mold. Also in Figure 3, one can clearly see that grain growth is less intense than that of a sample obtained by the reaction sintering method. The density of the samples tends to 100% of the theoretical density for both sintering methods, today this result is the best. We associate these density indices with the addition of a sintering additive Y₂O₃. Judging by the photographs (figures 2 and 3), it is not possible to clearly identify the grain boundary; the optimal method of grinding, polishing, and etching should be chosen to study the structure.

4. Conclusions

Samples of ceramics from aluminum oxynitride were obtained. It was possible to obtain a high AlON phase content and a density close to theoretical.

The reaction sintering method turned out to be more effective for ceramics made of aluminum oxynitride, since it was possible to achieve optical transmission with a high degree of compaction of the material. The addition of yttrium oxide had a good effect on compaction for both sintering techniques.

The HIP method turned out to be less suitable for sintering, since carbon is transferred from graphite molds to the bulk of the sample, and the grain size turned out to be smaller than with reaction sintering. These factors negatively affect the transparency of the samples.

It was found that the lattice parameter correlates with the AlN content in the initial composition. The lattice parameter increases with the AlN content.

In further works, it remains to be seen how to get rid of the second phase of aluminum oxynitride and what contributes to its appearance. It is necessary to develop sintering techniques and test other sintering additives.

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