Production of Al-O-N nanopowders in a plasma reactor with a limited jet flow

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Abstract. Experimental studies on the synthesis of aluminum oxynitride nanopowders in a reactor with a confined plasma jet by the interaction of disperse aluminum with ammonia and oxygen in a flow of nitrogen plasma generated in an electric arc plasma torch are performed. Preliminary calculations of the equilibrium compositions and thermodynamic characteristics of the multicomponent Al–O–N system are carried out.

1. Introduction

Aluminum oxynitride represents a compound of aluminum, oxygen, and nitrogen described by the formula Al23O27N5. This compound was synthesized relatively recently – in the 1950s [1–3]. Nowadays, the interest in this compound has grown repeatedly owing to the fact that, having a low crystalline symmetry, this material makes it possible to obtain transparent ceramics using conventional ceramic technology with no significant expenses. Currently, aluminum oxynitride is sold by Surmet Corporation under the commercial name ALON [4, 5]. The ceramics based on aluminum oxynitride have an average density and have a fairly high strength comparable with that of YAG (yttrium-aluminum garnet) and Fianite (stabilized zirconium dioxide), whereas according to the impact elasticity, the most important for armored protection, aluminum oxynitride surpasses all the transparent materials, including quartz glass [6]. Aluminum oxynitride, owing to a high optical transparency, hardness, and strength, is also used for the manufacture of lighting devices and infrared optical windows and domes and as a substrate for semiconductor integrated circuits.

The most widespread method for obtaining aluminum oxynitride compacts consists in mixing and subsequent sintering of aluminum oxide and aluminum nitride powders [7]

\[ 9\text{Al}_2\text{O}_3 + 5\text{AlN} \rightarrow \text{Al}_3\text{O}_7\text{N}_5 \]

The sintering makes it possible to obtain a singlephase material with a minimum porosity, which increases its transparency, since the pores and secondary phases are the centers of most intense light scattering. The production of transparent aluminum oxynitride is extremely difficult because its residual porosity should be reduced to a minimum, and there should be no secondary phases at all.

The direct synthesis of aluminum oxynitride nanopowders makes it possible to reduce the number of processing stages in the course of the production of transparent ceramics, as well as to avoid an uneven mixing of initial aluminum oxide and nitride powders.
One of the most efficient methods for obtaining any nanopowders of metals and their compounds (nitrides, oxides, etc.) is plasma-chemical synthesis, the main advantages of which consist in the possibility of achieving a high mass-average temperature (up to 5000 K), a short reaction time, and a relative simplicity and versatility of the design of experimental plants, as well as the ease of scaling and a wide range of productivity.

The purpose of this work consisted in the implementation of a production process of aluminum oxynitride nanopowders by means of plasma-chemical synthesis with controlled product properties.

2. Experimental Setup
The experimental studies on the synthesis of aluminum oxynitride nanopowders were carried out using a plasma installation (figure 1) based on an electric arc generator of thermal plasma with a nominal power of 25 kW [8]. Nitrogen was used as a plasma-forming and a transporting gas. Dispersed aluminum was introduced into the plasma jet. Upon evaporation of aluminum, its vapor was formed in the plasma, which was chemically quenched using a gas mixture consisting of ammonia, nitrogen, and air. The rapid cooling of the aluminum vapor was accompanied by chemical oxidation and nitridation reactions to form nanoparticles inherent in the Al–O–N system. The resulting particles were deposited onto the water-cooled walls of the plasma reactor, a part of the obtained product was scavenged on a filter.

![Figure 1. IMET setup for plasma-chemical synthesis.](image_url)

The physicochemical analysis of the obtained nanopowders involved:

- X-ray diffraction (XRD) phase analysis using filtered Cu Kα radiation (Rigaku Ultima-4 diffractometer equipped with a high-speed D/teX detector, PDXL software package, and PDF-2 database);
- the determination of the total oxygen and nitrogen content (LECO analyzers);
- the measurement of the specific surface area of powders by means of BET method (Micromeritics TriStar 3000 specific surface and porosity analyzer);
- SEM and TEM (Jeol JSM-6700F scanning electron microscope and FEI Tecnai G2 F20 transmission electron microscope).

3. Results and discussion
Experimental studies were preceded by the calculations of equilibrium compositions and thermodynamic characteristics of a multicomponent Al–O–N system in the temperature range from 400 to 5000 K using the TERRA software package for modeling phase and chemical equilibria in multicomponent systems, with the corresponding database containing the thermodynamic properties of the components.

As a result of calculations in which aluminum oxynitride $\text{Al}_{23}\text{O}_{27}\text{N}_5$ was considered in an approximation of an ideal $\text{Al}_2\text{O}_3$--$\text{AlN}$ solution, the yield of the target product and the energy consumption for its production were determined as a function of the temperature and the initial elemental composition of the $23\text{Al} + 13.5\text{O}_2 + x\text{N}_2$ system, where $x = 1, 2, 4, 8$. It is established that the equilibrium yield of the target products ($9\text{Al}_2\text{O}_3$--$5\text{AlN}$) close to 100% is provided at a temperature lower than 2400 K for the systems of any initial composition (figure 2).

![Figure 2. Yield of the Al2O3-AlN solution with different amounts of nitrogen in the system.](image)

In the experiments, a prechamber was used for preliminary evaporation of aluminum, wherein the aluminum powder was introduced into a flow of nitrogen plasma, and thus a high-temperature flow containing aluminum vapor was formed. At the outlet of the prechamber, a quenching gas was introduced consisting of ammonia, nitrogen, and air to provide the reaction of aluminum vapor with atmospheric oxygen and with the products of ammonia dissociation under the conditions of rapidly decreasing temperature.

To study the effect of the structural design of the reactor prechamber exerted on the quality of the obtained nanopowder and on the resource of continuous operation, three different schemes for organizing the process were proposed as follows. In the first case, the mixing of the plasma jet and the dispersed raw material with the further evaporation of the aluminum powder occurs within a prechamber with water-cooled walls. In the second case, the mixing of the plasma jet and the dispersed raw material occurs in a channel bounded by quartz walls, whose temperature does not exceed 1000 °C. In the third case, as the prechamber, a graphite channel is used having hot walls and a heat-isolated external surface to reduce heat loss in the zone of mixing of raw materials with a plasma flow, in order to increase the wall temperature to prevent the formation of condensed products on the wall surface.

The specific surface area of the obtained powders was 25.4, 31.7 and 34.9 m²·g⁻¹ for the schemes with the quartz tube, the graphite channel, and the watercooled prechamber, respectively. According to the results of XRD phase analysis, it was found that the powders obtained in all cases consisted of aluminum oxynitride, aluminum nitride, a small amount of aluminum oxide, and traces of metallic aluminum (figure 3). On the basis of analysis of the entire set of data on the properties of these...
powders (the average size of the particles, their phase composition), as well as the operating life of each of the tested schemes, it was decided to conduct further experiments using the assembly with a graphite channel.

Figure 3. X-ray diffraction pattern for Al–O–N nanopowders for different prechamber design: (a) water-cooled prechamber; (b) quartz prechamber; (c) graphite prechamber.

As a result of the experiments, powders with a particle size ranging from 10 to 200 nm (figure 4) were obtained, the color of which varied from white to dark gray. Most of the particles were spherical, and some particles had a hexagonal shape.

An elemental microanalysis of the obtained Al-O-N system nanopowders was carried out by energy dispersive X-ray spectroscopy (figure 5). As can be seen from the obtained data, aluminum, oxygen and nitrogen are present in all particles of the powder. The distribution of nitrogen and oxygen is not uniform, due to the presence of different phases of aluminum oxynitride. According to the results of the fractional analysis, oxygen and nitrogen in the obtained powders are in a tightly bound state; the content of molecular adsorbed forms slightly (less than 0.5%).

Figure 4. SEM and TEM images of the obtained nanopowders.
To study the effect of the amount of quenching gas supplied to the system exerted on the phase, disperse, and chemical composition of the nanopowder obtained, the quenching gas was supplied to the reaction chamber at the outlet of the prechamber in the form of a system of jets. The amount of ammonia and air introduced into the system remained constant for any flow rate of the quenching gas.

According to the XRD phase analysis, at a minimum consumption of quenching gas, a large amount of metallic aluminum (figure 6, XRD pattern d) and alumina Al₂O₃ are present in the resulting powder. This is caused by an insufficient impetus of the quenching gas, which leads to a decrease in the quality of mixing of the aluminum vapor with the gas reagents of the quenching gas, in particular, with atomic nitrogen occurring in the course of ammonia decomposition.

As the flow rate of the quenching gas increases and, consequently, the rate of its outflow in the form of jets increases, the conditions for the mixing of aluminum vapor with atmospheric oxygen and atomic nitrogen take a turn for the better, which leads to the formation of aluminum oxynitride and aluminum nitride (figure 6).

With an increase in the flow rate of the quenching gas from 1.8 to 6.0 m³·h⁻¹, the specific surface area of the powders increases from 20 to 71 m²·g⁻¹, which can be explained by an increase in the cooling rate in the reaction zone, a significant increase in the supersaturation of the vapors of condensed components, and the inhibition of coagulation processes. The nitrogen content in the nanopowders in this case increases from 3.6 to 14.7 wt %, whereas the total amount of oxygen in the nanopowders decreases from 35.5 to 25.5 wt %.

Figure 5. Z-contrast images for nitrogen and oxygen distribution in the particles of Al–O–N nanopowders.

Figure 6. X-ray diffraction pattern for Al–O–N nanopowders obtained at a flow rate of the quenching gas (m³·h⁻¹): (a) 6.0; (b) 4.5; (c) 2.7; (d) 1.8.
The effect of the amount of ammonia introduced into the system exerted on the phase composition of the powders was investigated at a constant molar ratio between atmospheric oxygen and aluminum [O]/[Al] = 1.2 in the system. The values of the molar ratio between ammonia and aluminum (hereinafter NH3/Al) were 6, 10, and 15 (at an aluminum consumption of 2.1 g·min⁻¹) and 23 and 30 (at an aluminum consumption of 1.0 g·min⁻¹). With a decrease in the consumption of aluminum and an increase in the amount of quenching gas, the cooling rate of the vapor of the condensed components increased, which resulted in a considerable increase in the specific surface area of the powder ranging from 25–29 m²·g⁻¹ at NH3/Al = 6–15 to 51.6 m²·g⁻¹ at NH3/Al = 30. According to XRD phase analysis data, with increasing NH3/Al ratio from 6 to 15, the content of the aluminum oxide phase in the powder composition decreases. At high NH3/Al values amounting to 23 and 30, the aluminum oxide phase in the powders is completely absent; however, additionally, a polytypic cubic phase of aluminum oxynitride occurs. The nitrogen content in the powders increases from 0.72 wt % at NH3/Al = 6 to 11.3 wt % at NH3/Al = 30.

Using a laser diffraction method (SALD 7101 Shimadzu) histograms of particle size distributions of the studied powders (figure 7) were obtained, from which it can be seen there are agglomerates of particles ranging in size from 1 to 50 µm in the resulting powder. Ultrasonic treatment of powder suspensions allowed to destroy the agglomerates and obtain more uniform nanopowders.

![Figure 7. Histograms of the distribution of powder particles by the initial sizes before (above) and after ultrasonic treatment (below).](image-url)

4. Conclusion
A design of a plasma reactor has been developed and tested that makes it possible to perform the synthesis of Al–O–N nanopowders upon the interaction of a metallic aluminum powder with ammonia and air in a flow of thermal nitrogen plasma generated in an electric arc plasma torch. The modes of the plasma-chemical process that provide the production of aluminum oxynitride nanopowder with a cubic structure containing the main component in an amount of 98–99% are experimentally determined. The specific surface area of the obtained powders ranges from 30 to 60 m²·g⁻¹, which corresponds to an average particle size ranging from 25 to 50 nm. The phase,
chemical, and disperse compositions of the obtained nanopowders are established as a function of the plasma process parameters and the reactor design.

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