PAPER • OPEN ACCESS

Methods and techniques for producing ceramics from aluminum oxynitride

View the article online for updates and enhancements.

IOP ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

Methods and techniques for producing ceramics from aluminum oxynitride

D V Prosvirnin, A G Kolmakov, M D Larionov, M E Prutskov and A V Levina

Baikov Institute of metallurgy and materials Science, RAS, Moscow, Russian Federation

E-mail: mail.imetran@gmail.com

Abstract. In this paper, we analyzed the literature on the subject of obtaining transparent ceramics from aluminum oxynitride (AlON). In the ceramic industry there are a large number of methods for the synthesis of raw materials and their sintering, in this paper we reviewed the main approaches given in the literature and analyzed the results.

1. Introduction

Oxinitride ceramics (AlON) is a very promising material today. AlON ceramics is used in many areas of technology: engineering, aviation, instrument making and others. Ceramics of aluminum oxynitride has a combination of properties that are not inherent in one material, durability, transparency and low density. However, 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 Al_2O_3 - AlN. The composition of AlON is consistent with the formula $Al_{(64 + x)/3} O_{32-x}N_x$, where the composition with $x = 5$ is the main stable phase in the γ-AlON region. Thus, its stoichiometric formula is $Al_{23}O_{27}N_5$. The mechanical properties given by Surmet [1] are presented in table 1.

The ceramic material in the Al_2O_3-AlN system has a stable γ phase like cubic spinel [2]. For the first time, the possibility of the existence of this phase in the Al2O3-AlN system was announced by Japanese scientists Yamaguchi and Yanagida, this discovery occurred in 1959 [3]. Later, other independent research teams confirmed the existence of this phase. In 1964, the first phase diagram of this system was presented (figure 1a) [4] and then, following this diagram, other phase equilibria of the system [5] were found (figure 1b). Such data became a prerequisite for obtaining a dense material, based on the phase of cubic spinel Al-O-N in the system of aluminum oxide - aluminum nitride. In 1976, according to literary sources, the first samples were obtained with transparency (figure 2) [6]. In 1979, a refined state diagram for the γ phase of aluminum oxynitride obtained by MacCool (figure 3) [7] was presented.

The required γ phase (AlON) is in the range of 64–78 mole percent Al_2O_3, the beginning of the formation of this phase with a composition of 72–73 mole percent aluminum oxide in the region of 1640 ºC, this concentration allows to achieve the lowest possible temperature in a double system without sintering additives.
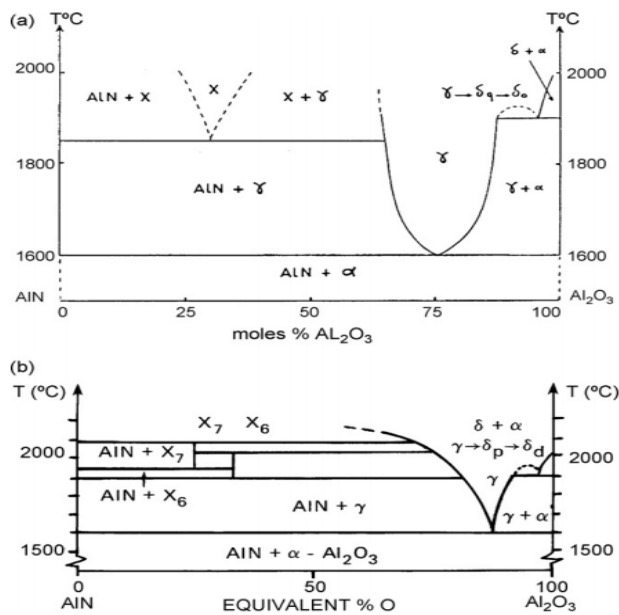
Figure 1. (a) Al2O3-AlN [4] state diagram, (b) Refined Al2O3-AlN state diagram from source [5]
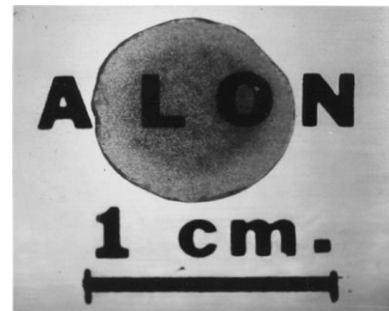

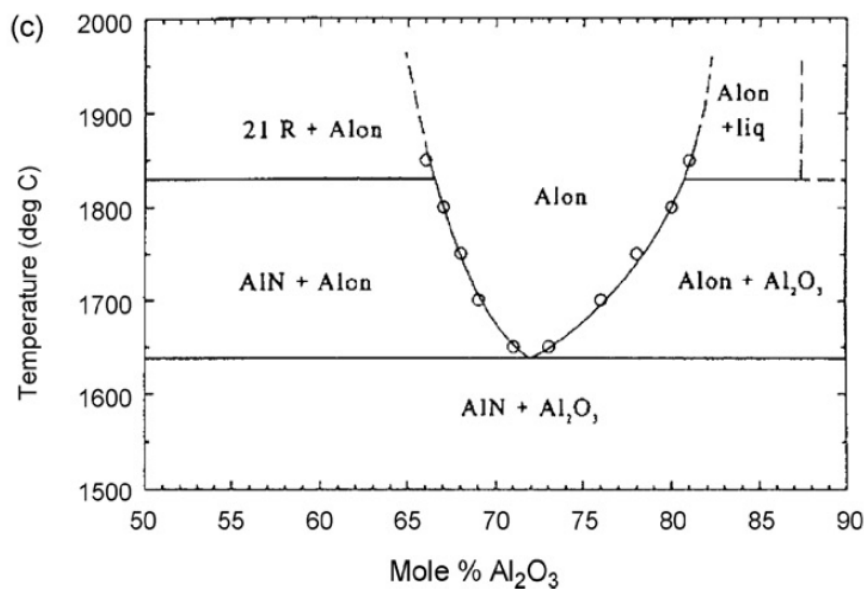**Figure 2.** Refined part of the phase equilibrium diagram. [5]

Figure 3. Refined part of the phase equilibrium diagram. [7]

Table 1. Characteristics of Al_2O_3 and AlN powders

Material	Flexural strength, MPa	Hardness according to Knoop, kg / mm^2	Young's modulus, GPa	Density, g / cm^3	Temperature Melting, °C
ALON	379 -700	1850	380	3,69	2140

2. Synthesis

The initial powders of aluminum oxide and nitride (Al_2O_3 and AlN) are subject to the strictest requirements for chemical purity and dispersion of particles [8,9]. For example, in the work of the researcher Kong [8], the initial powders had a chemical purity of 99.99% and an average particle size for Al_2O_3 - 1 μm, and for AlN - 0.5 μm.

It should be noted that in the production of oxynitride ceramics micro-additives of sintering components such as: Y_2O_3, Sc_2O_3, Lu_2O_3, La2O3, and others are used.

Y_2O_3, the main sintering additive used in oxynitride ceramics, as a promising optical material, has excellent physical and chemical properties, such as high melting point (2430 ° C), wide transparency range (0.2-8 microns), high corrosion resistance, a density of 5.01 g cm-3 and a boiling point of 4300ºC. The sintering additive of yttrium oxide can cause the formation of a liquid phase during sintering, which is beneficial for compacting and removing pores. Y^{3+} ions increase the mobility of grain boundaries and accelerate grain growth.

Lanthanum oxide (La_2O_3) has the opposite effect. A small amount of La^{3+} ions can significantly slow down mass transfer and, therefore, suppress grain growth. Such additives can be used together to compensate for the negative effects of both additives and to reduce porosity and intergranular defects [10].

Self-propagating high-temperature synthesis. This process, being locally initiated, then propagates itself in the form of a reaction wave; "High-temperature" - because it is accompanied by the release of heat, which heats the substance in the reaction zone to a high temperature; and the word "synthesis" indicates that during this process valuable substances and materials can be synthesized [11]. According to the researcher Borovinskaya [12], experiments on the synthesis of AlON using the SHS method - the joint production of two or more target products were carried out. As a result of the conducted studies of the phase composition and structure of the combustion products of $Al - Al_2O_3$ mixtures at high pressures of gas-like nitrogen (10–100 MPa) under conditions of CBC-gas gassing, optimal parameters for the synthesis of powders (γ-ALON) were found. Experiments using highly exothermic coupled boron combustion reactions in gaseous nitrogen for additional heating of the initial mixtures showed the possibility of obtaining in the SHS mode not only powders with clearly formed layered particles collected in mosaic macrostructures, but also glassy polycrystalline mass with areas of transparency in the visible region (figure 4).
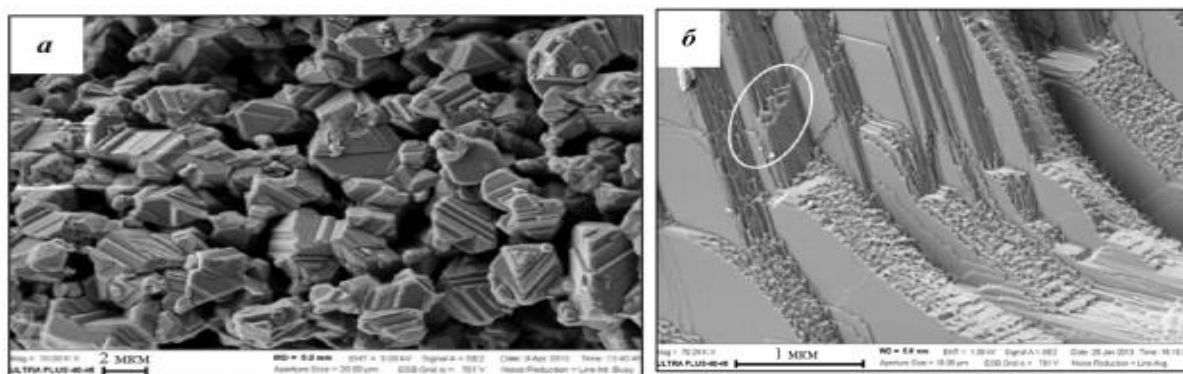

Figure 4. The microstructure of the particles of the powder γ-AlON (a); nanostructure of the layers of the particle γ-AlON (b) [13]

Plasma chemical synthesis. The synthesis of oxides in a plasma arc discharge is carried out by evaporation of the metal, followed by oxidation of the vapor or oxidation of the metal particles in an oxygen-containing plasma [13]. The characteristics of the obtained powders depend on the raw materials used, the synthesis technology and the type of plasmatron. The particles of plasma-chemical powders are single crystals and have sizes from 10 to 100-200 nm and more.

Carbothermic reduction method with nitriding. In the work of Chinese researchers [14], AlON powder was synthesized from nano-sized γ-Al_2O_3 of high chemical purity (99.99%) and carbon with a purity of 99.95%. The powders were mixed in a zirconium oxide microreducer for 12 hours, followed by drying at 80 ° C for 4 hours.

Then, the resulting mixture of γ-Al_2O_3 and carbon powder were placed in a crucible and heated under nitrogen atmosphere inside a graphite furnace. The mixture was first heated at a heating rate of 10 to 1550 ° C for 1 hour to obtain AlN and then heated at a heating rate of 3 ° C / min to 1650, 1750 and 1800 ° C for 2 hours to obtain AlON powders. The resulting powders were treated for 4 hours in air at 700 ° C to remove excess carbon or impurities.

However, in this work, the best results were obtained at 1750 ° C with a powder size of 42 μm. Such a particle size does not satisfy the sintering conditions, however, it should be noted that the required phase is formed as a result of the application of this method (figure 5).
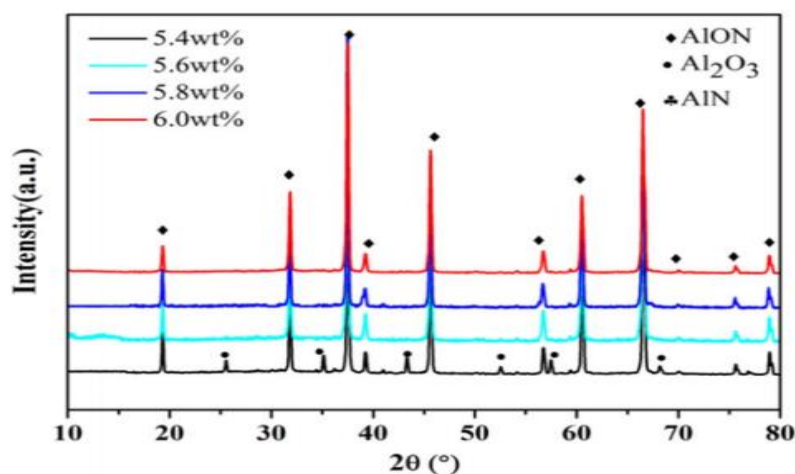

Figure 5. Diffraction patterns of the obtained powders with different mass percent carbon addition [14]

3. Sintering

Sintering is one of the key stages in the creation of ceramics from aluminum oxynitride, since the required (γ-phase AlON) and compaction of the product is formed during the sintering process. An important parameter is the density of the finished product, namely, 97 percent or more of the theoretical density, since below this threshold the optical properties drop to almost zero. Thus, the key points in this process are the balance between pressure, temperature and the environment in which sintering takes place. The difficulty lies in the choice of such parameters, which will allow to achieve the desired compaction at the lowest temperatures and pressure, since this directly affects the complexity of production and the cost of the finished product.

Reaction sintering. Sintered material is compacted by the formation of a new crystalline substance by the reaction between the solid-phase substance in the body of the product as one component and the vapor phase of the other substance. There is a kind of impregnation of the porous body with a vaporous substance, which reacts with the main or specially introduced phase to carry out the reaction. In this case, the formation of oxynitride is influenced by the medium, namely the chamber with the sintered compact is subjected to purging with nitrogen. Therefore, the denser and larger the product, the more difficult is the process of reaction sintering, what means that the force during compaction also affects the sintering process.

The reaction sintering is carried out at a temperature of 1700-1900 ℃, consistent with the phase equilibrium diagram [7, 15]. The disadvantages of this method are the following factors: a sufficiently long exposure time (from 12 hours) and the difficulty of finding the optimal pressing force and porosity of a compact, for the passage of diffusion between the gas and solid phases.

The research group Revva IB and Ditz A.A. [16] investigated in their work the effect of pressing force on the synthesis of oxynitride using the method of reaction sintering. Samples were compressed with different forces, 20, 70, 140 and 210 MPa. Sintering was carried out at a temperature of 1750-1800 °C. According to X-ray phase analysis, samples pressed under a pressure of 70 MPa have the greatest amount of the target phase (figure 6).
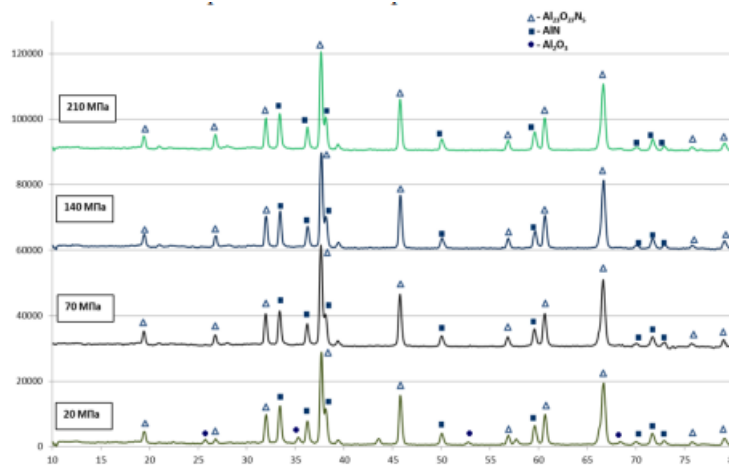

Figure 6. X-ray diffraction patterns of samples calcined at 1,800 ° C, molded at different pressures [17].

These data show that the reaction proceeds more intensively in samples compacted with a force of 70 MPa, since there remains sufficient porosity for the reaction of the solid phase with the gas.

Hot pressing method. The process is a simultaneous pressing and sintering. The mixture is placed in a mold, which walls are coated with an alcohol-based boron nitride coating to prevent the introduction of elements constituting the mold. During the sintering process, the vacuum chamber is subjected to "nitrogen flushing" cycles, the specimen is subjected to mechanical pressing during sintering. This method is more expensive than the reaction sintering method, since mechanical pressure is used in combination with vacuum and high temperature.

The advantage of hot pressing is the possibility of carrying out the process at temperatures lower than the sintering temperature in the free unloaded condition, since compaction is also achieved due to mechanical effort and the healing of the pores occurs at lower temperatures than with reaction sintering.

There is a variety of hot pressing, namely hot isostatic pressing. The process of simultaneous heating and forming of a powder billet, in which the powder is contained in a sealed sheath of flexible tin or glass, and thus the contained powder is subjected to equal pressure in all directions at a temperature high enough to cause plastic deformation and sintering.

In the work of a group of researchers from China, led by Junming X. [17], sintering was performed by hot isostatic pressing at various temperatures of 1800, 1850, and 1900 ° C. A mixture of powders with a composition of 67.5 mol% Al2O3, 33.5 mol% AlN and 0.5 wt% Y_2O_3 was sintered, the powders were mixed for 12 hours and dried at 80 ° C. The duration of the sintering process at different temperatures was the same and was 120 minutes. Sintering took place with a pressure of 20 MPa in a nitrogen atmosphere. The test results of sintered samples are presented in table 2.

Table 2. Mechanical properties of samples [18]

Sample	Sintering temperature ° C	Density g/cm^3	Hardness HV$_{10}$ (GPa)	Crack resistance K$_{1C}$ (MPa·m$^{1/2}$)
a	1800	3.68	14.67	2.45
b	1850	3.67	14.97	2.91

| c | 1900 | 3.65 | 15.66 | 3.37 |

According to the work, it was possible to achieve a high density of 3.65-3.68, (theoretical density of 3.69 g / cm^3). Although the density at a temperature of 1850-1900 ºC is lower, but the mechanical characteristics are higher. The sample in Figure "c" has a more uniform grain size and an optimal structure, which has a positive effect on the light transmission of the sample.

Sintering using plasma sparks. This method allows to reduce the sintering temperature up to 1650, provided that the sintering additive Y_2O_3 is added, the exposure time is also shortened.

Spark plasma sintering (SPS - Spark plasma sintering), also known as field assisted sintering technique (FAST), is a process of rapid sintering to obtain a fully dense and fine-grained ceramic at a low temperature with a short holding time.

The driving force of the SPS method is the cumulative effect of force, heat, electric field and plasma generated by a pulsed current within the entire volume of the sample. It differs from the usual sintering force created by external heating elements, in which heating occurs through radiation and convection [18].

In the work of the group of researchers Patel P., Gilde G. and McCauley J. W. [19], sintering was performed with a temperature of 1600 ° C, a dwell time of 15 minutes and a pressure of 20 to 50 MPa. The compacts had a different composition, namely, the mass percentage of the Y_2O_3 additive differed. The research results showed that the optimal concentration for the lowest activation energy and the greatest compaction is 0.6 wt% Y_2O_3 (table 3). Figure 7 shows the porosity of the samples obtained, the pores are circled.

Table 3. Density of samples with the addition of Y_2O_3 [19]

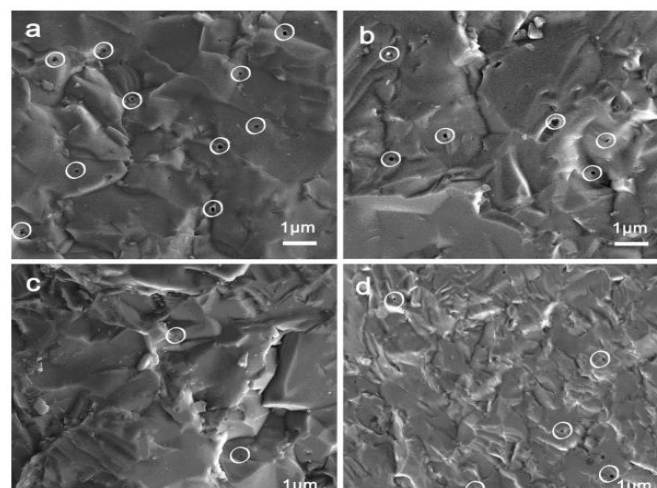| Mas% Y_2O_3	0	0,3	0,6	1,2
Density from theoretical in%	96,0	98,3	99,2	97,2

Figure 7. X photographs of the structure of samples with different Y_2O_3 contents:
a - 0; b - 0.3%; c - 0.6%; d - 1.2% [19].

This result is due to the fact that when adding 1.2% Y_2O_3, the formation of the $Y_3Al_5O_{12}$ (YAG) phase occurs, this phase adversely affects the mechanical characteristics of the sintered samples, in turn, a concentration below 0.6% does not allow for the desired compaction and elimination of pores and defects. Figure 8 shows the dependence of the phase reflections on the concentration of the sintering additive Y_2O_3.

The obtained density of samples with the optimal concentration of the sintering additive Y_2O_3 (0.6%). In conjunction with not great sintering temperatures and holding time, it makes it possible to declare the

viability of this method, however, the high complexity and high cost of the installation are an undoubted disadvantages.
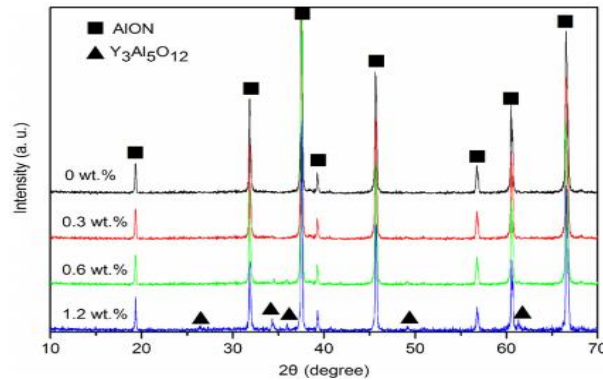

Figure 8. XRF samples [19]

Liquid sintering. Another sintering method used in the production process is transparent ceramics, in particular γ-AlON, to eliminate porosity and reduce secondary phases that are crucial for transparency. Dr. Patel investigated transient liquid phase sintering of AlON ceramics as a technology for the manufacture of dense transparent material [19].

This method consists in heating in two stages in a vacuum oven in a nitrogen atmosphere (N_2). In the first stage, the mixture of powders is heated to the temperature of the heterogeneous region of existence of the liquid and γ-AlON and held for a long time at a temperature of about 2150 ° C. In the second stage, the temperature is reduced until the homogeneous γ-AlON phase is reached(figure 9). The meaning of the temperature change is that in the first stage we obtain the liquid phase, which, when the temperature drops, allows the pores to heal in the specimen. Micro pores and intercrystalline defects are completely filled with the liquid phase, which makes it possible to obtain a dense product with light transmittance (transparency) during cooling (Figure 10).

As part of the work, the loss of specimen mass was detected at temperatures above 1950 ° C. So in the next work of Patel [20], the mass loss due to a change in the lattice parameter was explained. The loss of mass is due to a change in the relative composition determined by the lattice parameters. This mass loss and change in the lattice parameters are probably due to the formation of the vapor phase at elevated temperatures, either from a liquid or from a solid phase. It was found that at elevated temperatures, the composition migrates to the lattice parameters of the layer and, consequently, to a higher nitrogen content.
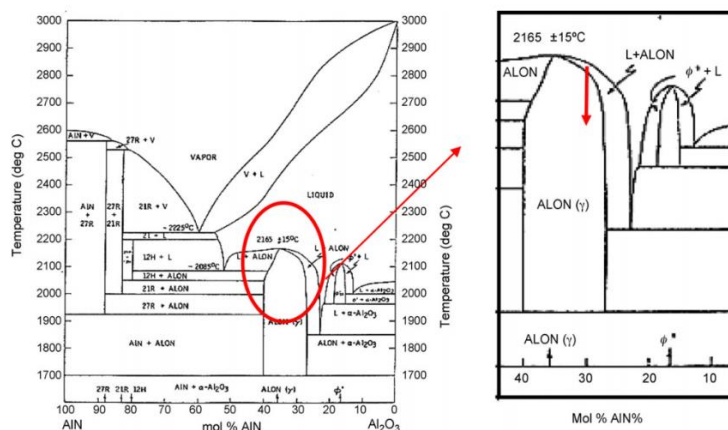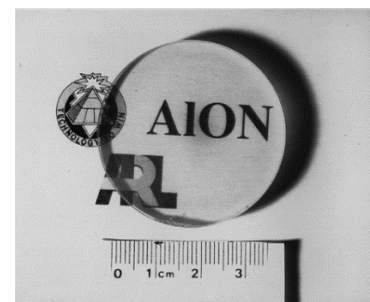

Figure 9. Liquid sintering method [19]

Figure 10. The sample obtained by the method of liquid-phase sintering [19]

Figure 11 shows the surprisingly strong dependence of the lattice parameter AlON, at a nitrogen pressure and a temperature of 2000 ° C, which leads to a loss of weight as the temperature rises to 2000 °C. A reduced lattice parameter will mean a loss of nitrogen or a shift in the composition towards Al_2O_3. An increase in nitrogen content is equivalent to a decrease in oxygen content, and this is a relative change in the ratio, which is reflected in the lattice parameter. However, the observation reveals a decrease in the percentage of nitrogen, in the ratio of nitrogen - oxygen, with increasing pressure of nitrogen. One explanation is the suppression of the oxygenated vapor phase in the form of Al_2O, [21] with increasing pressure. It is believed that nitrogen does not react under these conditions and there is no significant dissolution of nitrogen in AlON. It was determined that the lattice parameter AlON decreased from 0.7960 to 0.7926 nm, since the excess pressure was increased from 0.11 MPa to 0.2 MPa.
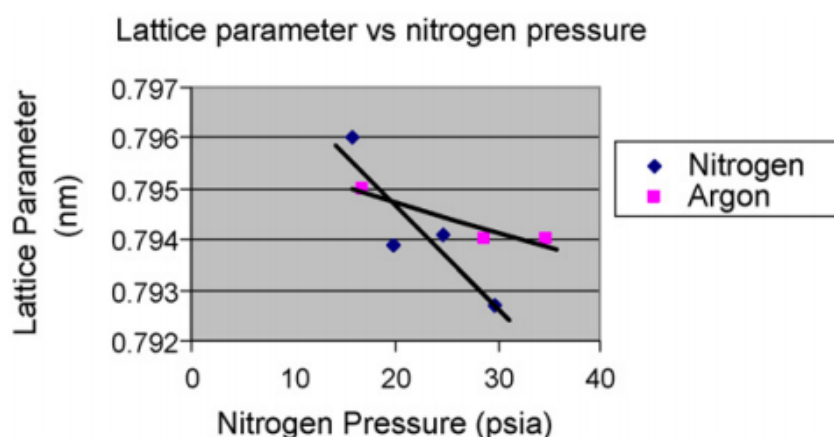

Figure 11. Dependence of gas pressure on the lattice parameter AlON [20]

The following conclusions were made: the lattice parameter increases with the nitrogen content, the lattice parameter decreases with increasing oxygen content, increasing the pressure of nitrogen or argon stabilizes the system, suppressing the loss of oxygen (Al_2O).

Liquid-phase sintering has positive sides: high compaction and defect elimination, due to the liquid phase, but the disadvantages of this method are that high temperatures up to 2200 °C and exact compliance with the nitrogen pressure parameter to control mass loss are required

4. Conclusions

There are quite a number of methods and approaches to the synthesis and sintering of ceramic material from aluminum oxynitride. Powders obtained by different methods have different characteristics of dispersion and purity, but in all methods they tend to obtain powders with particles of nano size and purity up to the second decimal place, i.e. 99.99%. The literature data under study are not straightforward, since in each individual case researchers resort to different methods of synthesis and sintering with their technological features and in many cases claim to obtain transparent samples, but not large.

Literary data is required to be reproduced experimentally, in order to evaluate the results and determine the optimal technological regimes, the compositions of powder mixtures, the modes of synthesis, pressing and sintering. It should be noted that today there is no proven technology for the production of oxynitride aluminum ceramics, both in Russia and in other countries. Accordingly, research in the field of obtaining a transparent ceramic material from aluminum oxynitride is necessary, since this material can replace a whole class of transparent structural materials.

References

[1]. Goldman L M et al. 2010 ALON® optical ceramic transparencies for sensor and armor applications *Structure* **380** 700

[2]. Kingery W D et al. 1976 *Introduction to ceramics*. (New York: Wiley) p 500.

[3]. Yamaguchi G and Yanagida H 1959. Study on the reductive spinel—a new spinel formula AlN–Al2O3 instead of the previous one Al3O4. *Bulletin of the Chem. Soc. of Jap.* **32** №. 11, pp. 1264-65.

[4]. Lejus A 1964 Formation at high temperature of nonstoichiometric spinels and of derived phases in several oxide systems based on alumina and in the system alumina–aluminum nitride. *Rev. Int. Hautes Temp. Refract.* **1** pp 53-95

[5]. Gauckler L J and Petzow G 1977 In representation of multi-component silicon nitride based systems *Nitrogen ceramics* ed F L Riley (Leyden: Noordhoff) pp 41–62.

[6]. McCauley J W 1974 Viechnic. Dj. Reaction studies in SI3N4-AL2O3 system *Amer. Cer. Soc. Bull.* , (Westerville: Amer Ceramic Soc) **53** № 8 pp 620-620.

[7]. McCauley J W Corbin N D 1979 Phase relations and reaction sintering of transparent   cubic aluminum oxynitride spinel (ALON) *Journ. of the   Amer. Cer. Soc.* **62**   № 9- 10 pp 476-479

[8]. Kong L B et al. 2015 Transparent Ceramic Materials *Transparent Ceramics* (Cham: Springer)pp 29-91.

[9]. Cheng J et al 2001 Microwave reactive sintering to fully transparent aluminum oxynitride (ALON) ceramics *Journ. of Mater. Sc. Let.* **20** №. 1 pp. 77-79.

[10]. Wang J et al 2015 Effect of Y2O3 and La2O3 on the sinterability of γ-AlON transparent ceramics *Journ. of the Eur. Cer. Soc.* **35** № 1 pp 23-28.

[11]. Merzhanov A G 2006 Self-propagating high-temperature synthesis: about the past, nowadays, and future *Izv. Vysh. Ucheb. Zav. Tsvet. Met.* **5** pp 5-8.

[12]. Borovinskaya I P et al. 2016 Structuro I fasoobrasovanie productov goreniia pri sinteze γ-ALON v rezhime svs-gazostatirovaniia *Izv. Vysh. Zav. Por. Met. I Funct. Pokr.* **3** pp 23-30

[13]. Gusev A I and Rempel A A 2001 *Nanocrystalline materials* (Moscow: Nauka) 224

[14]. Sahin F C, Kanbur H E and Apak B 2012 Preparation of AlON ceramics via reactive spark plasma sintering *Journ. of Eur. Cer. Soc.* **32** №4 pp 925-929

[15]. Prosvirnin D V et al. 2017 Effect of reaction sintering conditions on properties of ceramics based on alumina oxynitride *Materialovedenie* **10** pp 45-48

[16]. Revva I B, Ditz A A and Shulzhenko A S 2015 Vliyanie davleniia pressovaniia na sintez oxinirida aluminia *Vysokie tehnologii v sovremennoy nauke I tehnike: sbornik nauchnih trudov IV mezhdunarodnoi nauchno-tehnicheskoi konferencii molodyh uchenyh, aspirantov i studentov* (Tomsk: Izdatelstvo Topskogo polytehnicheskogo universiteta) pp 164-167

[17]. Junming X et al. 2008 Hot-pressed translucent aluminum oxynitride (AlON) ceramics *Key Eng. Mat.* **368-372** pp 450-452.

[18]. Li X, Luo J and Zhou Y 2015 Spark plasma sintering behavior of AlON ceramics doped with different concentrations of Y2O3 *Journ. of the Eur. Cer. Soc.* **35** № 7 pp 2027-32.

[19]. Patel P 2000 Phase equilibrium and kinetics in the multi-component non-oxide Al–O–N system Ph. D. (Baltimore: The Johns Hopkins University).

[20]. Patel P, Gilde G and McCauley J W 2006 Transient liquid phase reactive Sintering of Aluminum Oxynitride (AlON) Patent US-7,045,091 B May 16, 2006.