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Consolidation of Transparent ALON by Spark Plasma Sintering Methods

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Abstract. The paper studies the prospects of spark plasma sintering of aluminum oxynitride, determines the optimum modes and parameters of compacting. Optimum modes of preparing a powder mixture for sintering are determined. The structure and properties of sintered samples are studied. The factors affecting the transparency of the finished products are ascertained, and the ways that allow obtaining a high light transmittance are identified.

1. Introduction

There is a currently observed rise of penetrative power of small arms and small caliber artillery. That is forcing ammunition developers to seek new opportunities to improve performance of armor materials and protective structures. It especially concerns transparent armor materials. One of the most promising material in this class is transparent polycrystalline ceramics, such as ceramics based on aluminum oxynitride (ALON). This material possesses a unique combination of properties required for use in armored protection devices and furthermore does not require the use of overly expensive technologies for production. Manufacturing transparent product of complex shape from this material is possible by using of molding and sintering traditional for ceramic technology processes. Development of armored protection made of the aluminum oxynitride attracts an active international interest, especially from the companies working for defense industries.

Among all the ceramics nowadays an average density aluminum oxynitride has a significantly high strength comparable to the YAG (yttrium aluminum garnet) and cubic zirconia (stabilized zirconium oxide). It is also the most advanced armored protection comparing its impact strength. ALON surpasses all transparent materials, including quartz glass (fused quartz, spinel and leucosapphire).

Aluminum oxynitride is a compound of aluminum, oxygen and nitrogen described by the formula $Al_{23}O_{27}N_5$. This compound was synthesized as a powder quite recently - in the 50s. In the late 80s and early 90s a technology for producing transparent products of complex shape was developed. In Russia no attempts of such production have been made yet. Nowadays the interest for the aluminum oxynitride has greatly increased. With low crystal symmetry – cubic crystal system - the material makes it possible to produce transparent ceramics using conventional ceramic technology.

Aluminum oxynitride is usually made from powder compounds of aluminum oxide and aluminum nitride. There are two main objectives in the sintering process: to provide a single-phase material, and to minimize porosity. Pores and second phases are the most intense centers of light scattering. These requirements does not apply to conventional ceramic materials.

The main objectives of this research were choosing the raw material, determination of the optimum sintering methods and modes for aluminum oxynitride, and identification of factors affecting its transparency.

2. Research methods and equipment

Micrographs of the surface structure of the obtained samples were examined with an optical metallographic microscope MMP-3. For obtaining a homogeneous mixture of the oxide and nitride powders the ultrasonic dispersing in alcohol with an ultrasonic disperser Sonicator Q500 on 50% of its capacity was used. Duration of dispersion was 40 min.

Spark plasma sintering (SPS) was conducted in a LABOX machine model 625 (Sinter Land, Japan). The sintering procedure was standard: the graphite matrix with an additional layer of graphite paper between the matrix and the powder filling, and between the graphite punches and the powder to prevent the latter and the equipment from sintering. The temperature control was performed with an optical pyrometer with a measuring range 573°C to 3000 °C, directed to the matrix through a hole cut in the graphite felt, which was used as thermal insulation to prevent heat loss by radiation.

The sintered pellets were subjected to grinding and polishing by diamond pastes on the automatic polishing machine Mecatech 234. The microhardness of the samples was measured by the Vickers hardness test with a microhardness tester FM-800 (Future-Tech). The density of the samples was calculated according to the data of hydrostatic weighing with a high-accuracy analytical balances 210 G X 0.1 Mg

The bending strength characteristics of the sintered disk sample were measured on a universal testing machine 50 Quasar. A disk sample of height *h*, placed on a support ring, was forced by the truncated cone-shaped punch. Maximum load P was assumed for calculating the ultimate strength prior to the sample failure by the formula [1].

$$\sigma = \frac{3P}{8\pi h^2}\left[4-(1-\mu)\left(\frac{d}{D}\right)^2+4(1+\mu)\ln\left(\frac{D}{d}\right)\right] \quad (1)$$

where d – punch diameter, mm, μ - Poisson's ratio, *D* – diameter of the bearing ring.

X-ray phase analysis was conducted on the D8 Discover system. The break structure of the samples was studied with a scanning electron microscope (SEM) TESCAN (model VEGA 3).

3. Experimental results

3.1 Spark plasma sintering of aluminum oxynitride powder

In the first stage the sintering was conducted on already prepared powders obtained in the mode of self-propagating high-temperature synthesis (SHS), followed by pulverizing, which were produced by the Institute of Structural Macrokinetics and Materials Science RAS (Russian Academy of Sciences) in Chernogolovka city, Moscow region. The average particle size amounted to 80 microns (Fig. 1).

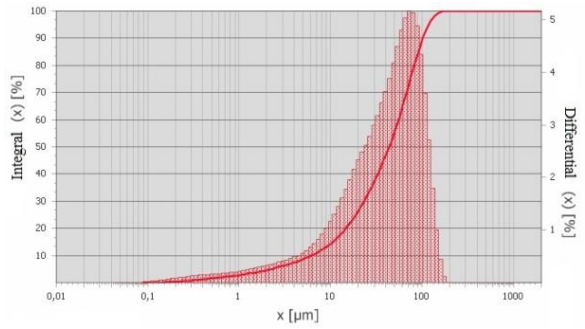

Figure 1. The particle size distribution of the aluminum oxynitride powder produced by the Institute of Structural Macrokinetics and Materials Science RAS

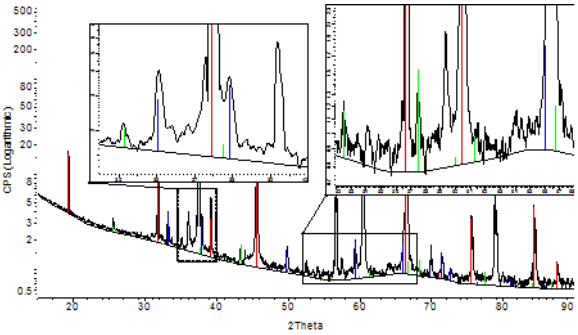

Figure 2. The X-ray spectrum of the aluminum oxynitride powder produced by the Institute of Structural Macrokinetics and Materials Science RAS (on a logarithmic scale)

Figure 2 shows the data of the X-ray analysis, which allows assessing the quality of the supplied aluminum oxynitride powder. According to the results of quantitative analysis, in the aluminum oxynitride powder produced by the Institute of Structural Macrokinetics and Materials Science RAS ISMAN there is a proportion of following phases: ALON - 96% (red), Al2O3 - 1,4% (lime), AlN - 2,6% (blue).

The mode of spark-plasma sintering was selected empirically based on maximum achievable density, microhardness and the presence of transparency. The maximum density (3.64 g / cm3, or 99.1% of the theoretical), and microhardness (18.6 GPa) were obtained with a 10-minute exposure at 1850 ° C, a pressure of 40 MPa, a heating and cooling rate of 100°C/min and 50°C/min respectively. The grain size at 10 minute exposure was equal 95 microns, and with increasing exposure time to 60 minutes the grain size increased to 120 microns, however the density and microhardness decreased. Bending strength in these samples ranged from 214 - 261 MPa, and conditional modulus varied from 172 GPa to 198 GPa. The maximum shrinkage during the sintering occurred at the temperature range 1800°C to 1850 °C. At the same time some transparency was observed in compacts with a diameter of 15 mm sintered in this mode, as illustrated by Figures 3 and 4.

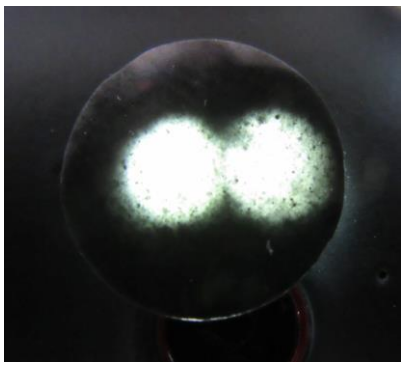

Figure 3. A polished sample, 1 mm thick, positioned on two LEDs

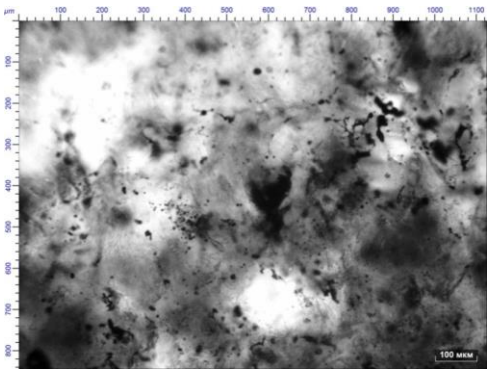

Figure 4. Image of a sample, 1 mm thick from a transmission electron microscope

As seen from the presented figures, there are small nontransparent inclusions along with transparent grains. These nontransparent inclusions may be pores or inclusions of second phase. To determine their nature an X-ray spectrum of the compact was taken. The proportion of phases: ALON - 95,4%, Al7O3N5 - 4,2%, AlN - 0,4%, which is also close to the composition of the starting powder.

The microanalysis of the sample fracture performed on a SEM, which is presented in Figure 5, showed that in contrast to large grains of ALON small inclusions contain admixtures of sulfur and iron, as indicated in Table 1, obviously residual products of thermal reaction preceding the production of ALON.

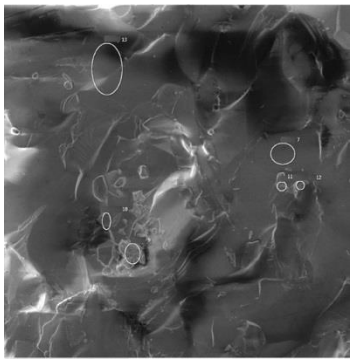

Figure 5. Areas of fracture sample, the chemical composition in which was studied.

Table 1. Chemical composition of studied areas.

№ specter	Chemical composition (at. %)				
	N	O	Al	S	Fe
7	15.64	64.71	19.55	0.09	
9	10.00	52.24	29.00	8.76	
10	12.89	60.60	26.48	0.03	
11	3.16	23.10	21.79	28.15	23.81
12	9.81	63.41	25.59	1.19	

Consequently, the ALON powder produced by the Institute of Structural Macrokinetics and Materials Science RAS, Chernogolovka city, is well sintered, shows acceptable mechanical properties, but doesn't have a sufficient purity to produce a transparent material.

3.2. Solid-phase synthesis of aluminum oxynitride

The phase diagram of Al2O3-AlN system shows that aluminum oxynitride has a sufficiently broad homogeneity region that allows varying the composition of the starting mixture. [2] However, it can be assumed that the material will have the maximum properties in the middle of the range of existence of the γ-aluminum oxynitride phase. For this reason, the starting components were taken by the following proportion: 64,3 at% of Al_2O_3 64,3 at% and 35,7 at.%. of AlN. The powders were mixed by specified proportion in alcohol in an ultrasonic disperser in alcohol for 40 minutes, and then air dried.

Sintering of all the samples was carried out in a nitrogen atmosphere at pressure equal 105 Pa. This is because the nitrogen in aluminum nitride may transit into the gas phase consequently reducing the quantity of AlN. Conversely, because of the ability of aluminum to alter its valence to 1 at high temperatures, there is a possibility that nitrogen will displace oxygen in aluminum oxide. In this case, the divergence of stoichiometry will occur in the opposite direction.

Analysis of the Al2O3-AlN system state chart revealed that the formation of γ-aluminum oxynitride phase starts at 1650 ° C. The literature also shows that 1650 ° C is the temperature at which starting materials completely transform to aluminum oxynitride [3-7]. These were the reasons why the holding temperature was 1700 °C which is slightly above the theoretical value. The available evidence seems to suggest that there is a temperature gradient in diameter of the mold, i.e. areas directly adjacent to the inner walls of the matrix may not undergo the transformation. In addition, a grain has to be grown to size of about 100 microns to ensure transparency. Higher temperature will also contribute to this. Heating and cooling rate remained the same.

Empirically determined that the optimum pressure during sintering is 40 MPa. Pressure rise does not improve characteristics of compacts. The optimal exposure time at 1700 °C is 30 minutes. The increasing of the exposure time has no significant effect on the properties of materials.

Characteristics of aluminum oxide and aluminum nitride powders synthesized in the Institute of Structural Macrokinetics and Materials Science RAS, by the plasma-chemical method, are shown in Figure 6. Table 2 presents properties of the sintered samples.

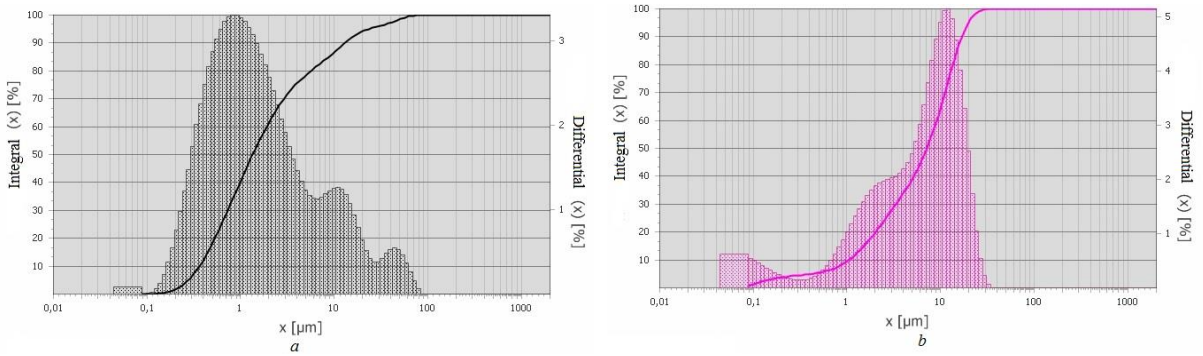

Figure 6. Particle size distribution of the powder: (a) aluminum oxide, (b) aluminum nitride

Table 2. Properties of the sintered samples.

Name	Density (g/cm^3)	The proportion of the theoretical density (%)	The average microhardness (GPa)	Tensile strength (MPa)	The presence of transparency
ALON-1	3.66±0.01	99.8	18.7±0.2	175	+
ALON-2	3.63±0.02	98.9	18.6±0.1	178	+
ALON-3	3.62±0.01	98.1	18.6±0.1	174	+
ALON-4	3.65±0.01	99.2	18.7±0.1	169	+
ALON-5	3.68±0.02	99.9	18.8±0.1	185	+
ALON-6	3.68±0.01	99.9	18.8±0.1	187	+

Samples have transparency, as shown in Figure 7.

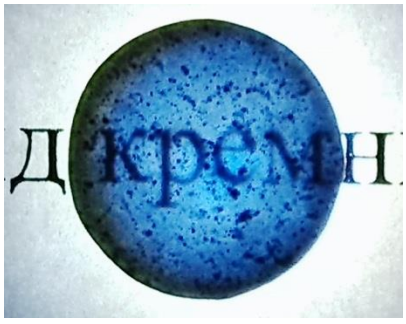

Figure 7. Sample ALON-6.

According to the results of the quantitative analysis, the sample contains traces of the starting powders.

4. Discussion of the results

Direct research of the aluminum oxynitride powder produced by the Institute of Structural Macrokinetics and Materials Science RAS) revealed that it contains only 95% of aluminum oxynitride. The same amount of aluminum oxynitride is contained in the sintered samples, i.e. the material is not single-phase. Secondary phases of non-cubic structure act as additional light scattering centers, which leads to a significant reduction in light transmission.

Furthermore, studies with the use of SEM prove the presence of sulfur and iron admixtures in significant quantities, which leads to the formation of additional phases in the material.

Consequently, satisfactory transparency was not achieved due to a high content of secondary phases (according to literature data, small amounts of secondary phases - about 1% - do not introduce significant changes to transparency).

The samples sintered using the solid-phase synthesis reaction, exhibit satisfactory transparency despite the fact that their structure contains secondary phases. This may occur due to a non-optimal ratio of starting powders or the fact that the synthesis reaction has not been fully completed. In addition, carbon can penetrate the material during the sintering. However, the analysis did not confirm its presence, which may be due to the lack of it, as well as the methods applied.

5. Conclusions

The data gathered in this study seem to prove that the spark-plasma sintering of aluminum oxynitride powder obtained by the SHS method on existing technology did not allow obtaining transparent material. The solid-phase synthesis of ALON with the spark-plasma sintering yielded positive results. The use of which makes it possible to produce transparent aluminum oxynitride for the first time in. However, obtaining single-phase transparent material requires further adjustment of the composition of the starting mixture.

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