ISSN 2075-1133, Inorganic Materials: Applied Research, 2018, Vol. 9, No. 4, pp. 599–602. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © D.V. Prosvirnin, M.D. Larionov, A.G. Kolmakov, A.S. Alikhanyan, V.I. Antipov, A.V. Samokhin, A.S. Lysenkov, D.D. Titov, 2017, published in Materialovedenie, 2017, No. 10, pp. 45–48.

Effect of Reaction Sintering Conditions on Properties of Ceramics Based on Alumina Oxynitride

D. V. Prosvirnin[a, *], M. D. Larionov[a], A. G. Kolmakov[a], A. S. Alikhanyan[b], V. I. Antipov[a], A. V. Samokhin[a], A. S. Lysenkov[a], and D. D. Titov[a]

[a] *Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, Moscow, Russia*
[b] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia*
**e-mail: imetran@yandex.ru*

Received July 6, 2017

Abstract—A comparative analysis of the physicomechanical characteristics and phase composition of $Al_{23}O_{27}N_5$ ceramic obtained by reaction sintering of the mixture of Al_2O_3 and AlN powders at different temperatures and pressures is carried out. The samples obtained had properties that correlated well with the published data.

Keywords: alumina oxynitride, structure, strength, hardness, speed of sound, reaction sintering
DOI: 10.1134/S2075113318040317

INTRODUCTION

Shock-resistant ceramic with a sufficient degree of transparency, including on the basis of alumina oxynitride $Al_{23}O_{27}N_5$, is a sought-after material in various fields of engineering, such as automobile manufacture, aircraft industry, and production of protective devices and structures [1–7]. One of the promising methods for the synthesis of alumina oxynitride is reaction sintering of the mixture of alumina powder Al_2O_3 and alumina nitride AlN [4–11]. In this case, an important task is to find the optimal methods of powder synthesis, sintering parameters, temperature regimes, and other criteria for obtaining material with a certain level of necessary properties. To achieve the required structure and level of properties, a number of additional techniques are used; in particular, uniaxial or isostatic pressure is applied during sintering, alloying additives are added to reduce the time and/or lower the sintering temperature, and the SPS process (spark-plasma sintering) and liquid phase sintering are used [6–11]. In any case, it is noted that the structure and mechanical characteristics of oxynitride ceramics are largely determined by the sintering temperatures.

In this paper, a comparative analysis of the physical and mechanical characteristics and phase composition of $Al_{23}O_{27}N_5$ ceramic obtained by reaction sintering of the mixture of Al_2O_3 and AlN powders at different temperatures and pressures was carried out.

MATERIALS AND METHODS

Powders of Al_2O_3 and AlN obtained by the method of plasma-chemical synthesis [12, 13] were used as starting material for synthesis of the samples of $Al_{23}O_{27}N_5$ ceramic. The parameters of the powders are given in Table 1. The powders were mixed in a planetary micro mill in the ratio of 40 : 60 for 50–60 min. The process was carried out in isopropyl alcohol to prevent agglomeration of powder particles and abrasion of drum walls by grinding bodies made from 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 the mixture of powders followed by reaction sintering. The pressing was carried out in a press mold under a pressure of 50 MPa. Sintering was carried out in a vacuum chamber for 30–120 min at temperatures of 1700—1800°C. In this case, the chamber was subjected to two consecutive cycles of "nitrogen purge"—pumping to residual pressure of 10^{-2}–10^{-3} mmHg. The pressed billets were placed in a crucible made of boron nitride. Samples of type II were prepared by hot pressing of a mixture of powders at temperatures of 1700—1900°C

Table 1. Characteristics of the starting powders

Initial powder	Chemical purity, %	Average particle size, μm
Al_2O_3	98.0	0.1
AlN	98.0	10.0

Table 2. Elemental analysis by XRPA method of AlN powder in at %

Al	N	O	C	Si	Cl	Other impurities
40.54% (64.48%)	44.72% (30.24%)	3.91% (3.02%)	0.65% (0.38%)	0.46% (0.62%)	0.22% (0.37%)	≤0.1%

and pressure of 500 kg/cm^2 for 12 min. 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 samples of both types were subjected to grinding and polishing.

A Tescan Vega scanning microscope was used for testing and investigation of compacts and powders. The XRPA 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 in accordance with GOST 9450-76 at the load of 500 g and test time of 10 s. The strength characteristics were determined on an INSTRON 3382 universal testing machine according to the three-point bending scheme. Measurements of the rate of longitudinal ultrasonic waves were carried out according to a standard procedure, using a Panametrics EPOCH-4 ultrasonic flaw detector at the frequency of 10 MHz according to a scheme of combined transducers. The velocity of longitudinal ultrasonic waves V was calculated from the formula $V = 2d/t$, where d is the thickness of the sample and t is the propagation time of the ultrasonic signal at the measurement point, and the attenuation coefficient of the longitudinal ultrasonic waves was calculated from the ratio $\alpha = [1/(2d)]\ln(A1/A2)$, where $A1$ and $A2$ are the amplitudes of two consecutive ultrasonic pulses.

RESULTS AND DISCUSSION

XRPA data showed that Al_2O_3 powder is a mixture of metastable phases of alumina oxide; the phase of alumina nitride is a hexagonal modification. Also in the powder, a small number of reflexes of impurity phases were detected. The data of elemental analysis by the MRSA method of AlN powder is presented in Table 2. Quantitative phase analysis of the powders showed that the ratio of the components in the weight volume in the powder mixture was 23% AlN–77% Al_2O_3. The XRPA of the compacted AlN–Al_2O_3 mixture showed that the pressing did not affect the composition of the mixture.

A diffraction pattern for the samples of type I after reaction sintering is shown in Fig. 1. The presence of alumina oxynitride, as well as small amounts of alumina nitride, corundum (Al_2O_3), and also alumina oxycarbide and alumina carbonitride, has been revealed. Apparently, the presence of these substances is due to insufficient annealing time for complete interaction, as well as the presence of carbon-containing substances in the mixture of impurities.

Performing XRPA of the samples of type II after hot pressing at temperatures of 1700–1900°C showed the presence of alumina oxynitride and residual alumina in the samples (Fig. 2).

A general view of the samples of both types is shown in Fig. 3. The samples obtained are gray and dark gray disks with a height of 10–15 and a diameter of 65 mm. The samples of type I had a uniform gray color (Fig. 1a). The samples of type II after pressing at 1700°C had a light gray color with whitish spots 1–3 mm in size. The lack of transparency of these two groups of samples is due to incompleteness of the formation of alumina oxynitride and the presence of porosity (Fig. 4). A

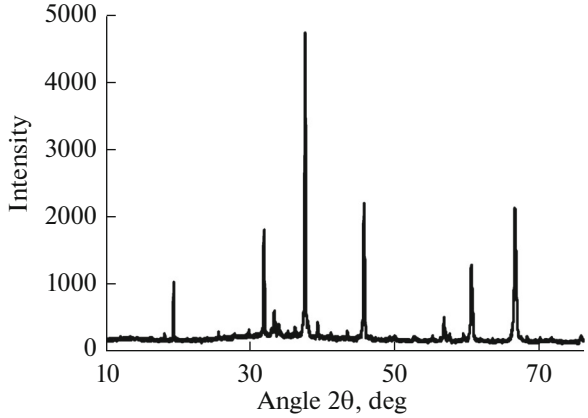

Fig. 1. X-ray diffraction pattern for the samples of type I after reaction sintering.

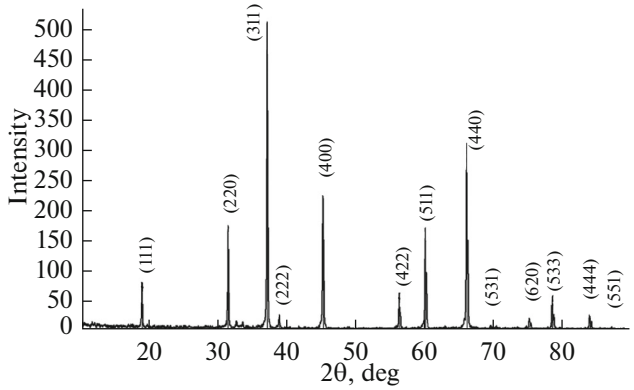

Fig. 2. X-ray diffraction pattern for the samples of type II after hot pressing.

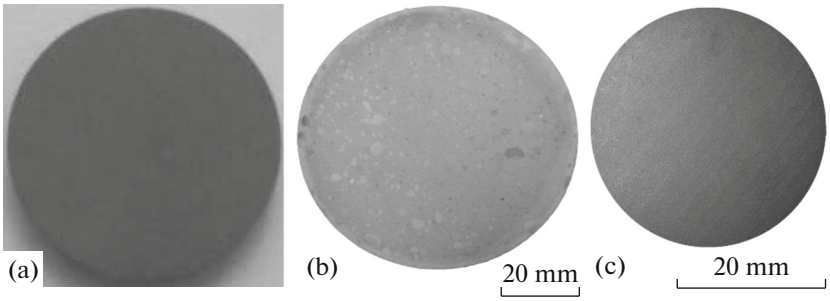

Fig. 3. General view of the samples of $Al_{23}O_{27}N_5$: (a) sample of type I obtained by technology of reaction sintering; (b) sample of type II obtained by technology of hot pressing at temperature of 1700°C; (c) sample of type II obtained by technology of hot pressing at temperature of 1900°C.

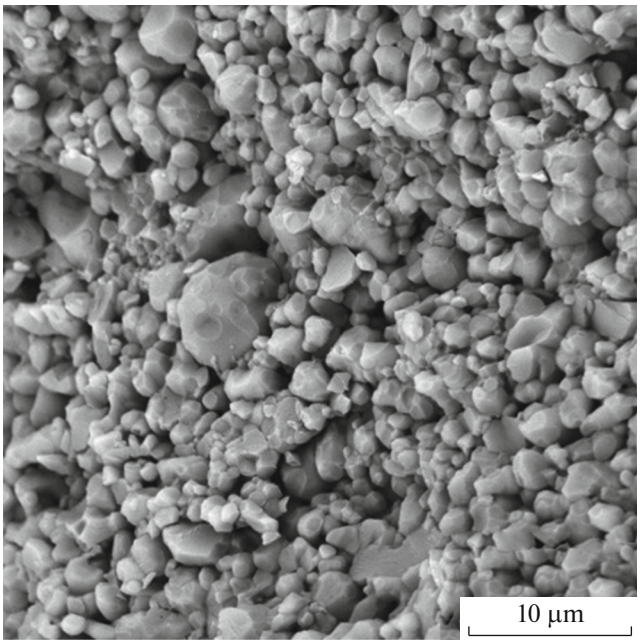

Fig. 4. Typical view of the surface of broken sample of type II (1700°C) at three-point bending.

sample of type II after pressing at 1900°C had a dark gray color and had a certain optical transparency in thin sections. The dark color is associated with diffusion of carbon through the gas phase into the sample, which is promoted by high temperature and vacuum. Thus, it has been found that the use of a coating prevents only direct diffusion of carbon in the solid phase from graphite molds.

The physical and mechanical characteristics of the samples under study are given in Table 3.

Higher values of the attenuation coefficient and low speed of sound propagation in the samples of type I indicate that they have a larger number of inhomogeneous regions (pores, defects, impurities) compared to the samples of type II. The values of the speed of sound and the attenuation coefficient obtained for the samples of type II practically coincided for 1700 and 1900°C and were close to the data given in the literature.

In general, the samples of both types showed a rather high level of mechanical characteristics. The best characteristics were obtained for a sample of type II (1900°C). If we compare the obtained values with the data usually given in different sources for oxynitride ceramic of the trademark AlON, it turns out that the obtained materials exceed it by 2–2.4 times with respect to the values of K_{IC}, they are comparable in hardness, but they are inferior by about a factor of two with respect to flexural strength.

Study of the surface of failure of the samples of type II (Fig. 4) revealed an intercrystalline type of destruction of the presence of pores in the material and also showed relatively large dispersion of the size of crystallites (1–5 μm). The pattern of failure for a sample of type I was not fundamentally different, but the porosity was more pronounced. The presence of porosity has a negative effect on the spread of mechanical properties and their level.

Thus, to obtain the necessary level of physical and mechanical properties and good transparency, it is necessary to eliminate diffusion of carbon and increase the values of temperature and exposure time. Currently available hot pressing technology, unfortunately, does not reliably prevent diffusion of carbon from graphite molds.

Table 3. Physical and mechanical characteristics of ceramic samples based on $Al_{23}O_{27}N_5$

Samples	V_{av}, m/s	α_{av}, dB/mm	$HV_{0.3}$	$\sigma_{bending}$, MPa	K_{IC}, MPa/m^2
Type I	9304 ± 46	0.6 ± 0.03	958 ± 99	122 ± 13	4.0 ± 0.37
Type II	10127 ± 506	0.18 ± 0.01	1336 ± 144	139 ± 11	4.5 ± 0.21

CONCLUSIONS

1. The samples of ceramic based on $Al_{23}O_{27}N_5$ obtained by two technologies have a close and sufficiently good set of physical and mechanical characteristics, correlating with the published data. To obtain the necessary working properties, it is required to increase the sintering temperature to about 2000°C and exposure time to 10–12 h.

2. The technology of obtaining alumina oxynitride from the mixture of Al_2O_3 and AlN powders by reaction sintering now can be considered more promising than hot pressing, because it allows achieving greater chemical purity of the material and obtaining products of complex shape. Increasing the temperature and exposure time of the process in combination with additional technological methods will make it possible to obtain products with necessary characteristics without the use of complex and insufficiently technologically effective equipment for hot pressing.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (grant no. 16-08-00815 A).

REFERENCES

1. Arzhakov, M.S., Zhirnov, A.E., Arzhakov, S.A., Lukovkin, G.M., Kolmakov, A.G., and Zabolotnyi, V.T., Glass ceramic and polymer impact-resistant materials and protective constructions based on them, *Russ. Metall.* (Engl. Transl.), 2015, vol. 2015, no. 10, pp. 800–804.
2. Arzhakov, M.S., Lukovkin, G.M., Kolmakov, A.G., Arzhakov, S.A., Zhirnov, A.E., and Parfenov, A.A., Transparent shock-resistant composites with orthogonal distribution of elements and protective constructions based on it, *Integral*, 2015, nos. 1–2 (81–82), pp. 50–53.
3. Gribchenkova, N.A., Smorchkov, K.G., Kolmakov, A.G., and Alikhanyan, A.S., Vaporization in the Al_2O_3–MgO system, *Inorg. Mater.*, 2017, vol. 53, no. 5, pp. 514–518.
4. Lysenkov, A.S., Timoshkin, I.A., Kargin, Yu.F., Titov, D.D., Fedotov, A.Yu., Ashmarin, A.A., and Baranchikov, A.E., Synthesis of aluminum oxynitride (AlON) and study of the properties of ceramics based on it, *Inorg. Mater.: Appl. Res.*, 2016, vol. 7, no. 4, pp. 517–519.
5. Gribchenkova, N.A., Beresnev, E.N., Smorchkov, K.G., Mikhailov, M.A., Shcherbakov, A.V., Ivanova, T.A., and Alikhanyan, A.S., ALON: Synthesis and thermal properties, *Russ. J. Inorg. Chem.*, 2015, vol. 60, no. 9, pp. 1137–1142.
6. Kolmakov, A.G., Prosvirnin, D.V., Alikhanyan, A.S., Kopiev, G.V., Samokhin, A.V., Antipov, V.I., and Chernyi, V.A., Synthesis of the composite material of the Al–O–N system, *Perspekt. Mater.*, 2016, no. 11, pp. 77–84.
7. Takao, Y. and Sando, M., Al-system non-oxide spherical powder synthesis by liquefied petroleum gas firing, *J. Am. Ceram. Soc.*, 2005, vol. 88, pp. 450–452.
8. Bakas, M.P., Lillo, T.M., and Chu, H.S., US Patent 7833922, 2010.
9. Huang, S., et al., AlON phase formation in hot-pressing sintering Al_2O_3/AlN composites and their oxidation behavior, *J. Alloys Compd.*, 2016, vol. 685, pp. 309–315.
10. McCauley, J.W., et al., AlON: a brief history of its emergence and evolution, *J. Eur. Ceram. Soc.*, 2009, vol. 29, no. 2, pp. 223–236.
11. Sahin, F.C., Kanbur, H.E., and Apak, B., Preparation of AlON ceramics via reactive spark plasma sintering, *J. Eur. Ceram. Soc.*, 2012, vol. 32, no. 4, pp. 925–929.
12. Alekseev, N.V., Samokhin, A.V., and Tsvetkov, Yu.V., RF Patent 2311225, 2007.
13. Samokhin, A.V., Sinayskiy, M.A., Alexeev, N.V., Rizakhanov, R.N., Tsvetkov, Yu.V., Litvinova, I.S., and Barmin, A.A., Synthesis of nanoscale zirconium dioxide powders and composites on their basis in thermal DC Plasma, *Inorg. Mater.: Appl. Res.*, 2015, vol. 6, no. 5, pp. 528–535.

Translated by Sh. Galyaltdinov