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The process of nitration of aluminum and aluminum-containing mixtures in the regime of self-propagating high-temperature synthesis with a high pressure (up to 300 MPa) of the reacting gas (nitrogen) is considered. The dependences of ignition temperatures and also burning temperatures and burning rates of these initial mixtures on test conditions (nitrogen pressure and composition of the initial mixture) are studied. The dependence of the burning rate of initial mixtures on factors affecting spreading of the liquid component (melt containing aluminum and nitrogen) over the surface of the second component (aluminum nitride or titanium diboride), such as the equilibrium wetting angle, interaction at the interface, and melting of the second component, is studied. The microstructure and some properties of materials obtained are examined. Based on these studies, the combustion mechanism is determined, a mechanism of phase formation in combustion of these mixtures is suggested, and the structure of the combustion wave is determined.

Key words: aluminum nitride, melting, combustion and phase-formation mechanism, wave structure.

INTRODUCTION

Products of aluminum-nitride-based materials, owing to specific physicochemical properties of this substance, can find wide application in various branches of industry. Therefore, self-propagating high-temperature synthesis (SHS) of such materials is an urgent problem. The SHS gas-static technology of dense materials unites two processes in space and time: synthesis of the compound itself and sintering of a dense material from it. Therefore, in studying aluminum-nitride-based SHS materials, it is necessary not only to consider the laws of burning of porous aluminum-containing specimens in nitrogen but also to determine the optimal conditions for obtaining dense materials.

In synthesis of dense aluminum-nitride-based materials under traditional conditions, the main restrictions of SHS are the insufficient initial concentration of nitrogen in pores of initial aluminum-containing specimens, filtrational difficulties in the course of self-propagating high-temperature synthesis, and dissociation of combustion products. To eliminate these restrictions, the process was performed at high pressures (up to 300 MPa) of the reacting gas (nitrogen) in SHS gasostats [1, 2].

TEST TECHNIQUE

The initial components in all experiments were ASD-1 or ASD-4 aluminum powders and SHS powders of aluminum nitride and titanium diboride. The powders were mixed in ball mills. The initial specimens 30-80 mm in diameter and 20-300 mm high, with porosity $\Pi = 40-50\%$, were obtained by uniaxial pressing in steel press-forms and isostatic pressing in rubber shells (gas-statically or hydrostatically). The specimens were placed into an SHS gasostat. The synthesis was performed in a nitrogen medium at pressures of 10–300 MPa. The burning temperature was measured by 5/20 tungsten/rhenium thermocouples 100-200 μ m thick. The mean burning rate was determined by two thermocouples located at a fixed distance in the upper and lower parts of the specimen. The relative measurement errors of burning temperatures and rates were smaller than 5 and 7%, respectively [3, 4].

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Fig. 1. Burning temperature of the "aluminum + aluminum nitride" burden versus nitrogen pressure.

The density of combustion products was measured by a hydrostatic method on an analytical balance. The macrohardness was determined by the Rockwell scale, and the microhardness was determined by a PMT-3 device by standard techniques. The specific features of the microstructure and the phase composition of materials were studied by the Jeol-JCXA-733 x-ray microanalyzer, "Neofot-30" microscope, and "Dron-2" x-ray diffractometer. The chemical analysis of the products was performed by standard techniques. The accuracy of thermal conductivity measurement corresponds to the GOST 8.140-82 Russian standard.

TEST RESULTS

The burning of pure aluminum in nitrogen was studied on specimens with a porosity of 40–50%. The burning rate and temperature remained unchanged with nitrogen-pressure variation from 50 to 100 MPa and were equal to 15 mm/sec and 2273 K, respectively. Combustion products contained aluminum and aluminum nitride (Table 1). The mass content of free aluminum was 10-15%.

The study of combustion of the initial mixture consisting of aluminum and aluminum nitride (aluminum concentration in the mixture varied from 35.5 to 60%) under nitrogen pressure $p_{N_2} = 15\text{--}300$ MPa showed that the maximum content of nitrogen in compact combustion products was 32.8%, and it was reached at $p_{N_2} \ge 100$ MPa. The measured burning rate of specimens with an initial porosity of $\approx 50\%$ and a mass content of aluminum nitride in the initial mixture of $\approx 50\%$ is plotted in Fig. 1 as a function of nitrogen pressure.



Fig. 2. Typical structure of AlN fracture $(\times 400)$.

Thermograms contained typical plateaus at the maximum burning rates. For contents of aluminum nitride in the initial specimens within 40-60%, the burning rate remained unchanged for identical nitrogen pressures. The burning rate was measured at different nitrogen pressures and was 1–2 mm/sec for $p_{\rm N_2} \approx 15 \text{ MPa}$ (bulk density) and 3–5 mm/sec for $p_{N_2} = 100-300$ MPa $(\Pi \ge 40\%)$. The minimum porosity of the end product, aluminum nitride, that could be obtained in these tests was 20-25%. A photograph of the typical structure of fracture of aluminum nitride with a porosity of $\approx 20\%$ is shown in Fig. 2. The mass content of free aluminum in this specimen was approximately 0.1%, and the thermal conductivity was $\lambda = 50 \text{ W/(m \cdot K)}$. It is seen in the photograph that the structure of the product resulted from melting, and it is impossible to distinguish grains of aluminum nitride formed by aluminum burning and grains of aluminum nitride used as a diluent.

In studying combustion of specimens of a mixture of aluminum and titanium diboride, it was found that the burning rate is significantly higher than for specimens of a mixture of aluminum and aluminum nitride under identical conditions. The results of these measurements are listed in Table 1. The phase composition of the resultant product is a mixture of aluminum nitride and titanium diboride. The mass content of free aluminum is $\leq 0.8\%$. A photograph of the thin section of the microstructure of the materials obtained is shown

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Phase composition	$p_{N_2},$	u,	T, K	$C_{Al},$	$C_{N_2},$	$C_{ m N_2}^0,{ m g/cm^3}$			
of products	MPa	$\mathrm{mm/sec}$,	$\rm g/cm^3$	$\rm g/cm^3$	300 K	950 K	1300 K	1800 K
No. 1: $Al + AlN$	100	15	2273	1.35	0.7	0.285	0.13	0.1	0.076
No. 2: AlN + TiB_2	100-300	15	2623-2773	0.845	0.438	0.285 - 0.373	0.13 - 0.245	0.1 - 0.211	0.076 - 0.173
No. 3: AlN	100-300	5	2623-2773	0.739	0.383	(400 K)	(1000 K)		

Note. u and T are the burning rate and temperature of the specimens, respectively, C_{Al} is the amount of aluminum in 1 cm³ of the initial specimen ($\Pi = 50\%$), C_{N_2} is the amount of nitrogen necessary for complete nitration of aluminum in 1 cm³ of the initial specimen ($\Pi = 50\%$), and $C_{N_2}^0$ is the amount of nitrogen in pores in 1 cm³ of the initial specimen ($\Pi = 50\%$).



Fig. 3. Photograph of the thin section of the typical structure of the composite material 60% AlN+40% TiB₂ (×440).

in Fig. 3. The density of materials is 92% of the theoretical value, the flexural hardness is 200–250 MPa, the Rockwell hardness (scale A) is 70–80 units, the grain microhardness is 25,750–31,800 MPa, and the matrix microhardness is 10,720–12,250 MPa. The material has practically no pores, it is uniform, and titanium diboride grains are distributed over the matrix of melted aluminum nitride. The values of grains (titanium diboride) and matrix (aluminum nitride) microhardness correspond to the values typical of single crystals of titanium diboride and aluminum nitride. The data of the x-ray microanalysis are shown in Fig. 4. Distinct interfaces between titanium diboride and aluminum nitride phases are clearly visible, and the elements (titanium and aluminum) are definitely distributed over the compounds, which indicates that there is no interaction of the liquid phase formed during SHS and nitrogen with titanium diboride grains. A comparison of porosity of the material of pure aluminum nitride $(\Pi \approx 20-25\%)$ and the composite material "aluminum"



Fig. 4. Data of x-ray microanalysis of the composite material 60% AlN+40% TiB₂: K α -Ti (a) and K α -Al (b).

nitride–titanium diboride" ($\Pi \approx 8\%$) shows that porosity is significantly lower in the second case, whereas the content of free aluminum in the materials differs insignificantly.

The dependence of the ignition temperature of aluminum and aluminum-containing mixtures on nitrogen pressure and composition of the initial burden was studied using a compression furnace developed at the Institute of Structural Macrokinetics and Material Science of the Russian Academy of Sciences (ISM)² on the basis of the SVS-8 reactor (Fig. 5), which allows experiments with nitrogen pressure up to 30 MPa and temperature up to 2273 K. The measurement results are plotted in Fig. 6. It is seen that ignition of aluminum-containing mixtures occurs at heating temperatures higher than the melting point of aluminum (931 K).

²The furnace was developed by A. V. Losikov.



Fig. 5. Layout of the compression furnace on the basis of the SHS-8 reactor: 1) casing; 2) gate; 3) heater; 4) heating zone; 5) thermocouple; 6) thermal insulation; 7) cooling channels; 8) electrical inputs; 9) power source of the heater.



Fig. 6. Ignition temperature of the burden versus the content of aluminum in it and nitrogen pressure (the heating rate is 30 K/min).

DISCUSSION OF RESULTS

It is experimentally found that aluminum melts at initiation of the nitration reaction, but the melted drops are protected from contacting nitrogen by a continuous oxide film without pores. Aluminum volume increases upon melting and further increase in melt temperature [5]. At a certain temperature, the oxide film is broken, and the subsequent process of nitration depends on the following factors:

1) mechanism of interaction of liquid aluminum with nitrogen;

2) wettability of the second component (aluminum nitride or titanium diboride) by the melt (the melt content will be discussed later);



Fig. 7. Thermal conductivity of the composite material 60% AlN+40% TiB₂ versus temperature (porosity is $\approx 8\%$).

3) chemical interaction of the melt with the second component and violation of the interface between the components;

4) melting capability of the second component and associated violation of the interface between the components.

Let us consider the effect of these factors in the case where the second component of the initial mixture is titanium diboride. It is shown in [6-12] that the equilibrium wetting angle of titanium diboride by aluminum in vacuum or an inert gas at a temperature higher than 1573 K tends to zero; in this case, titanium diboride does not interact with liquid aluminum. The results of the present work show that the melt formed in the SHS zone does not interact with titanium diboride either (see Fig. 4). It should also be noted that the burning temperature of the 50% Al + 50% AlN mixture reaches 2773 K. This value is much lower than the melting point of titanium diboride (3223 K). Hence, titanium diboride in the SHS zone does not melt, and the interface between the melt and titanium diboride (namely, the surfaces of titanium diboride grains) is not violated and does not prevent spreading of the melt formed in the SHS zone over the surface of titanium diboride grains. Thus, the results obtained and their comparison with available data show that factors 2–4 (see above) do not decelerate spreading of the melt formed in the combustion zone over the surface of titanium diboride particles.

We consider the aggregate state and elementary composition of the nitrated product in the zone of the fast reaction and afterburning. The following experimental data of the present work give grounds to state that, during SHS of the considered materials in the reaction zone, the substance formed by aluminum nitration is in a melted form:

- the presence of a typical plateau on thermograms in measurements of the maximum burning temperatures;
- the presence of a matrix of melted aluminum nitride with a stoichiometric composition (Fig. 3) whose existence is also confirmed by the measurements of thermal conductivity of the material "aluminum nitride-titanium diboride" (Fig. 7): the value of the thermal conductivity $\lambda = 150$ W/(m × K) can be caused only by the presence of the aluminum nitride skeleton [for titanium diboride, $\lambda = 150$ W/(m · K), and for the Elantinit [AlN-based ceramic material with high thermal conductivity, technical specifications No. 974-87 (ISM) obtained by recrystallization of aluminum nitride through the liquid phase, $\lambda = 120-150$ W/(m · K)];

Formation of melted final materials obtained under similar conditions was also reported in [13, 14].

It seems of interest to find the melt composition in the reaction zone and the possibility of existence of the aluminum nitride melt with a stoichiometric composition in the zone of the maximum temperature of the combustion wave.

It is shown in [15, 16] that the pressure $p_{\rm N_2}$ = 10-50 MPa allows obtaining the aluminum nitride melt 50–300 μ m thick, which is in thermodynamical equilibrium with the ambient gas (nitrogen). Typical values of physicochemical parameters and conditions of SHS of aluminum nitride and its melting by laser radiation are listed in Table 2. The SHS conditions in the present work almost coincide with the conditions of [15, 16]. The difference between the burning temperature measured in the present work and the melting point of aluminum nitride in [13, 14] is within the measurement error of the maximum burning rate. The coincidence of parameters and obtaining a material with a matrix of melted aluminum nitride due to SHS allow us to conclude that a melt of stoichiometric aluminum nitride can exist in the wave of SHS materials obtained from the burden "aluminum + titanium diboride or aluminum nitride" under test conditions used.

It is important to find in which zone of the combustion wave this melt is formed. The maximum burning rate (2773 K) is close to the adiabatic burning temperature of aluminum in nitrogen, calculated under the condition of formation of a stoichiometric composition and without allowance for melting heat (2900 K) [17]. This indicates that aluminum in the reaction zone absorbs the maximum possible amount of nitrogen, and the maximum amount of heat is released thereby. This is also confirmed by the analysis of the change in specimen porosity due to shrinkage. Table 3 shows the change in porosity due to various factors. It is seen that porosity of specimen 2 changes by 30% due to shrinkage. This is possible if sufficient fluidity of the resultant melt is retained, which is most probable at the melting point of the melt or temperatures close to it, i.e., in the combustion zone. Hence, the melt of stoichiometric aluminum nitride is formed in the combustion zone.

The study of aluminum nitration in the case where the second component of the initial mixture is aluminum nitride showed that melting of the aluminum nitride being formed and initial aluminum nitride diluent occurs during combustion (see Fig. 2), i.e., the interface "liquid aluminum–aluminum nitride" is violated in the course of combustion.

It is known from publications that the equilibrium wetting angle of aluminum nitride by aluminum at temperatures higher than 1573 K tends to zero, whereas below the temperature of 1573 K, it is greater (80°) than the equilibrium wetting angle of titanium diboride [10, p. 169; 11, pp. 164–165, 190]. It is also known that interaction occurs at a temperature of 1473 K at the interface "liquid aluminum–aluminum nitride": nitrogen passes from aluminum nitride to liquid aluminum, which generally increases the equilibrium wetting angle [6; 7; 11, p. 165].

Thus, the above-noted processes decelerate spreading of liquid aluminum over the surface of aluminum nitride particles, which, probably, is the reason for the decrease in the burning rate (see Table 1).

An analysis of porosity behavior during SHS shows that the decrease in porosity due to shrinkage in combustion of the 50% Al + 50% AlN is 15% mixture. The final porosity of the specimen is 20-25%, which is the limit where nitrogen filtration into the specimen is terminated. Since the final specimen has a stoichiometric composition, aluminum nitration is finished before the specimen porosity reaches 20-25%.

The experimental data obtained, namely, the form of thermograms with a typical plateau obtained in measurement of the maximum temperatures and the presence of final materials with melted structures, show that the description of the mechanism of combustion of aluminum and aluminum-containing mixtures under conditions of the present work can involve the concepts of the elementary combustion models of the II kind, namely, the models of high-temperature melting [18– 20]; hence, it is possible to develop qualitative ideas on possible ways of phase formation in the combustion wave. To explain the mechanism of phase formation in combustion of aluminum in nitrogen, one should also involve the concept of the nonequilibrium mechanism of phase formation. The assumption of the existence of such a mechanism of interaction between

TABLE 2

	Test conditions				
Parameters	SHS of aluminum nitride*	Melting of aluminum nitride			
		by laser radiation***			
Nitrogen pressure, MPa	10-300**	10-50			
Burning temperature, K	2773**				
Melting temperature, K		2950			
Burning rate, mm/sec	5-15**				
LR scanning rate, mm/sec		2.5			
Conversion factor, mm/sec	≈1**	≈1			
Heating rate of the substance, K/sec	$10^3 - 10^6$	$10^4 - 10^5$			
Width of the synthesis zone, μm	100 - 5000	—			
Width of the melting zone, μm	_	50-300			
Residence time of the substance at the melting temperature, sec	≼1	≤1			

Note. Data of [18–20] are marked by one asterisk, data of the present work are marked by two asterisks, and data of [15, 16] are marked by three asterisks; LR is laser radiation.

TABLE	3
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Specimen number	Mass composition of the initial mixture, $\%$	$\Pi_{\rm in},\%$	$\Pi_{\rm fin,exp},\%$	$\Pi_{\rm fin, calc},\%$	$\Pi_{\rm shr},\%$
1	50% Al+50 $%$ AlN	43	20 - 25	35	15 - 10
2	50% Al + $50%$ TiB ₂	47	8	38	30

Note. Π_{in} is the initial porosity, $\Pi_{fin,exp}$ is the final experimental porosity, $\Pi_{fin,calc}$ is the porosity calculated under the condition of its reduction only due to the positive bulk effect of the aluminum-nitrogen reaction, and Π_{shr} is the change in porosity due to shrinkage ($\Pi_{shr} = \Pi_{fin,calc} - \Pi_{fin,exp}$).

metals and nonmetals was first put forward in [21] in studying combustion of transitional metals in nitrogen. Some experimental evidence of its existence were also obtained there. The existence of the nonequilibrium mechanism of phase formation in interaction of transitional metals with nitrogen at high pressures of the latter was confirmed later [22]. In describing the combustion-wave structure, two factors affecting nitration of specimens in all cases in the present work (see Table 1) should be noted. The calculations were performed for initial burdens with the following compositions: 100% aluminum, 50% aluminum + 50% titanium diboride, and 50% aluminum + 50% aluminum nitride. The amount of nitrogen contained in the pores $(\Pi = 50\%)$ for T = 300-1800 K is insufficient for complete nitration of aluminum; filtration of nitrogen from outside is always necessary (the amounts of nitrogen in pores were calculated in accordance with the data of [23–25]). In addition, in all cases, as was shown above, nitrogen pressure is sufficient for equilibrium existence

of the melt of stoichiometric aluminum nitride.

Based on the data obtained, it is possible to present the structure of the SHS wave with the following zonal distribution of physicochemical processes in the combustion wave.

I. Heating Zone. In case Nos. 1–3 presented in Table 1, aluminum during synthesis is heated to the melting point (951 K) and melts, but the aluminum melt is inside a continuous oxide film without pores. The film does not allow aluminum to spread, and there is no contact of nitrogen with liquid aluminum. During melting, the volume of aluminum increases (6.6% at 931 K and 13% at 1273 K) [5], the oxide film is broken, and liquid aluminum flows out, which leads to ignition, instantaneous nitration of aluminum, and drastic increase in temperature.

II. Fast Reaction Zone — Zone of the Maximum Heat Release. 1. Combustion of Aluminum. Nitration proceeds to a certain conversion depth η_1 caused by the amount of nitrogen in pores and the cur-

rent filtrational situation. The maximum amount of heat is released, which is sufficient for melting of the entire substance in the zone and its heating to a temperature of 2273 K, coalescence of homogeneous drops of the melt occurs, porosity is lost, and nitrogen filtration is terminated; the value of η_1 determines the burning rate $u_1 = 15$ mm/sec. Nitration results in the formation of a melt containing aluminum and nitrogen in a proportion corresponding to the conversion depth $\eta_1 < 1$.

2. Combustion of a Mixture of Aluminum and Titanium Diboride. Nitration of aluminum proceeds to a certain conversion depth η_2 caused by the amount of nitrogen in pores and the current filtrational situation. The maximum amount of heat is released, and the burning rate is $u_2 = 15 \text{ mm/sec.}$ As was shown above, the presence of titanium diboride in the initial burden does not affect melt spreading, and the burning rate determined by the maximum conversion depth η_2 remains unchanged. Hence, in the fast reaction zone, the maximum conversion depth in combustion of aluminum specimens equals the maximum conversion depth in combustion of specimens made of a mixture of aluminum and titanium diboride, i.e., $\eta_1 = \eta_2$. The temperature increases up to 2273 K. Titanium diboride grains prevent coalescence of melt drops. Porosity is retained, nitrogen filtration is possible, and the specimen retains its geometric shape. Nitration results in the formation of a melt containing aluminum and nitrogen in a proportion corresponding to the nitration depth $\eta_2 = \eta_1 < 1$.

3. Combustion of a Mixture of Aluminum and Aluminum Nitride. Aluminum nitration proceeds to the maximum conversion depth η_3 . The maximum amount of heat is released. Since the conditions responsible for the conversion depth η_3 do not differ from the conditions in case Nos. 1 and 2, we have $\eta_3 = \eta_2 = \eta_1$. The temperature increases up to 2273 K. The burning rate, however, is lower in this case: $u_3 = 5$ mm/sec, which is a consequence of the influence of certain factors, as was noted above. Porosity is retained, nitrogen filtration is possible, and the specimen retains its geometric shape. Nitration results in the formation of a melt containing aluminum and nitrogen in a proportion corresponding to the nitration depth $\eta_3 = \eta_2 = \eta_1 < 1$.

III. Afterburning Zone. 1. Combustion of Aluminum. The specimen lost its porosity, and nitrogen cannot be added to the interaction region by filtration. Nevertheless, the specimen temperature and nitrogen pressure predetermine the existence of another mechanism of nitrogen addition (determination of the nature of this mechanism requires additional studies), which provides addition of such an amount of the gas that the heat released due to interaction of the melt and nitrogen is sufficient for maintaining the melt temperature of 2273 K. Nitration depth increases but remains lower than unity. Nitration has no longer effect on the burning rate. Melt homogenization occurs. The thermogram of the maximum burning temperature acquires a plateau at the melting temperature of 2273 K. The crystallization process begins.

2. Combustion of a Mixture of Aluminum and Titanium Diboride. Nitration continues $(\eta_2 \rightarrow 1)$, the temperature in the zone increases $(T \rightarrow 2773 \text{ K})$, but this has no longer effect on the burning rate. Due to nitration, the amount of nitrogen in the melt and its melting point increase. The released heat, however, is always sufficient for melting of the newly formed products. At $\eta_2 \approx 1$ and T = 2773 K, there appears a plateau on the thermogram. In the afterburning zone, there exists a melt containing aluminum and nitrogen in a proportion corresponding to stoichiometric aluminum nitride and titanium diboride grains. Simultaneously with nitration, shrinkage of the specimens occurs. Nitration ends at $\Pi \approx 20-25\%$, but it can possibly end earlier. Shrinkage occurs to values of porosity $8 < \Pi < 20-25\%$ but also possibly to the final value of 8%.

3. Combustion of a Mixture of Aluminum and Aluminum Nitride. Nitration continues $(\eta_3 \rightarrow 1)$, the temperature in the zone increases $(T \rightarrow 2773 \text{ K})$, but this has no longer effect on the burning rate. Due to nitration, the amount of nitrogen in the melt and its melting point increase. The released heat, however, is always sufficient for melting of the newly formed products. Interaction of the melt with grains of aluminum nitride (grains) along the interfaces occurs. Owing to the high value of thermal conductivity, the temperature of aluminum nitride increases together with the melt temperature; at $\eta_3 \approx 1$ and $T \approx 2773$ K, the initial aluminum nitride also melts. The thermogram acquires a plateau at 2273 K. Melt homogenization occurs. Porosity decreases to 20-25%, and this is the threshold value at which nitrogen filtration into the specimen is terminated.

IV. Zone of Crystallization and Products. 1. Combustion of Aluminum. Crystallization occurs: the melt containing aluminum and nitrogen in a proportion corresponding to the conversion depth reached in the afterburning zone passes to the solid state (possibly, forming the solid solution of nitrogen in aluminum of the same composition). During cooling, it decomposes into a two-phase mixture of aluminum and aluminum nitride. Nitration continues, but its intensity decreases with the change in the aggregate state (crystallization). The released heat allows only a decrease in the cooling rate. The nitration depth increases to the final value but remains lower than unity. 2. Combustion of a Mixture of Aluminum and Titanium Diboride. Crystallization occurs: the melt containing aluminum and nitrogen in a proportion corresponding to the conversion depth $\eta \approx 1$ passes to the solid state (possibly, forming the solid solution of nitrogen in aluminum of the same composition). During subsequent cooling, its passes to single-phase stoichiometric aluminum nitride, forming an aluminum nitride skeleton with uniformly distributed grains of titanium diboride. Simultaneously, to a temperature of 2000 K, there occurs shrinkage, which compensates for a possible increase in porosity due to crystallization, or porosity decreases to 8% if it was $8 < \Pi < 20-25\%$ in the afterburning zone.

3. Combustion of a Mixture of Aluminum and Aluminum Nitride. Crystallization occurs: the melt containing aluminum and nitrogen in a proportion corresponding to the conversion depth $\eta \approx 1$ passes to the solid state (possibly, forming the solid solution of nitrogen in aluminum of the same composition). During subsequent cooling, its passes to single-phase stoichiometric aluminum nitride. Simultaneously, to a temperature of 2000 K, there occurs shrinkage, which compensates for a possible increase in porosity due to crystallization.

It should be noted that there are no yet direct experimental data confirming the presence of the mechanism we suggested for phase formation in the zone of crystallization and products in the case of combustion of aluminum and aluminum-containing mixtures in nitrogen.

CONCLUSIONS

1. It is shown that SHS of aluminum nitride and composite materials on its basis in high-pressure nitrogen occurs with formation of the aluminum-nitride melt, and the measured melting point is 2773 K. It is also found that a typical feature of the composite material "aluminum nitride–titanium diboride" is the presence of a matrix of melted aluminum nitride.

2. A dependence of the combustion-front velocity in the case of aluminum–nitrogen interaction on physicochemical properties of the second component (aluminum nitride or titanium diboride) present in the front is found.

3. It is shown that the mechanism of aluminum combustion in high-pressure nitrogen corresponds to the elementary model of combustion of the II kind.

4. The structure of the combustion wave with a zonal distribution of physicochemical processes is suggested. An assumption is made on the presence of a nonequilibrium mechanism of phase formation in the case of aluminum–nitrogen interaction.

REFERENCES

- V. I. Ratnikov and V. K. Énman, "Compressor facility with a hydraulic drive," Inventor's Certificate No. 761744, Byul. Izobr., No. 33, 179 (1980).
- V. I. Ratnikov and V. K. Énman, "Equipment for SHS processes with superhigh pressure of the gas," in: *Problems of Technological Combustion* (collected scientific papers) [in Russian], Vol. 2, Chernogolovka (1981), pp. 8–12.
- A. S. Mukas'yan, V. M. Martynenko, A. G. Merzhanov, et al., "Mechanism and principles of silicon combustion in nitrogen," *Combust. Expl. Shock Waves*, 22, No. 5, 534–539 (1986).
- V. M. Maslov, I. P. Borovinskaya, and A. G. Merzhanov, "Peak-temperature measurement for self-propagating high-temperature synthesis processes," *Combust. Expl. Shock Waves*, 14, No. 5, 618–622 (1978).
- A. I. Belyaev, *Metallurgy of Light Alloys* [in Russian], Metallurgiya, Moscow (1970).
- G. A. Yasinskaya, "Wettability of refractory carbides, borides, and nitrides by melted metals," *Poroshk. Metallurg.*, No. 7, 53–56 (1966).
- A. D. Panasyuk and A. B. Belykh, "Investigation of contact interaction of aluminum nitride and liquid copper, silicon, aluminum, and nickel," in: *Adhesion of Melts* and Soldering of Materials (collected scientific papers) [in Russian], No. 6 (1980), pp. 73–76.
- S. K. Rhee, "Wetting of ceramics by liquid aluminum," J. Am. Ceram. Soc., 53, No. 7, 386–389 (1970).
- P. S. Kislyi, M. A. Kuzenkova, L. I. Struk, et al., "Industrial exploitation of aluminum evaporators in vacuum from melts based on refractory compounds," *Poroshk. Metallurg.*, No. 1, 40–47 (1976).
- P. S. Kislyi et al., Physicochemical Fundamentals of Obtaining Refractory Superstrong Materials [in Russian], Naukova Dumka, Kiev (1986).
- P. S. Kislyi et al., *Cermets* [in Russian], Naukova Dumka, Kiev (1985).
- A. D. Panasyuk, V. S. Fomenko, and G. G. Glebova, Stability of Nonmetal Materials in Melts: Handbook [in Russian], Naukova Dumka, Kiev (1986).
- I. P. Borovinskaya, V. É. Loryan, and G. Yu. Shekk, "Obtaining AlN-based ceramics in the combustion mode and its properties," in: *Structures and Technology of Obtaining Articles from Nonmetal Materials*, Proc. XIII Conf., Obninsk (1992), p. 6.
- S. D. Dunmead, J. B. Holt, and Z. A. Munir, "Simultaneous combustion synthesis and densification of AlN," *Am. Ceram. Soc. Bull.*, 67, No. 9, 1506 (1988).

- V. L. Vinogradov, V. A. Kostanovskii, and A. V. Kirillin, "Determination of melting parameters of aluminum nitride," *Teplofiz. Vys. Temp.*, **30**, No. 4, 731– 737 (1992).
- A. V. Kostanovskii, "Remelting of the surface layer of AlN-based ceramics under the action of laser radiation," *Teplofiz. Vys. Temp.*, **32**, No. 5, 742–748 (1994).
- N. P. Novikov, I. P. Borovinskaya, and A. G. Merzhanov, "Thermodynamic analysis of self-propagating hightemperature synthesis reactions," Preprint of the Institute of Chemical Physics, Acad. of Sci. of the USSR, Chernogolovka (1975).
- A. G. Merzhanov, "Combustion processes in chemical technology," Preprint, Joint Inst. of Chem. Phys., Acad. of Sci. of the USSR, Chernogolovka (1976).
- A. G. Merzhanov, *Solid-Flame Combustion* [in Russian], Inst. of Struct. Macrokinet. and Mater. Sci., Chernogolovka (2000).
- A. G. Merzhanov, Combustion Processes and Synthesis of Materials [in Russian], Inst. of Struct. Macrokinet. and Mater. Sci., Chernogolovka (1998).

- I. P. Borovinskaya, "Formation of refractory compounds in combustion of heterogeneous condensed systems," in: *Combustion and Explosion*, Proc. IV All-Union Symp. on Combustion and Explosion [in Russian], Nauka, Moscow (1977), pp. 138–148.
- I. P. Borovinskaya, G. A. Vishnyakova, and V. É. Loryan, "Mechanism of phase formation in combustion of titanium and zirconium in nitrogen," in: *Problems of Structural Macrokinetics* (collected scientific papers) [in Russian], Chernogolovka (1991), pp. 5–23.
- D. S. Tsiklis, *Dense Gases* [in Russian], Khimiya, Moscow (1977).
- A. A. Vasserman et al., Thermophysical Properties of Air and Its Components [in Russian], Nauka, Moscow (1966).
- A. A. Antanovich and M. A. Plotnikov, "Experimental determination of nitrogen density at high pressures and temperatures," *Dokl. Akad. Nauk SSSR*, **226**, No. 4, 809–811 (1976).