ISSN 0010-5082, Combustion, Explosion, and Shock Waves, 2016, Vol. 52, No. 2, pp. 184–192. © Pleiades Publishing, Ltd., 2016. Original Russian Text © Z.A. Mansurov, S.M. Fomenko, A.N. Alipbaev, R.G. Abdulkarimova, V.E. Zarko.

# Aluminothermic Combustion of Chromium Oxide Based Systems under High Nitrogen Pressure

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**Abstract:** The aluminothermic reduction of some oxide systems in the solid-state combustion mode in nitrogen in a high-pressure reactor has been studied for the purpose of obtaining nitride-containing composites. The properties of the synthesis products obtained at various nitrogen pressures were determined.

*Keywords*: self-propagating high-temperature synthesis, high pressure, oxide systems, nitrides, composites.

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# INTRODUCTION

Nitride-containing ceramic powders obtained by combustion of mixtures of metal nanopowders in air are promising materials for applications. Under certain conditions, an aluminum nitride phase (more than 80% by weight) is stabilized in the final products of combustion of aluminum nanopowders in air [1]. Combustion of commercial powders of aluminum, titanium, zirconium, lanthanum, and other metals also produces corresponding nitrides [2]. Various compounds of refractory metals with nitrogen, silicon, and carbon are new composite materials, many of which are successfully used in electronics, modern mechanical engineering, metallurgy, chemical industry, electrical engineering, and other industries [3]. Refractory compounds are the main components in the manufacture of ceramicsone of the priority areas of modern materials science [4]. which is impossible without the development of many

industries, primarily engineering and electronics. The high physicomechanical properties of these compounds have led to interest in developing new methods for the production of ceramic materials.

Of particular interest are nitrides—compounds of refractory metals with nitrogen, many of which have high fire resistance, unique semiconducting and dielectric properties, and high chemical stability [5]. Important issues in the production of high-temperature nitride ceramics at a high pressure of reactive nitrogen are not only methods of synthesizing the compounds but also the formation of the structure of the material. its geometric shape [6]. Researchers have used various methods to produce nitride ceramics. In this paper, one of them is considered in detail. Earlier we have studied some features of combustion of oxide systems under high nitrogen pressure [7]. The obtained composites had insufficient strength and density. To improve the strength characteristics in the systems studied, it is proposed to use chromium oxide (III)—a strong oxidizer [8].

#### EXPERIMENTAL

Self-propagating high-temperature synthesis (SHS) under high nitrogen pressure was conducted in the setup shown schematically in Fig. 1. The design of the setup

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**Fig. 1.** SHS high-pressure reactor: (1) vacuum pump; (2) transformer; (3) ammeter; (4) reactor top cover; (5) reactor bottom cover; (6) tubular heating furnace; (7) thermocouple; (8) sample; (9) reactor body; (10) manometer; (11) inlet and outlet valves; (12) nitrogen flasks; (13) LTR-U-1 data acquisition system; (14) computer.

provides a nitrogen pressure of up to 10 MPa in the reactor.

To increase the concentration limits of the synthesis, a tubular heating furnace allowing preheating of the sample to  $1000^{\circ}$ C was placed in the reactor.

In the experiments, the following components were used: the PA-4 (99.0%) aluminum powder, zirconium concentrate from the Obukhov Ore Dressing and Processing Enterprise (Kazakhstan, 98.1% ZrSiO<sub>4</sub>), silicon and zirconium powders, silicon and chromium oxides (chemically pure grade), natural quartzite (97.0% SiO<sub>2</sub>), silica sol manufactured by DeguDent GmbH (Germany), and high purity nitrogen in flasks (volume fraction not less than 99.9% N). The grain size of the starting components was less than 90  $\mu$ m. The components were weighed on a VLE-134 electronic balance and thoroughly mixed in a porcelain mortar. Then, we added a small amount of silica sol sufficient for the preparation of a semi-dry mixture suitable for pressing. The water content of the mixtures was 5–10%.

Samples were prepared in the form of cylinders 20 mm in diameter and 40 mm high by pressing in a mold at a pressure of about 70 MPa. Dried samples were placed in a tubular furnace located in the high-

**Table 1.** Composition of the initialAl-ZrSiO<sub>4</sub>-C mixtures

Component	Mass content, $\%$				
Al	25	30	25	30	
$\mathrm{ZrSiO}_4$	65	60	70	65	
Zr	5	5	5	5	
С	5	5	0	0	

pressure reactor, where heating in nitrogen to a temperature of 1100–1150 K led to their autoignition and SHS of nitride-containing composites. Temperature control in the reactor furnace was performed with a thermoregulator. The temperature of the samples was measured with thermocouples. The compressive strength of the products was determined by a standard method on a setup consisting of a press and a dynamometer.

The initial nitrogen pressure in the reactor was varied in the range of 0.5–2.0 MPa. The composition of the test samples is given in Tables 1 and 2.



Fig. 2. Relative change in the mass of the samples synthesized in the Al–ZrSiO<sub>4</sub>–Zr system (Table 1) with different aluminum contents and with (a) and without (b) added graphite versus nitrogen pressure in the reactor.

Table 2. Composition of the initialAl-ZrSiO<sub>4</sub>-Cr<sub>2</sub>O<sub>3</sub> and Al-SiO<sub>2</sub>-Cr<sub>2</sub>O<sub>3</sub> mixtures

Component	Mass content, $\%$					
Al	10	13	13	15		
$\mathrm{ZrSiO}_4$	38	35		_		
$\mathrm{Cr}_2\mathrm{O}_3$	50	50	50	50		
$SiO_2$			37	35		
$CaF_2$	2	2		_		

# **RESULTS AND DISCUSSION**

Presumably, the mechanism of chemical reactions in the Al–MeO– $N_2$  system has the form

$$MeO + Al \rightarrow Al_2O_3 + Me,$$
 (1)

$$2Me + N_2 \rightarrow 2MeN,$$
 (2)

where  $MeO = Cr_2O_3$ ,  $SiO_2$ ,  $ZrSiO_4$ .

A practically important approach to the formation of the structure and morphology of nitride SHS ceramic is to use the effect of increasing mass of the sample upon interaction of the reduced metal with nitrogen. With increasing nitrogen pressure to 2.0 MPa (Figs. 2 and 3), the mass of all samples increases due to the reactive capture of nitrogen. This effect is most pronounced for compositions with a high content of aluminum in the mixture.

An important parameter that influences the structure formation and physical properties of composites is the combustion temperature (Figs. 4 and 5). Combustion temperature decreases monotonically with increasing nitrogen pressure. This is because the heat release of exothermic compositions is caused by the aluminothermic reduction of metal oxides. Increasing the nitrogen pressure enhances the heat release from the samples, which leads to an increase in the heat loss and a decrease in the combustion temperature in the system.

To investigate the possibility of obtaining carbonitride composites, to some test samples we added a small amount (5%) of carbon in the form of graphite. This led to only a slight increase in the combustion temperature (see Fig. 4), which was 1670 K at a nitrogen pressure of 0.5 MPa and an aluminum content of 30%. However, under conditions of preheating of the system, gaseous carbon nitride, so called cyanogen is formed, which is confirmed by chromatographic analysis [9]:

$$2C + N_2 \to (CN)_2. \tag{3}$$

Carbide phases in the final product of the synthesis were not detected.

The energy capacity of aluminothermic systems based on zirconium and silicon oxide is low, and accordingly, the reaction temperature is low, whereby the synthesized samples were not sufficiently strong. To increase the synthesis temperature and improve the mechanical properties of the composites, we introduced a stronger oxidizer — chromium oxide (III)—into the system.

The following mechanism of chemical reactions in the  $Al-ZrSiO_4-Cr_2O_3-N_2$  system is presumed:

$$Cr_2O_3 + Al \rightarrow Al_2O_3 + Cr,$$
 (4)

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Fig. 3. Relative change in the mass of the samples synthesized in the Al–ZrSiO<sub>4</sub>–Cr<sub>2</sub>O<sub>3</sub> (a) and Al–SiO<sub>2</sub>–Cr<sub>2</sub>O<sub>3</sub> (b) systems versus nitrogen pressure in the reactor (see Table 2).



Fig. 4. Combustion temperature of the samples synthesized in the  $Al-ZrSiO_4$  system with different Al contents and with (a) and without (b) added (5%) graphite versus nitrogen pressure in the reactor.

$$\operatorname{ZrSiO}_4 + \operatorname{Al} \to \operatorname{Al}_2\operatorname{O}_3 + \operatorname{Zr} + \operatorname{Si},$$
 (5)

$$\operatorname{Cr} + \operatorname{N}_2 \to \operatorname{Cr}_2 \operatorname{N},$$
 (6)

$$\operatorname{Zr} + \operatorname{N}_2 \to \operatorname{ZrN},$$
 (7)

$$3\mathrm{Si} + 2\mathrm{N}_2 \to \mathrm{Si}_3\mathrm{N}_4. \tag{8}$$

Thus, the formation of the nitride-containing composite may be a multi-stage process, in which the main heat release occurs in the first stage of aluminothermic reduction of the metal oxide, and the nitriding of the reduced metal takes place at the final stages of the synthesis. The absence of elemental zirconium in the synthesis products indicates that the aluminothermic reaction first leads to reduction of zirconium, which is an active reagent and which immediately reacts with nitrogen to form zirconium nitride. When increasing the aluminum content, we also detected the formation of aluminum nitride. Excess aluminum causes complete reduction of silicon and zirconium, which form zirconium disilicide (Table 3).

The addition of chromium oxide to the  $Al-ZrSiO_4$ and  $Al-SiO_2$  systems significantly increases the combus-



Fig. 5. Combustion temperature of the samples synthesized in the Al–ZrSiO<sub>4</sub>–Cr<sub>2</sub>O<sub>3</sub> (a) and Al–SiO<sub>2</sub>–Cr<sub>2</sub>O<sub>3</sub> (b) systems versus nitrogen pressure in the reactor.

$ZrSiO_4 +$	Al + Zr	$+ N_2$	$p_{N_2}$ ,	Products, %						
$ZrSiO_4, \%$	Al, %	Zr, %	MPa	$ZrO_2$ (mono)	$\mathrm{ZrSi}_2$	ZrN	$Al_2O_3$	$Al_{2.81}O_{3.56}N_{0.44}$	ZrSi-bc (rhombic)	AlN
70	20	10		26.5	13.8	11.1	48.5	—	_	
65	25	10	0.5	15.1	12.6	12.5	47.7		7.3	
60	30	10	0.5	10.6	21.6	12.4	53.5		5.6	_
55	35	10		0.5	19	0.6	47.8	23.9	19	_
70	20	10		19.6	16.2	14.9	49.2	—	_	_
65	25	10	1.0	13.7	17.8	10.7	47.8		9.1	
60	30	10	1.0	2.7	2.1	4.5	36.3	36.0	18.4	
55	35	10		2.2	2.0	1.1	28.3	30.2	18.1	7.1
70	20	10		18.9	13.7	17.3	50.1		_	_
65	25	10		15.2	14.5	12.2	57.0		1.1	
60	30	10	2.0	3.8	4.1	7.2	29.4	41.9	13.6	
55	35	10		2.4	3.6	2.1	10.0	49.1	22.2	10.6
_	_	100	5.0	23.8	2.5	55.5			_	_

Table 3. Results of x-ray diffraction analysis of SHS products in the Al-ZrSiO<sub>4</sub>-Zr system

tion temperature (see Fig. 5), which reaches 1770 K in the Al–SiO<sub>2</sub> system with an aluminum content of 15% at a nitrogen pressure of 0.5 MPa.

Table 4 shows the results of x-ray diffraction analysis of SHS products in the Al–ZrSiO<sub>4</sub>–Cr  $_2O_3$  system. It can be suggested that in the aluminothermic reaction under the experimental conditions, more active chromium is the first to be reduced and immediately reacts with nitrogen to form nitride. It should be noted that the amount of chromium nitride in the SHS products increases with increasing nitrogen pressure. A small portion of metallic chromium is not nitrided and remains in the form of reduced metal. Under these conditions, silicon and zirconium nitrides are not formed.

In the study, the main physic-mechanical characteristics of the synthesized nitride-containing composites were determined. The compressive strength  $\delta_{\text{comp}}$ 

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A1 0Z	n atm	${\rm Products},\%$							
AI, 70	p, atm	$ZrO_2$ (mono)	$\mathrm{Cr}_2\mathrm{O}_3$	$\mathbf{Cr}$	$(Al,Cr)_2O_3$	$\mathrm{Cr}_2\mathrm{N}$	$\mathrm{ZrSiO}_4$	$SiO_2$ (cristobalite)	
	10	34.1	29	13.4	9.7	9.2	3.3	1.3	
10	15	42.1	5.8	24.7	16.9	7.7	1.4	1.3	
	20	52.1	7.1	19.5	_	16.8	4.5	—	
	10	35.3		19.7	32.1	11.6	13	1.4	
	15	45.3	9.5	8.7	14.8	18.8	2.9	—	
	20	32.1	_	10.9	25.1	28.1	3.8	—	

Table 4. Results of x-ray diffraction analysis of SHS products in the  $Al-ZrSiO_4-Cr_2O_3$  system



**Fig. 6.** Strength of the samples synthesized in the Al–ZrSiO<sub>4</sub>–Zr (a) and Al–ZrSiO<sub>4</sub>–Zr–C (b), systems versus nitrogen pressure in the reactor.

of all the synthesized samples increased with increasing nitrogen pressure  $p_{\rm N_2}$  and aluminum content (Fig. 6). The addition of graphite reduced the strength due to the formation of gaseous carbon compounds, which led to an increase in porosity and weakening of the composite.

Figure 7 shows the dependence of the compressive strength of the composites synthesized in the Al– ZrSiO<sub>4</sub>-Cr<sub>2</sub>O<sub>3</sub> and Al–SiO<sub>2</sub>-Cr<sub>2</sub>O<sub>3</sub> systems with different aluminum contents on the nitrogen pressure in the reactor. As the nitrogen pressure in the reactor and the aluminum content in the Al–SiO<sub>2</sub>-Cr<sub>2</sub>O<sub>3</sub> system are increased, the compressive strength of the composite increases monotonically and reaches 100 MPa. The compressive strength of the zirconium-containing system reaches 120 MPa at a nitrogen pressure of 1.5 MPa, which is more than twice the compressive strength of the samples not containing chromium oxide.

The morphology and microstructure of the composites were studied in relation to the experimental conditions and the ratio of the starting components. The topography and microstructure of the surface of the samples and the qualitative and quantitative compositions in point areas were determined on a Quanta 3D 200i multifunction scanning electron microscope with integrated focused ion beam systems and an energy dispersive spectrometer in the National Nanotechnology Laboratory of the al-Farabi Kazakh National University.

The study of the microstructure of sections in the composite samples synthesized in the Al–ZrSiO<sub>4</sub> system (Fig. 8) showed morphological differences in the structures of the composites with and without graphite. In samples containing graphite, along the length of acicular rods there are round-shaped structures which have a more complex composition, comprising silicides, nitrides, and oxides of aluminum. A round-shaped structure is usually formed in crystal growth by the vapor–liquid–crystal mechanism. Under the conditions of the experiment, the liquid phase in the system can be aluminum and aluminum silicides. According to elemental analysis, the rod-like structures consist mainly of zirconium nitride.



Fig. 7. Strength of the samples synthesized in the Al–ZrSiO<sub>4</sub>– $Cr_2O_3$  (a) and Al–SiO<sub>2</sub>– $Cr_2O_3$  (b) systems versus nitrogen pressure in the reactor.



Fig. 8. Microstructure and appearance of sections in the samples synthesized in the Al–ZrSiO<sub>4</sub>–Zr–C (a) and Al–ZrSiO<sub>4</sub>–Zr (b) systems.

Investigation of the microstructure of the samples synthesized in the Al–ZrSiO<sub>4</sub>–Cr<sub>2</sub>O<sub>3</sub> system showed the presence of filamentary swirling spirals (whiskers) in the composite structure. In the samples containing chromium nitride (Fig. 9a), whiskers have spherical formations at the ends. It is this form of the whiskers that imparts strength to the composite. In the Al–SiO<sub>2</sub>–Cr<sub>2</sub>O<sub>3</sub> system, the matrix of the composite consists of irregularly shaped crystals of chromium-aluminum spinel (Fig. 9b).

The fire resistance of the materials was determined by a standard method involving temperature measurements at the beginning of deformation of the cones made of the test material using an infrared radiation pyrometer. Pyramidal cones 35 mm high were mounted on an alumina support, placed in a Tammann furnace, and heated at a rate of  $10^{\circ}$ C/min. The results are shown in Table 5.

To determine the corrosion resistance of the nitridecontaining composites to metal melts, we made crucibles of the composite materials 80 mm height with an outer diameter of 50 mm, a wall thickness of 7 mm, and a bottom thickness of 15 mm. These crucibles were used for melting of Duralumin (at 950°C) and copper and bronze (at 1400–1450°C) in the Tammann furnace for 15 min. The resistance to melts was determined from the change in the mass of the crucible due to dissolution or chemical interaction with the molten phase. All cru-



Fig. 9. Microstructure, appearance, and characteristic sizes of the composite crystals synthesized in the Al–ZrSiO<sub>4</sub>– $Cr_2O_3$  (a) and Al–SiO<sub>2</sub>– $Cr_2O_3$  systems (b).

System	Fire resistance, $^{\circ}\mathrm{C}$
Al–TiO <sub>2</sub>	1550
Al–ZrSiO <sub>4</sub>	>1750
$Al-ZrSiO_4-C$	>1750
Al–SiO <sub>2</sub>	1600
Al–SiO <sub>2</sub> –C	1700
$Al – Zr SiO_4 – Cr_2O_3$	1600
$Al-ZrSiO_4-V_2O_5$	1550
Al–SiO <sub>2</sub>	1600

Table 5. Fire resistance of nitride-containing composites

synthesized from different systems in nitrogen

cibles of the nitride containing composites showed high corrosion resistance to melts (mass loss of 0-5%) and virtually zero wettability with the molten metal.

# CONCLUSIONS

The experiments in the high-pressure reactor with preheating of the samples showed stable autoignition and the process of SHS in the aluminothermic compositions containing zirconium and silicon and chromium oxides. The external nitrogen pressure in the reactor had no appreciable effect on the autoignition temperature, which was 1100–1120 K.

The x-ray phase composition and strength characteristics of the SHS products of a number of samples of zirconium and silicon and chromium oxides were determined in relation to the content of the active components and the nitrogen pressure in the reaction vessel. Along with metal nitrides and alumina, the composite contains appreciable amounts of silicides and oxynitrides.

The electron microscopic study of the SHS products using energy dispersive elemental analysis clearly indicates the reinforcing and strengthening role of the rod-shaped and filamentary structures of nitrides and metal oxynitrides in the oxide matrix of the composite.

The studies have shown that SHS processes in multicomponent systems in nitrogen under high pressure can be used to obtain nitride-containing composite materials that not only have high refractory properties and resistance to metals but also show high strength characteristics.

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