SHS - Processes in the Carbonaceous Oxide System at High Nitrogen Pressure Values

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Abstract

This paper contains study results of the nitride containing composites features formed in the compacted Al-TiO_2-C-Si samples inside a high pressure reactor with various nitrogen pressure values. The nitriding and carbide-formation processes take place simultaneously with aluminothermic reduction of titanium oxide in the self-propagating high-temperature synthesis (SHS) mode. It has been found that the nitrogen pressure effect is manifested as insignificant reduction of the combustion temperature and increased durability of the synthesized composite. The SHS process in the nitric environment leads to practically complete reduction of titanium oxide, the free titanium being absent. The X-ray analysis has revealed that the basic SHS products are refractory compounds such as metal nitrides, carbides, and oxides. Increase in nitrogen pressure results in decrease of the specific electric resistance of the synthesized composites caused by growth of the electroconductive phases i.e. titanium carbides, nitrides, and silicides. Performed electron microscopic study including the energy dispersion analysis of the morphology and structure of the SHS products has revealed formation of the nano-sized titanium silicide crystals distributed between the complex carbonitride particles.

The complex carbonitride composites synthesized in the high pressure reactor are of interest as high-refractory and abrasive materials considering their physical and chemical properties.

Introduction

The currently performed study deals with synthesis of the new ceramic composite materials consisting of two and more refractory compounds [1] and high constant microscopic durability. These materials are of a particular interest as they are mechanically and chemically stable upon heating. Based on the principles of the sol-gel and SHS-technologies, there have been earlier synthesized the inorganic carbonaceous composites that have unique properties when they are used to line the induction furnaces [2, 3]. From the scientific point of view this synthesis can be carried out as one stage synthesis (direct synthesis) of the multicomponental ceramic materials consisting both of the single-phase compounds (e.g. carbonitrides, compound carbides and nitrides, etc.) and the heterogeneous systems based on nitride, boride, carbide, and metal and nonmetal oxides [1]. The actual objectives of producing the high-temperature nitride ceramics at high reacting nitrogen pressures are not only compounds synthesis but also formation of the material structure and its geometry. One of the most important techniques of the nitride SHS-ceramics structure and geometry formation is use of the reaction volume effect i.e. increase in the substance mass due to reactionary trapping of nitrogen [4, 5].

Application of the two phase maturing of the samples in Al_2O_3 – Ti at 1620 K and changing the nitrogen pressure from 6 up to 196 MPa has allowed the authors of this paper [6] to obtain sintered composite material consisting of the Al_2O_3 and TiN phases with relative density above 98,5 %.

Study [7] in the Ti-Al-C and Ti-Al-N systems using the hot pressing techniques resulted in the production of the promising composites containing up to 96 % of the so-called MAX phase (Ti_2AlC, Ti_2AlN).

Integrated studies of the synthesis processes by means of combustion in Si-Al-Ti-O-N system allowed the authors [8, 9] to produce quite a large number of the complex composite materials with dense nano-sized grain structure of various morphology.

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By study of the titanium nitride synthesis conditions depending on the compaction pressure and nitrogen pressure in the reactor, the authors [10] have established the optimum experiment conditions for production of titanium nitride with the highest contents of atomic nitrogen (46.5 %). These are 98 MPa compaction pressure and 200 MPa nitrogen pressure in the reactor.

Of major interest are studies related to production of the nano-sized titanium nitride powders by means of pulse voltage applied to titanium wire in the nitrogen atmosphere. Used voltage is 11.4 kV and nitrogen pressure varies from 0.2 up to 1.5 MPa. The synthesis process is carried out in the explosion mode. Formed titanium nitride particles are of cubic form and their size is less than 200 nm [11, 12].

The present paper contains the study results of certain nitride-containing composites formation features in the pressed Al-TiO_2-C-Si samples at various nitrogen pressures. Sintering of the initial components and formation of nitrides highly depends on degree of titanium reduction at the aluminothermic reaction and thus results in different phase compositions on the surface and in the centre of the pressed samples.

Methodology of Experiment

The conditions of the TiO_2 based nitride-containing composites synthesis have been studied using:

- High pressure reactor with preliminary heating up to 1170 K accompanied by spontaneous ignition of the samples;

- Constant pressure bomb (pressure chamber) with combustion initiated at the ambient temperature using the nickel-chromium spiral and iron-aluminum termite.

In both cases the 2 cm diameter and 4 cm high cylindrical samples made up by the pressed powder mixtures with addition silica sol have been used as the study object. The nitrogen pressure varied within 0-2.5 MPa atmospheres.

Figure 1 below illustrates the high pressure reactor block diagram. Its key element is the 45 liter reactor case equipped with the top and bottom covers. The thermocouple outlet and power supply are provided by means of the feed nozzles in the bottom cover. Delivery and release of gas is provided through the high pressure flexible hoses supplied with the make-and-break coupling installed on the top cover. To increase the concentration limits of the SH-synthesis, the tubular heating furnace allowing for preliminary heating of the sample up to 1270 K has been installed inside the reactor. Temperatures of the SH-synthesis have been monitored using the automated temperature recording device. By means of the direct measurement method, the signal from the thermocouples installed inside the reactor has been transferred through the power feed nozzles in the bottom cover along the shielded wire up to the crate LTR-U-1 system. The products of the combustion process are subject to X-ray analysis using DRON-3M diffractometer device. Topography and microstructure of the sample surface have been studied and both the qualitative and quantitative analysis of the component composition in certain points has been carried out using the JSM-6510LA JEOL raster electronic microscope.

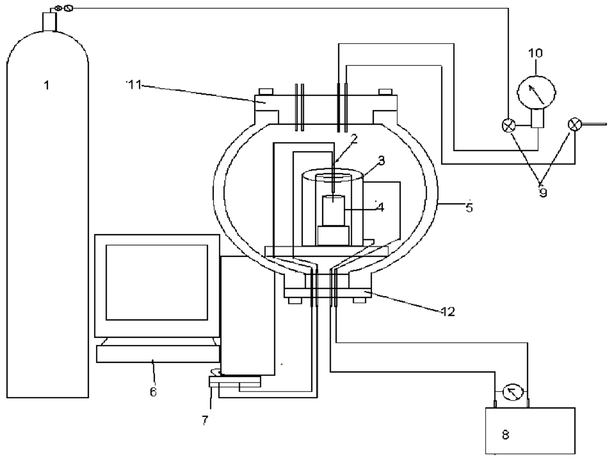


Fig. 1. High pressure SHS-Reactor: 1 - nitrogen cylinder; 2 - thermocouple; 3 - tubular heating element; 4 - sample; 5 - reactor case; 6 - PC; 7 - data acquisition system LTR-U-1; 8 - transformer; 9 - inlet and outlet valves; 10 - manometer, 11 - reactor top cover; and 12 - reactor bottom cover.

Table 1
Compositions of the experimental samples are given

Component	Contens, % mass			
Al	20	25	30	35
TiO_2	65	60	55	50
C	10	10	10	10
Si	5	5	5	5

Results and Discussion

Experiments carried out in the high pressure reactor with preliminary heating of the samples have demonstrated stable spontaneous ignition and synthesis for all the compositions. The process has been accompanied by a significant, i.e. 10-15 % pressure increase in the reactor, this fact testifying to intensification of the gaseous products formation reactions in the SHS process. The most probable reaction in the conditions of the preliminary heating is formation (1) of the gaseous carbon nitride or so-called dithiane.

$$2C + N_2 \rightarrow (CN)_2 \qquad (1)$$

Reaction (1) is highly endothermic, its intensity increasing with pressure that leads to decrease of the synthesis temperature (Fig. 2a). A tendency towards temperature decrease is typical for all the substance compositions.

The maximum combustion temperature is 1820 K for the compositions with 30% aluminum and 0.5 MPa nitrogen pressure.

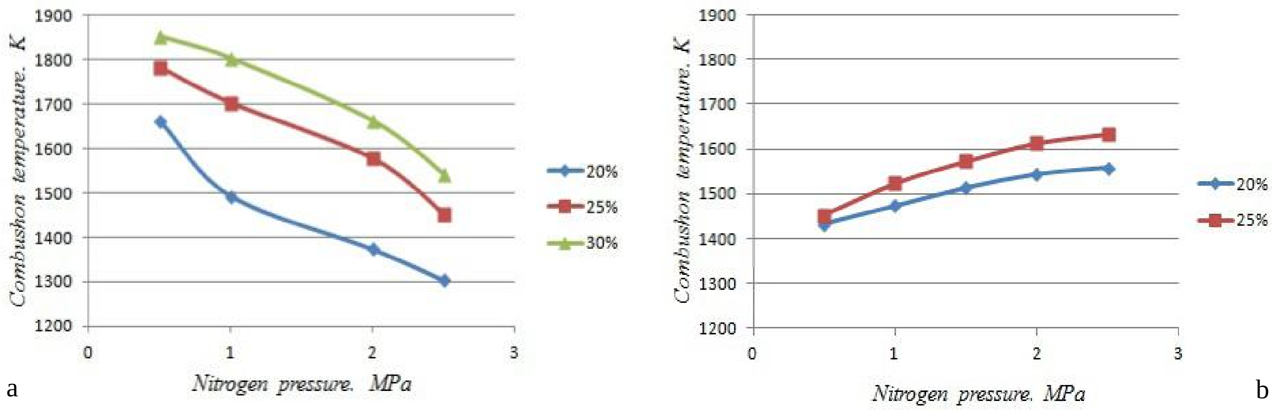


Fig. 2. Dependence of combustion temperature on nitrogen pressure in Al-TiO_2-C-N_2 system: a – in high pressure reactor with preliminary heating of the system; b – in the ambient temperature constant pressure bomb.

The external nitrogen pressure impact on the synthesis initiation temperature, i.e. 1120 K - 1140 K, is insignificant. The samples containing 35 % and more aluminum could not maintain their form after the synthesis due to submelting, therefore their heat-transfer properties could not be identified.

Studies carried out in the constant pressure bomb testify to the fact that SH-synthesis can be initiated at the ambient temperature probably in the case of 25% and 30% aluminum contents that are close to stoichiometry of full titanium reduction. No combustion was possible in the case of compositions with less than 25% and more and 30% aluminum within all the studied nitrogen pressure range. Noteworthy that in this case pressure does not increase in the constant pressure bomb during synthesis, formed products do not result in gas formation in these conditions, and the combustion temperature (Fig. 2b) considerably grows with pressure reaching 1650 K at 2.5 MPa and 25 % aluminum contents.

Identification of the compression strength range (Figs. 3a, 3b) has shown that the external nitrogen pressure considerably affects mechanical durability of the synthesized material and increases it up to 2-2.5 times. Synthesized products are more dense materials compared to the initial samples.

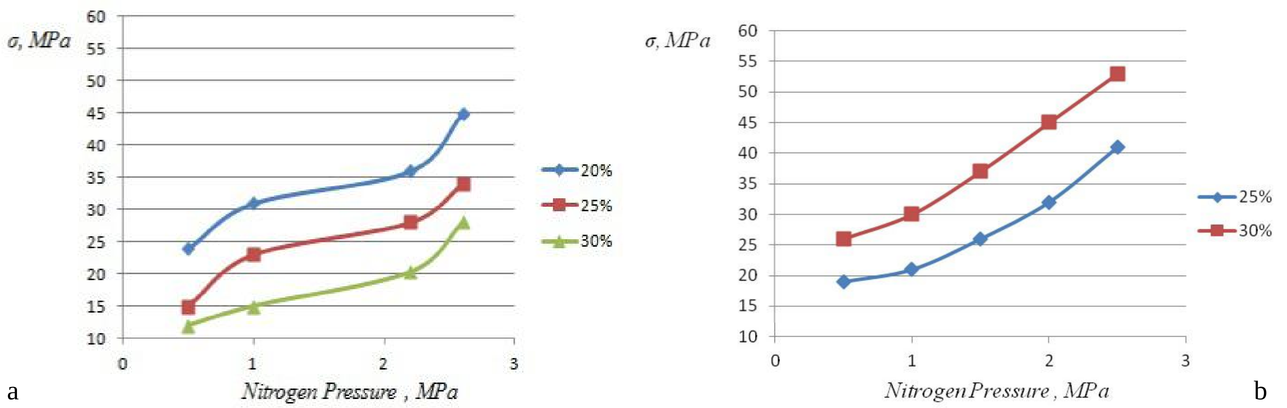


Fig. 3. Dependence of sample durability on nitrogen pressure: a – in high pressure reactor with preliminary heating of the system; b – in the ambient temperature constant pressure bomb.

Specific electric resistance of the synthesized composites samples has been measured and the results are provided in Fig. 4. It is apparent from Fig. 4 that growth of nitrogen pressure leads to increase in the contents of the electroconductive phases in the SHS-products the latter being manifested as reduction of the electric resistance. Such electroconductive compounds are titanium nitrides and silicides the contents of which increase with growing nitrogen pressure. Thus, electric conductivity of the nitride composites received by means of SHS in the nitrogen atmosphere is an adjustable functional characteristic, therefore is of practical significance for production of the electric heating elements.

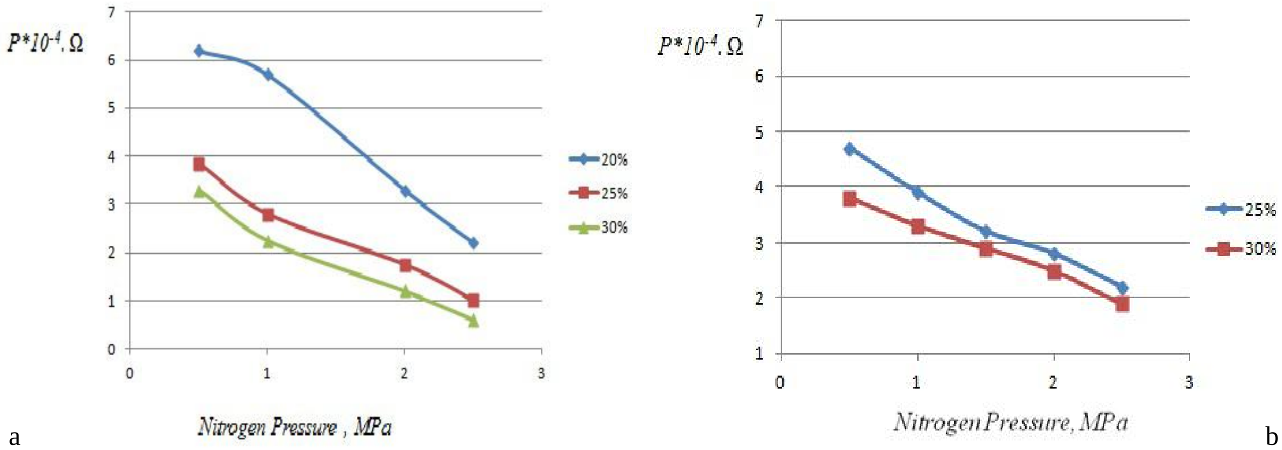
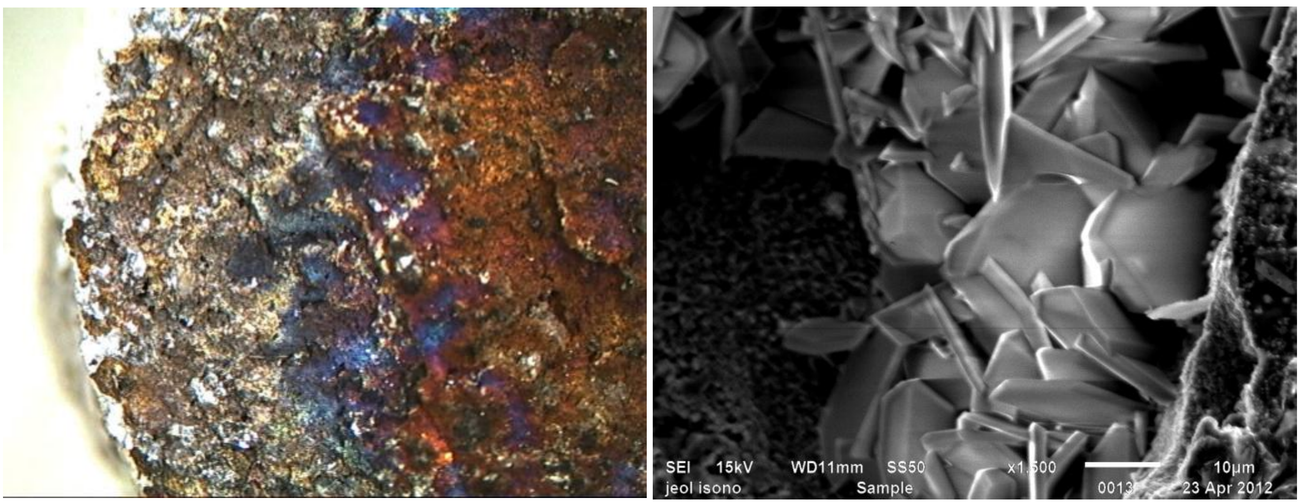


Fig. 4. Dependence of sample conductivity on nitrogen pressure: a – in high pressure reactor with preliminary heating of the system; b – in the ambient temperature constant pressure bomb.

Study of the cleaved sample microstructure (Fig. 5) has revealed not only surface to centre morphological difference in the composite material structure but also difference in the phase and chemical composition of the synthesized products. Nitrogen filtration deep into the cylinder shaped sample heavily depends on nitrogen pressure in the reactor. Energy-dispersion elemental analysis performed using JSM 6510 LA scanning electronic microscope testifies to the presence of metal oxides, nitrides, and silicides in the SHS products. Lighter crystals found closer to the surface correspond to metal oxides and nitrides, the contents of the nitrides being increased closer to the center of the sample.

The surface layer of the microstructure (Fig. 6) is made up by the angular and volumetric grey crystals of presumably 5-10 μm compound nitrides with nano-sized elongated broken-shaped titanium silicide crystals between them.



a b

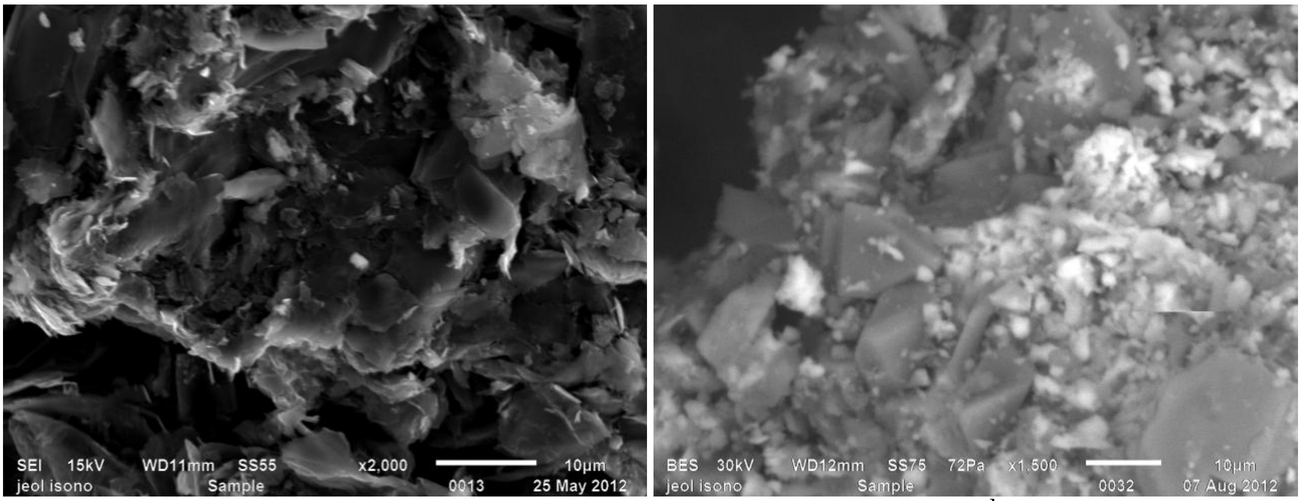


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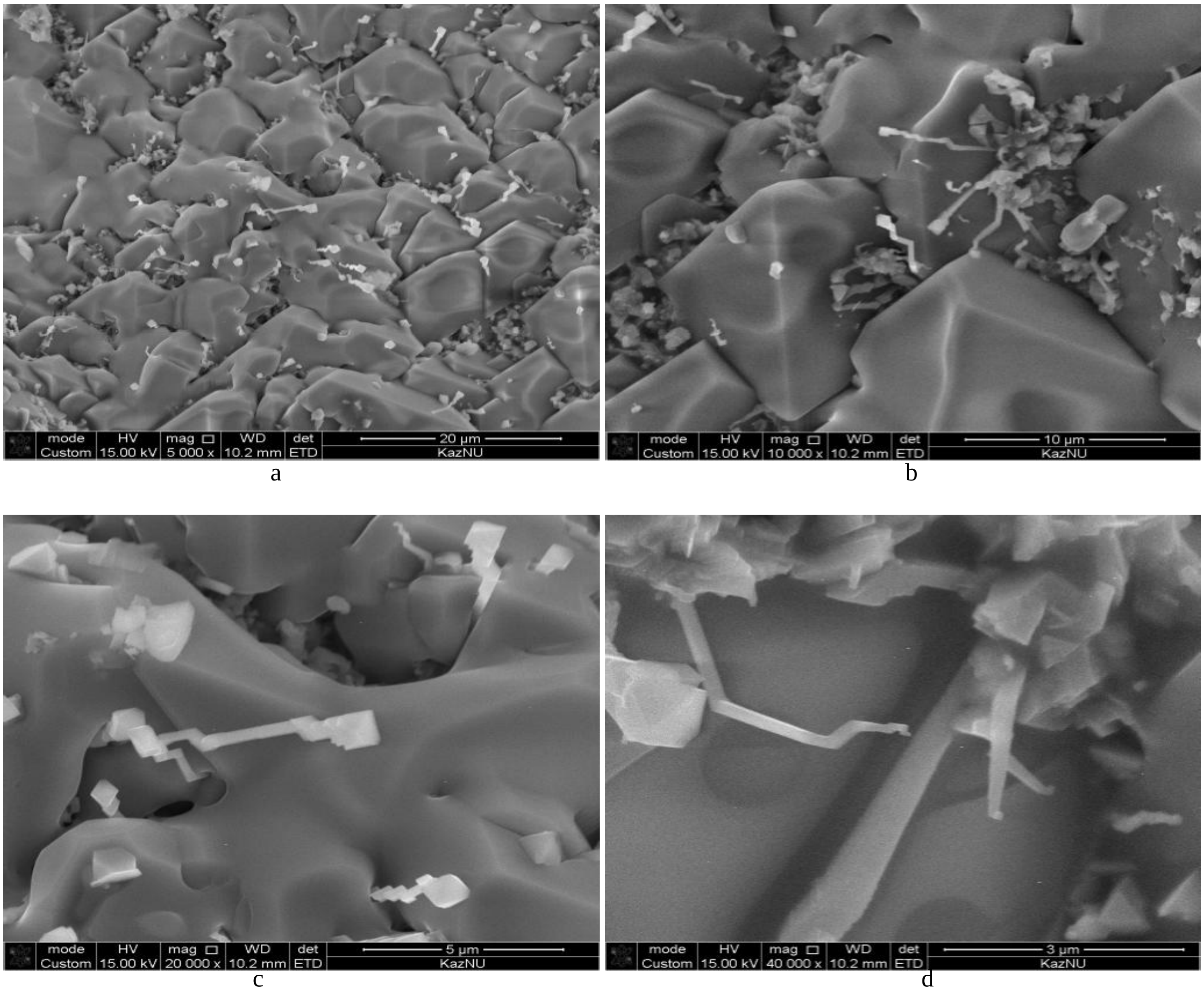
Fig. 5. Microscopic pictures of cleaved sample surface and its structure: a – general view of the cylindrical sample cross section; b – surface layer microstructure; c, d – structure of the sample central part cross section.



c d

Fig. 6. Microstructure of the surface area at various scales: a – 5000 magnification; b – 10000 magnification; c – 20000 magnification; d – 40000 magnification.

According to the results of X-ray phase analysis, the averaged powder composites mainly contain refractory compounds with high values of the microhardness and melting temperatures.

Table 2 below provides the results of the X-ray phase analysis of the SHS-products produced in the high pressure reactor at various nitrogen pressures in different parts of the cylindrical composite samples.

Table 2

SHS-products produced in the high pressure reactor at various nitrogen pressures

Compound	Pressure 0.5 MPa		Pressure 2 MPa		Pressure 2.5 MPa	
	Surface area, % mass	Central area, % mass	Surface area, % mass	Central area, % mass	Surface area, % mass	Central area, % mass
Aluminum oxide (corundum)	66.3	22.9	69.4	55.2	64.4	40.5
Aluminum γ-oxide	4.5	3.11	-	-	-	-
Titanium nitride	13.9	30.1	22.0	41.5	23.8	46.3
Silicon carbide	1.7	7.1	-	-	-	5.8
Titanium oxide	1.5	-	-	-	1.8	-
Titanium silicides	6.4	1.1	8.6	3.3	7.5	2.3
Silicon oxide	-	0.5	-	-	1.0	-

It is apparent from the Table given above that growth of nitrogen pressure leads to increase in the contents of titanium nitride, the central areas being richer in nitride than the surface ones. These results are also manifested in the nature of the change in the produced composite material compression strength. Increase in the titanium nitride contents in the central sample area is caused by practically full reduction titanim oxide in this area as a result of the aluminothermic reaction. According to Table 2, significant quantities of unreduced titanium oxide are found on the surface, whilst titanium oxide is absent in the center of the sample as well the free titanim that is partially combined with silicide. The study results prove that all reduced titanium can be transformed into a valuable product i.e. titanium nitride in the conditions of a high pressure reactor at rather moderate 2-2.5 MPa nitrogen pressure.

Table 3 below provides the results of the X-ray phase analysis of the SHS-products produced in the constant pressure bomb at various nitrogen pressures. All the products are highly refractory compounds with melting temperature exceeding 2170 K. Their chemical stability to any aggressive environments is high. Synthesized composite material is referred to extremely high-quality composites in terms of its chemical and phase compositions.

Table 3

SHS-products produced in the constant pressure bomb at various nitrogen pressures

Compounds	Conditions of Synthesis			
	Nitrogen pressure 0.5 MPa	Nitrogen pressure 2 MPa	Nitrogen pressure 0.5 MPa	Nitrogen pressure 2 MPa
	Al – 25 %	Al – 25 %	Al – 30 %	Al – 30 %
Aluminum oxide (γ + corundum)	60.3	25.3	47.2	37
Titanium nitride	30.5	34.2	27.2	23.1
Silicon carbide	2.9	3.3	5.3	4.1
Titanium silicides	1.9	2.5	1.8	0.9
Titanium oxide	2.5	3.3	2.1	1.8

Thus, the results of the electron-microscopic and X-ray phase analysis of the SHS-products at higher nitrogen pressures prove that the composite materials produced by means of these techniques mainly consist of the nitride-containing compounds with certain presence of the refractory oxides and silicides.

Conclusion

Obtained study results allow for the following conclusions:

- SHS-processes occurring in the multicomponent Al-TiO_2-C-Si system in the high pressure nitrogen environment result in the nitride-containing composite materials with high refractory properties and high stability;
- Nitrogen pressure effect is manifested as insignificant reduction of the combustion temperature and increased durability of the synthesized products;
- Increase in nitrogen pressure results in decrease of the specific electric resistance of the synthesized composites caused by growth of the electroconductive phases i.e. titanium carbides, nitrides, and silicides;
- The central areas have higher contents of titanium nitride compared to the surface ones due to more complete aluminothermic reduction of titanium oxide that is fully transformed to titanium nitride in the nitriding process;
- Conditions of the synthesis enable formation of the nano-sized titanium silicide crystals distributed between the complex carbonitride particles.

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