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PREPARATION BY SHS-EXTRUSION METHOD OF COMPACT CERAMIC MATERIALS BASED ON THE TI–B SYSTEM MODIFIED WITH NANOSIZE SI_3N_4 PARTICLES

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Compact ceramic materials based on the Ti–B system modified with 5 wt.% of nanosize Si_3N_4 particles are prepared by the SHS-extrusion method. Results of studying structure, phase composition, and physical and mechanical properties of the materials obtained are presented. It is shown that addition of Si_3N_4 promotes formation of new phases, in particular titanium diboride and nitride in the final product. It is found that introduction of modifying nanosize Si_3N_4 particles into an initial charge leads to an increase in hardness and microhardness by 15 – 20 %, as well as to an increase in crack resistance by a factor of 1.5 compared with unmodified samples.

Keywords: compact ceramic materials, modification, nanosize particles, SHS-extrusion, SHS-Az.

INTRODUCTION

Today for contemporary industry there is considerable interest in structural and functional materials exhibiting unique properties. Materials based on titanium alloys are highly recommended in rocket building, aviation technology and engineering due to high strength, corrosion resistance and a capacity to operate in corrosive media [1 – 4]. However, these materials exhibit low wear resistance and therefore often in order to improve wear resistance these materials are alloyed with titanium borides [5 – 7].

Titanium borides are ultrahard refractory heat-resistant materials that exhibit low LTEC. Titanium borides may be used as structural materials or as wear-resistant components of electrode ceramic materials with addition of a metal binder in order to reduce compound brittleness [8, 9]. A binder material should exhibit LTEC close to that of the wear-resistant component of a material and good chemical stability. Use of such electrode materials for creating protective coatings may lead to improvement of component operating properties in corrosive media. A method for applying these coatings is electric-spark alloying [10 – 12].

It is possible to prepare by SHS-extrusion compact ceramic materials based on titanium borides exhibiting minimum porosity [13, 14]. The essence of the method involves a combination of material heating and high-temperature deformation due to which the material undergoes significant structural changes. Previously [15] features of material phase formation based on titanium borides in the course of the SHS process and the effect of adding nanosize Si_3N_4 particles on the phase composition and structure of synthesized materials has been studied.

It has been established that addition of nanosize Si_3N_4 particles leads to formation of TiN phase that is a crystallization center for cubic TiB.

The aim of this work is preparation by SHS-extrusion of compacts of ceramic electrode materials based on the TiB system with an excess Ti content modified with 5% nanosize Si_3N_4 particles and also a study of the structure and properties of the materials obtained.

RESEARCH OBJECTS AND METHODS

The objects for study were powder stoichiometric mixtures. Compositions and the original properties of the com-

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TABLE 1. Original Powder Component Properties

Component	Component content, wt.%	Powder grade	Main substance content, wt.%, not less than	Main fraction particle size, μm
Ti	83 – 87	PTOM-1	98.8	45
B	12 – 13	B-99A	99.5	20
Si_3N_4	<5	SHS-Az	97.0	0.08 – 0.12

ponents are provided in Table 1. Nanosize Si_3N_4 particles used as modifiers were prepared by azide technology of self-propagating high-temperature synthesis (SHS-Az) in the Samara State Technical University (SamGTU) [16 – 18].

The original powder components previously dried in a drying cabinet at 80°C were weighed according to a calculated composition on CSAMWP-308 electronic scales and placed in a ball mill drum. The ratio of charge weight and milling ball weight was 1:3.5. A charge was mixed for 4 h with a drum rotation frequency of 0.6 rev/sec. In order to remove excess moisture after mixing a charge was screened and placed in a drying cabinet for 12 h.

Combustion properties (temperature and rate) of the selected compositions were studied in order to predict material behavior during SHS-extrusion. Experiments were conducted in a unit modeling actual synthesis conditions occurring in an SHS-extrusion mold. A tungsten-rhenium thermocouple (VR5-VR20 with diameter 200 μm) was installed into previously pressed specimens, after which a tungsten spiral initiated combustion from the uninsulated upper end of the charge workpiece, and the combustion front moved to the opposite end of the workpiece passing through the thermocouple. The thermocouple was connected to an LTR-U116-channel ADC the signal from which was processed in a computer in a real time regime.

In order to perform SHS-extrusion cylindrical workpieces were pressed from the charge obtained. Pressing was conducted in a metal mold in a hydraulic press with a prescribed value of load. The preliminary compaction pressure was selected from consideration of obtaining a relatively dense workpiece of 0.6 of the compact density. The workpieces obtained 25 mm in diameter were wrapped in asbestos heat insulation cloth 2 mm thick in order that the workpiece ends remained without insulation. Prepared workpieces before conducting SHS-extrusion were placed in a drying cabinet.

Specimens were studied using equipment of the ISMAN distribution center for collective usage: specimen phase composition was determined in a DRON-3M x-ray diffractometer, the microstructure of transverse microsections was studied in a LEO 1450 VP, Carl Zeiss microscope (SEM). Microhardness was measured in a PMT-3 instrument according to GOST 9450–76 with a load of 100g, Rockwell hardness was determined to GOST 9013–59 (ISO 6508–86) in a TN500–01 hardness meter, Vickers hardness was determined according to GOST 2999–75 hardness meter with a load of 10 kgf for 30 sec. Crack resistant K_{Ic} was determined by an equation

$$K_{Ic} = 0.048\left(\frac{l}{a}\right)^{\frac{1}{2}}\left(\frac{HV}{E\Phi}\right)^{\frac{2}{5}}\left(\frac{HV\cdot a^{\frac{1}{2}}}{\Phi}\right),$$

where l is crack length, μm; a is impression semi-diagonal, μm; HV is hardness, GPa; E is elasticity modulus, GPa; Φ is limitation factor, Φ = 3 (const).

RESULTS AND DISCUSSION

Previously a study has been made of combustion characteristics for a composition without addition of nanosize particles and with addition of 5 wt.% nanosize Si_3N_4 particles. It has been established that addition of 5 wt.% Si_3N_4 does not affect combustion rate (for both compositions it was 12 mm/sec), although the combustion temperature in this case increases from 1800 to 1950°C. This increase in temperature-time interval during which the synthesized material exhibits a capacity for extrusion.

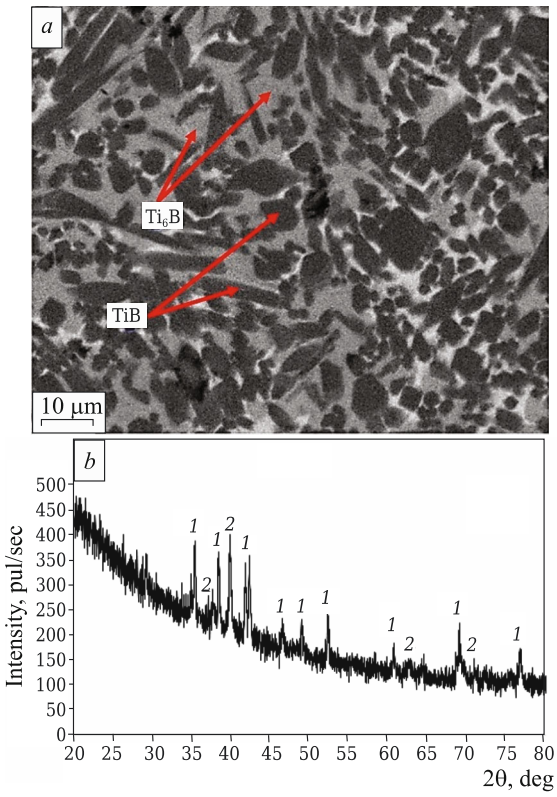

Fig. 1. SEM-microstructure (*a*) and diffraction pattern (*b*) of specimen based on Ti–B system without addition of nanosize Si_3N_4 particles: *1*) TiB; *2*) Ti_6B.

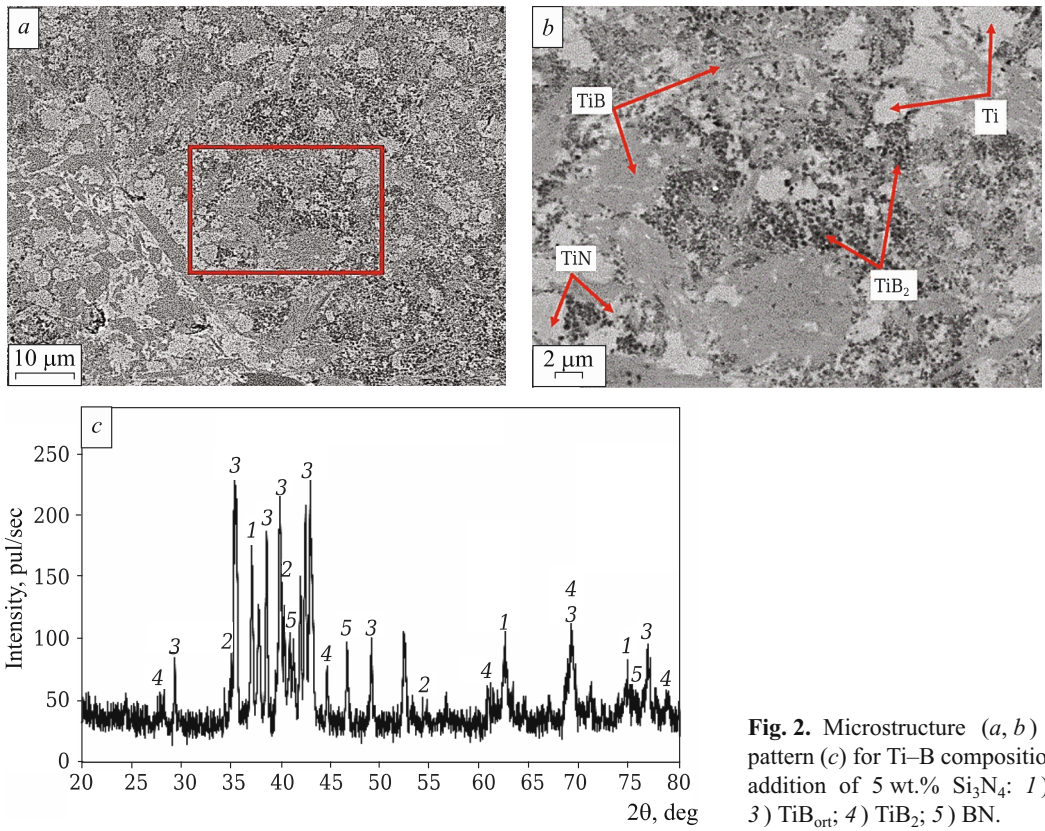

Fig. 2. Microstructure (*a*, *b*) and diffraction pattern (*c*) for Ti–B composition specimen with addition of 5 wt.% Si_3N_4: *1*) TiB_{cub}; *2*) Ti; *3*) TiB_{ort}; *4*) TiB_2; *5*) BN.

In the course of conducting experiments for SHS-extrusion as a result of treatment and optimization of production parameters compact ceramic materials were prepared without additive and with addition of nanosize Si_3N_4 particles. For specimens without additive the maximum electrode length was 200 mm, and with addition of 5 wt.% Si_3N_4 it was 180 mm.

SEM results are shown in Fig. 1 for a microsection cross section and also results of x-ray phase analysis (XPA) for compact ceramic materials based on the Ti–B system. It is seen that the typical structure of materials with addition is titanium monoboride whiskers (dark grey areas) located within a titanium matrix (see Fig. 1*a*). Results of XPA (see Fig. 1*b*) show presence of the main TiB phase arranged within a Ti matrix within which a small amount of boron is dissolved.

SEM results for a cross section of a microsection and XPA results for compact ceramic materials of TiB composition with addition of 5% Si_3N_4 are shown in Fig. 2*a*, *b*. It is seen that the material structure changed strongly with respect to unmodified material. XPA results (see Fig. 2*c*) show presence of four phases: basic TiB phase in the form of two modifications, i.e., orthorhombic and cubic, TiB and small BN inclusions; all phases are located within a solid solution of B in Ti. However, resting on SEM results and chemical analysis it may be concluded that within a specimens a fifth TiN phase is also present. Since peaks for TiN and TiB have a similar cell parameter the in a diffraction field they are superimposed upon each other that is confirmed by results of previous research [15].

Results are provided in Table 2 for measurement of the TiB composition material properties. It is seen that in material with addition of 5 wt.% Si_3N_4 the hardness and microhardness are higher than for unmodified materials on average by 15 – 20%. This may be explained on the basis of results of analyzing the structure and phase composition of the materials obtained. With addition to material of nanosize Si_3N_4 particles there is formation of new harder phases such as titanium nitride and titanium diboride.

TABLE 2. Results of Measuring Physicomechanical Properties of Ti–B Composition Materials

Material composition	Microhardness, kg/mm^2	Hardness		Crack resistance K_{Ic}, MPa·m$^{1/2}$
		Vickers *HV* 10/30, MPa	Rockwell *HRC*	
Ti–B:				
without additive	760 – 1504	907	67	3.36
with addition 5 wt.% Si_3N_4	1064 – 1682	1097	75	5.67

CONCLUSION

Compact ceramic materials based on the TiB system without addition and with addition of 5 wt.% Si_3N_4 (particle size 180 – 120 nm) have been prepared by SHS-extrusion. It has been established that modification with silicon nitride nanosize particles leads to an increase in material hardness and microhardness by 15 – 20%, and an increase in crack resistance by a factor of more than 1.5 compared with materials without added Si_3N_4. This is connected with formation of new harder phase in modified specimens. Material without addition is a composition of titanium boride grains within a titanium matrix. With addition to material of nanosize Si_3N_4 particles there is formation of titanium diboride, titanium nitride, small inclusions of boron nitride, and titanium boride is represented in two modifications, i.e., orthorhombic and cubic.

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