Non-isothermal synthesis of materials based on the MAX phases in the Ti-Si-C and Nb-Al-C systems

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Abstract The experimental results of self-propagating high-temperature synthesis of materials in Ti – Si – C and Nb – Al – C systems are presented. Mixtures of powders of Ti, Si, Nb, Al, and C were used as charge. The combustion thermograms of the Ti-Si-C system are investigated. It is shown that changes in the technological conditions of synthesis can substantially change the phase composition and microstructure of the final products. The optimal synthesis conditions were established, which made it possible to obtain a product with a maximum content of the target phases Ti_3SiC_2, Nb_2AlC, Nb_4AlC_3. Under all conditions studied, the SHS method fails to obtain 100% of the MAX phase of stoichiometric composition. To obtain 100% stoichiometric MAX phases, additional heat treatment of the ground SHS products is necessary. The products obtained by high-temperature synthesis were characterized by X-ray, optical and scanning electron microstructural analysis methods.

1. Introduction.

Creation of new materials and their production methods are one of the most important scientific and applied problems of physical materials science. At present, the obtaining of refractory high-strength materials possessing wear-resistance at elevated temperatures, high ductility at room temperature, and capable of operating under extreme conditions is an urgent problem.

MAX-materials are new materials and are of particular interest to develop refractory high-strength materials. These are ternary compounds that are described by the general formula $M_{n+1}AX_n$, where M is transition metal; A is the element of IIIA or IVA periodic group, X is carbon or nitrogen (or both) and, possibly, boron. A distinctive feature of these materials is the structure of hexagonal crystal lattices, in which the layers of atoms of the M and A elements alternate in a certain sequence, and carbon atoms (or nitrogen) are located in octahedral pores between atoms of the M element. The structure of their crystal lattices provides the unique combination of metal and ceramics properties. To obtain materials based on MAX - phases, various methods are used [1-7]. The basic method for the obtaining of materials based on MAX - phases is sintering which requires high power and time consumption. Self-propagating high-temperature synthesis (SHS) can be considered to be an alternative to sintering.

In this work, the phase composition, microstructure and some properties of SHS materials based on MAX-phases (Ti_3SiC_2, Nb_2AlC, Nb_4AlC_3) are studied.

2. Experimental procedure

Powders of titanium (TPP8 grade, Avisma company, Berezniki), silicon (KR-1 grade, <20 μm), carbon (PM75 grade, <0.033 μm), niobium (TU 48-4-284-73, > 63 μm), aluminum (ASD4 grade, ~ 8 μm), and amorphous boron were used for the preparation of reaction mixtures. The powders were thoroughly mixed in a porcelain mortar. Porous (40–45%) cylindrical samples with a diameter of 20 and a length of 30–32 mm were formed from the prepared mixtures on a hydraulic press. The SHS process was carried out in a constant pressure bomb in an argon atmosphere. A gasless combustion wave was initiated by a red-hot tungsten spiral. The maximum combustion temperature was determined by a tungsten – rhenium thermocouple TR5-TR20 with a diameter of 100 μm. The temperature was recorded using an analog-to-digital converter (ADC) LA-20USB.
The phase composition of synthesized materials was determined with a DRON-2 diffractometer ($CoK\alpha$ radiation). Optical (Axiovert 200M, Karl Zeiss) and scanning electron (SEM515, Philips) microscopes were used to study the microstructure.

3. Results and Discussion

Figure 1 shows the thermogram of combustion of Ti-Si-C (Ti_3SiC_2). The maximum combustion temperature is (2373 ± 25)K that is noticeably lower than the adiabatic combustion temperature (3008 K), but higher than the melting point of titanium (1937 K), silicon (1723 K), and double and triple eutectics in the test system.

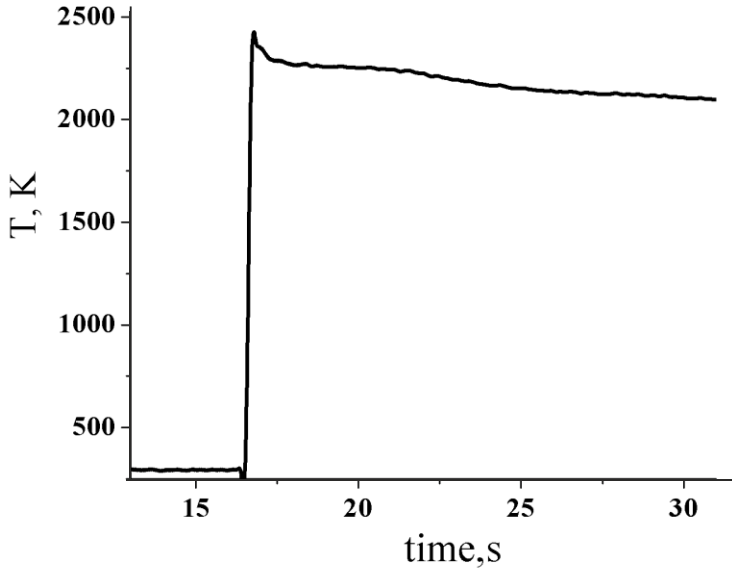

Figure 1. Thermogram of Ti - Si - C combustion.

Self-propagating high-temperature synthesis in the Ti-Si-C system with an excess of silicon forms a composite material Ti_3SiC_2 – (12-18) vol% TiC (Table 1). Traces of other phases TiSi and $TiSi_2$ are also observed. After additional sintering of the SHS product obtained by grinding at a temperature of 1473K for 4 hours in a vacuum of $13{,}33*10^{-3}$ Pa, the amount of the Ti_3SiC_2 phase increases to 92–98 vol%, while the amount of the TiC phase decreases. Traces of silicides are preserved. Increasing the annealing temperature to 1673 K during the sintering leads to the formation of a single-phase material Ti_3SiC_2 (Table 1).

Table 1. Phase composition of the composite material (Ti-Si-C system) depending on the processing mode.

№	Processing mode	Phase composition, vol%		
		Ti_3SiC_2	TiC	$TiSi_2$
1	SHS (porous product)	82-88	18-12	Traces
2	SHS + sintering of porous product at 1423K, 4h	92-93	7	Traces
3	SHS + breaking and grinding of porous product + sintering of powder at 1473K, 4h	93	7	Traces
4	SHS + breaking and grinding of porous product + sintering of powder at 1673K, 4h	100	Traces	-

Figure 2 shows the microstructure of breaks in the SHS-composite material Ti_3SiC_2 + 15vol%. TiC after mechanical compression tests. It can be seen that the material under loading underwent inter - and transcrystalline stratification.

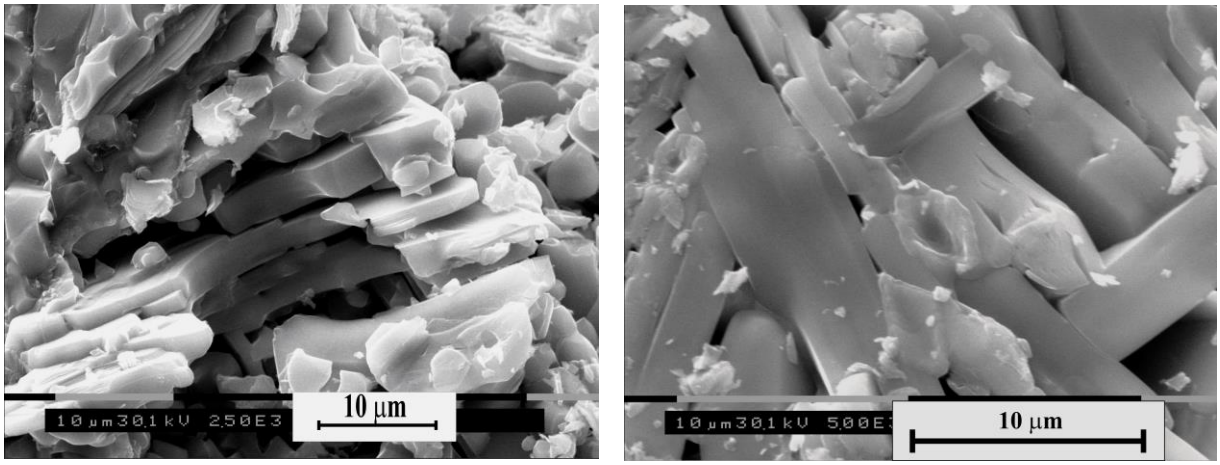

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Figure 2. Microstructure of breaks in the SHS-composite material Ti_3SiC_2 + 15vol%. TiC after mechanical compression tests.

Titanium carbosilicide TI_3SiC_2 is the most studied compound. In addition to Ti_3SiC_2, other compounds with a nanolaminate structure may also be of practical interest. The paper presents the SHS of MAX-phases in the Nb-Al-C and Nb-Al-C-N systems.

In the Nb-Al-C system, two compounds with a layered structure, Nb_2AlC and Nb_4AlC_3, were detected [8-15]. In these works, Nb_2AlC was obtained by hot isostatic pressing and Nb_4AlC_3 was obtained by annealing Nb_2AlC at a temperature of 1973K.

The combustion of a 2Nb + Al + C stoichiometric mixture proceeds in the spin mode. According to X-ray diffraction, the main phases in the synthesized product are Nb_2AlC, NbC.

Figure 3 shows the structure of the break surface of the SHS sample Nb_2AlC. Plate-shaped grains characteristic for MAX – phases are observed. Since the sample was not previously deformed, the layered structure of its grains was not detected.

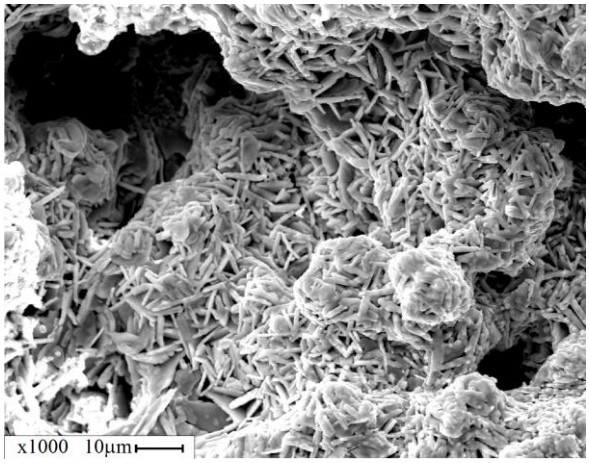

Figure 3. Break structure in the SHS sample Nb_2AlC.

Since a mixture of 2Nb + Al + C is low-exothermic, a high-quality product based on Nb_2AlC cannot be obtained by SHS without additional techniques.

The task of the study was to obtain a material with a nanolaminate structure in the four-component Nb-Al-C-N system (analogue to $Ti_2AlN_{0,5}C_{0,5}$) in the combustion mode [16]. The products of 2Nb + Al + 0.5C obtained in the combustion mode at a nitrogen pressure of 6, 3, 1,5 and 0,4 MPa were synthesized and analyzed. According to X-ray diffraction, multiphase products consisting of Al_2Nb_3C, $Nb_4N_{3,9}$, NbC are formed at a nitrogen pressures of 6, 3, 1,5 MPa (Figure 4). And only at a nitrogen pressure of 0.4 MPa, the diffractogram of the synthesized product contains reflections of Nb_2AlC. The material with the MAX-phase Nb_2AlC was also obtained by the SHS method in a chemical furnace (Figure 4d).

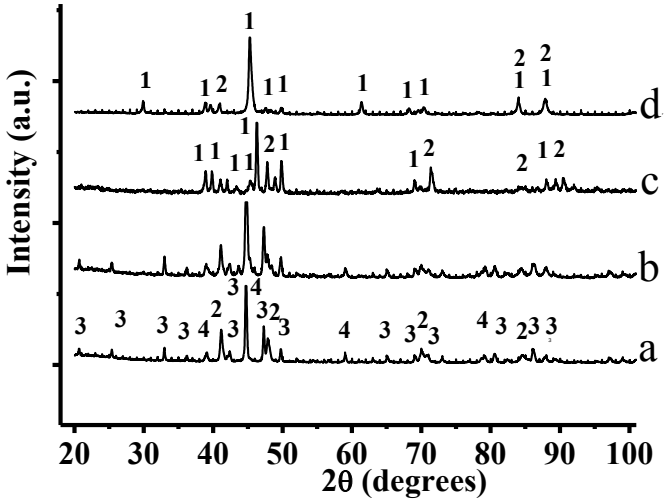

Figure 4. X-ray diffraction patterns of SHS products Nb-Al-C system, (Nb:Al:C=2:1:1 molar ratio) synthesized under the nitrogen atmosphere: (a) at a pressure of 6 MPa; (b) at a pressure of 1,5 MPa; (c) at a pressure of 0,4 MPa; (d) in a chemical furnace. 1 –Nb_2AlC; 2 – NbC; 3 –Al_2Nb_3C; 4 – $NbC_{0,5}$

Figure 5 shows the microstructure of the SHS products Nb-Al-C system, obtained at nitrogen pressure of 6 and 0,4 MPa. In the micrograph 5a, plate-shaped crystals belong to the ternary Al_2Nb_3C

compound, the round phases belong to $Nb_4N_{3,9}$ and NbC. Figure 5b shows the microstructure of the sample synthesized at a pressure of 0,4 MPa. Plate-shaped crystals typical for the samples with a nanolaminate structure are clearly observed.

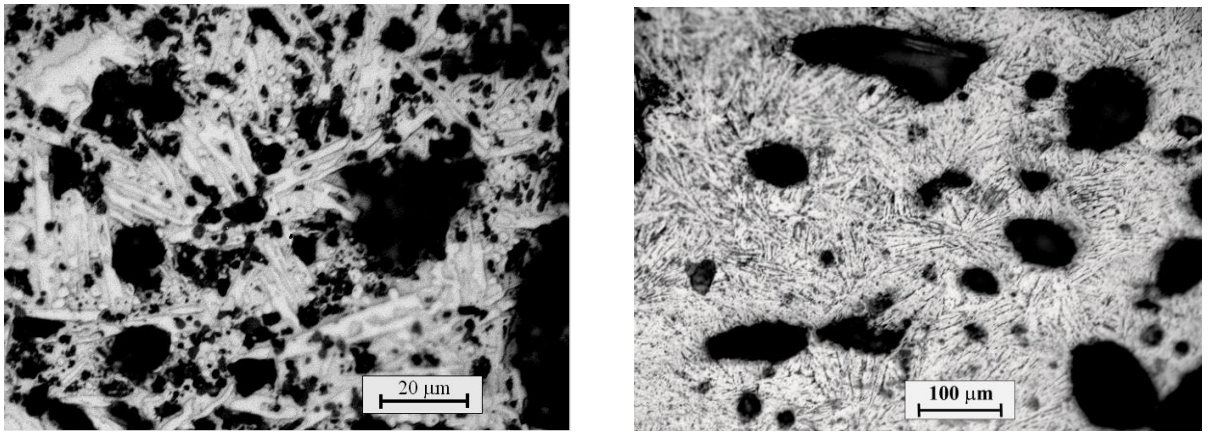

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Figure 5. Microstructures of the products (Nb-Al-C system) synthesized under the nitrogen atmosphere: (a) 6 MPa, (b) 0,4 MPa.

Figure 6 shows the microstructure of the 2Nb + Al + 0.5C sample synthesized by the SHS method in a chemical furnace. Most of the volume is occupied by plate-shaped crystals which, according to X-ray diffraction, are the Nb_2AlC phase. There are round areas, the appearance of which may be due to lack of carbon in the initial reaction mixture. The microstructure of 2Nb+Al+C samples does not contain such areas.

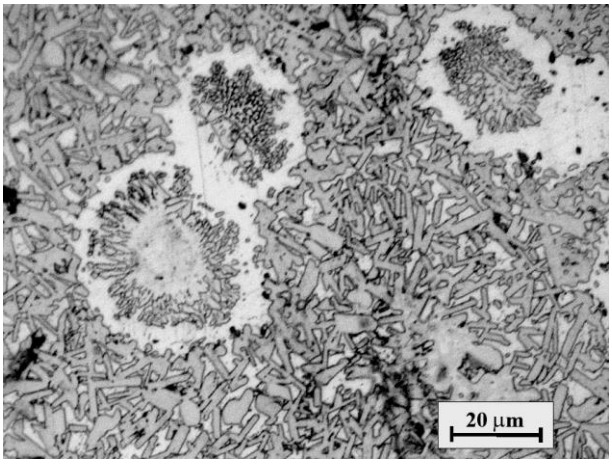

Figure 6. Microstructure of the 2Nb+Al+0.5C sample synthesized in a chemical furnace

As already mentioned, Nb_4AlC_3 MAX-phase was initially obtained by the high-temperature (1973K) heat treatment of the Nb_2AlC MAX-phase [8]. Later, single-phase Nb_4AlC_3 samples were synthesized by hot pressing and spark plasma sintering (SPS) [8, 9]. The microstructure and electrical, thermal and mechanical properties of synthesized Nb_4AlC_3 MAX-phases were studied in these works. Excellent mechanical properties of Nb_4AlC_3 at high temperatures were noted. The bending strength of Nb_4AlC3 (346 MPa) remains without worsening in the range from room temperature to 1673K, the Young's modulus of Nb_4AlC_3 can be maintained up to 1773K that is much higher than that of Nb_2AlC

(1673K), Ta_4AlC_3 (1473K) and Ta_2AlC (1473K), which indicates prospective using the MAX-phase (Nb_4AlC_3) at high temperatures.

Considering the above, the studies were conducted to find the optimal conditions for obtaining the Nb_4AlC_3 MAX- phase by the SHS method. As preliminary studies showed, the combustion of the 4Nb+1.2Al+2.7C mixture developed in a spin mode. To increase the exothermicity of the mixture, a mixture of Ti + 2B powders was added to the initial mixture in an amount of 1, 5, 10 wt.% as an additional source of heat.

Figure 7 shows the X-ray diffraction patterns of the SHS products based on Nb_4AlC_3 and with the addition of Ti + 2B powders.

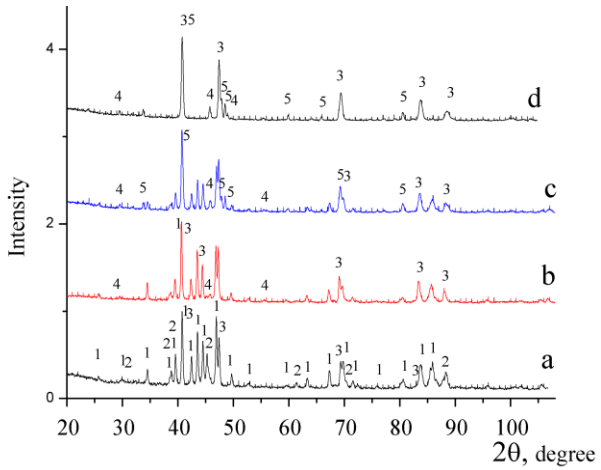

Figure 7. X-ray diffraction patterns of the SHS products Nb-Al-C system (Nb: Al: C = 4: 1.2: 2.7 molar ratio) and with the addition of exothermic Ti + 2B powders, (a) Nb: Al: C = 4: 1.2: 2.7; (b) 1wt.% of (Ti + 2B); (c) 5wt.% of (Ti + 2B); (d) 10wt.% of (Ti + 2B). 1 – Nb_4AlC_3; 2 – Nb_2AlC; 3 – NbC; 4 – $NbAl_3$; 5 – NbB

X-ray diffraction shows that the addition of 1wt.% Ti + 2B to the initial mixture during SHS forms a product consisting of Nb_4AlC_3, NbC and a small amount of the intermetallic phase $NbAl_3$. The addition of a larger amount of Ti + 2B leads to a significant decrease in the MAX-phase of Nb_4AlC_3 and the presence of niobium monoboride in the synthesized product. With the addition of 10wt.% Ti + 2B, the product consists of NbC, $NbAl_3$ and NbB.

4. Conclusion Materials based on the Ti-Si-C and Nb-Al-C systems were obtained by the SHS method. The combustion regimes of powder systems were studied. The structure and phase composition of SHS materials are investigated. Using the SHS method, it is not possible to obtain 100% stoichiometric MAX phases. The synthesis products contain carbides, silicides, and aluminides of titanium and niobium. To obtain 100% MAX phases of stoichiometric composition, an additional high-temperature heat treatment of ground SHS products is required. In the SHS products from the 4Nb-Al-3C system, two MAX phases are present. The introduction of a highly exothermic Ti-2B additive into the mixture leads to an increase in the content of the target Nb_4AlC_3 phase.

Notification-

SHS Self-propagating high-temperature synthesis

ADC - analog-digital converter

SPS - spark plasma sintering

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