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The Effect of Synthesis Conditions on Phase Composition and Structure of Combustion Products of Nickel-Bonded Titanium Carbide

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Abstract

The paper explores the regularities of synthesis of nickel-bonded titanium carbide from powdered and granulated charge of PTM and PTM-1 grades of titanium in a co-flow of inert and active gas. It was found that the combustion of Ti + C + 25 % Ni mixtures occurs differently depending on the specific surface and morphology of the titanium particles. For PTM grade titanium, the process involves a long afterglow following the passage of the combustion front, with the phase composition of the product (TiC, Ni) corresponding to thermodynamic calculations. To explain the synthesis features, a two-stage mechanism of interaction of the Ti + C + 25 % Ni system is proposed. When burning a mixture based on PTM-1 grade titanium, there was no afterglow, and the phase composition of the product included intermetallides. The experiments showed that the synthesis in a nitrogen flow changed the phase composition of the combustion products of a mixture based on PTM-1 titanium and a mixture of PTM and PTM-1 titanium in equal parts. The synthesis products prepared from granulated charge without a gas flow were granules that did not sinter together, which facilitated the process of their processing into powder. For a powdered system in the presence and absence of a gas flow, and for a granulated mixture in an argon stream, irrespective of titanium grades, the combustion products were a sintered mass that was impossible to grind under laboratory conditions.

Keywords

Granules; microstructure; nickel binder; phase composition; spec; synthesis; titanium carbide.

Introduction

Titanium carbide (TiC) based materials due to their hardness and wear resistance have a wide range of applications from abrasives and protective coatings to structural tribological alloys. To increase their plasticity, a metallic binder is introduced into the initial charge, such as nickel Ni [1, 2]. Currently, the main method of producing materials from the initial powders is sintering [1, 3], which requires a considerable amount of energy and time, as well as a large number of process operations traditional for powder metallurgy. An alternative to sintering is self-propagating high-temperature synthesis (SHS) [4], during which the heat necessary for obtaining the final product is released in the interaction of the initial reagents. A feature of SHS is melting of the most fusible components in the combustion process, which ensures the spreading of the melt and the self-dispersion of the initial reagents. However, as a result of the synthesis, a sintered mass is produced, the grinding of which presents great difficulties and requires considerable energy inputs.

In [5], the study of the regularities of combustion of Ti–C granular mixtures showed that after synthesis the granules retained their dimensions and did not sinter together. It can be expected that the use of granulated charge instead of powder for the synthesis of titanium carbide with a metal bond will make it possible to produce granules with dimensions of the order of 1 mm, the grinding of which to the powder state will be less energy-consuming.

Starting materials and experimental procedure

The starting materials used and their brief characteristics are given in Table 1.

The compositions were granulated as follows: the original Ti–C–Ni powdered mixture was stirred for 4 hours in a drum tumbler mixer. Then, 4 wt% of polyvinylbutyral solution in ethyl alcohol was added to the resulting mixture. The pasty mass obtained after mixing was mashed through a sieve with a cell size of 1.25 mm. To impart spherical shapes to the particles, they were rolled on a rotating horizontal surface. The particles were then dried in air for 10 hours and dispersed on a shaking sieve. In this research, we used granules with dimensions of 0.63–1.6 mm.

The regularities of combustion were studied on the original experimental setup. It can be used for synthesis with and without gas blow to measure the flow and pressure of the gas during combustion, and also to obtain video recordings of the combustion process (Fig. 1). Based on the frame-by-frame processing of video recordings, the speed of the combustion front was calculated. All the results of experiments in the concurrent gas flow described below were obtained with a pressure difference between the upper and lower end of the batch at 1 atm (the pressure at the upper end is 1 excess atmosphere). To avoid shrink-off of the unburned portion of the batch during combustion and to obtain stable results, before each experiment the sample was blown with argon flow at the same pressure drop.

The investigations were carried out for compositions where nickel was 25 % of the mass of the whole mixture, which provided a strong connection of titanium carbide with products under gas-flame spraying [6].

Table 1

Materials and reagents

Materials	Grade	Particle size to 50 wt%, μm	Particle size to 90 wt%, μm
Titanium	PTM	<61	<107
Titanium	PTM-1	<105	<169
Black	P-803	<2.5	<4
Nickel		<100	<150
Polyvinylbutyral			
Ethyl alcohol 95 %			

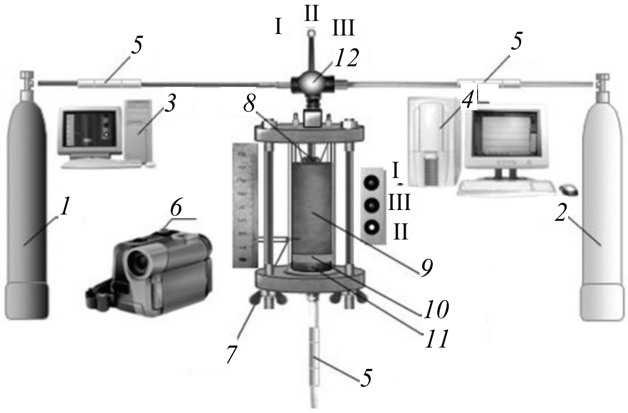


Fig. 1. Diagram of the experimental setup:
1 – nitrogen gas cylinder; *2* – argon gas cylinder; *3* – computer for recording a video signal; *4* – computer for recording the readings of sensors through the ADC; *5* – flow and pressure sensors; *6* – digital video camera; *7* – thermocouple of tungsten-rhenium 5/20 (not used in this work), *8* – electrical spiral; *9* – charge; *10* – layer of mineral wool; *11* – metal mesh; *12* – gas switch (I – nitrogen, II – argon, III – gas supply blocked)

Experimental results and discussion

The conducted studies showed that the combustion of the granulated SHS mixture of Ti + C + 25 % Ni with PTM grade titanium occurred in two stages. First, the combustion front lasted no more than 3 s, after which a brighter glow of the products was observed (we call it afterglow) for 6–8 s (Fig. 2).

In the combustion of granulated mixtures, this effect was observed for the first time, in the Ti + xC granules ($0.5 \le x \le 1$) previously studied, there was no afterglow.

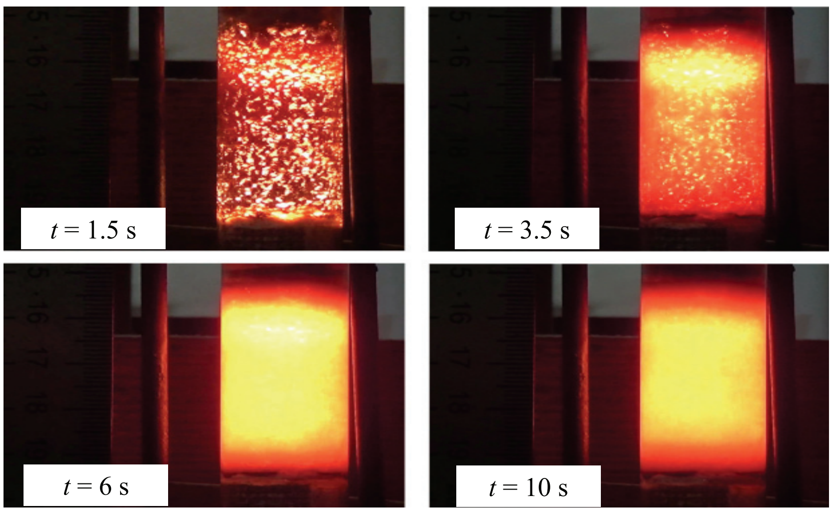


Fig. 2. Shots of the process of synthesis of granulated mixture of nickel-bound titanium carbide with PTM titanium at different times (this time is measured from the moment of ignition)

Previously, the afterglow was observed in [7] in the combustion of pressed samples of Ti + C + 20 % Ni. To test the existence of this effect in powdered mixtures of bulk density, experiments were conducted to burn Ti + C + 25 % Ni mixtures, which showed that the afterglow effect also occurred in them. This kind of combustion is explained by the fact that nickel, having a lower melting point (1726 K) than titanium (1933 K), melts in the combustion front and spreads over titanium particles, preventing the interaction of titanium with black. The inhibitory action of the nickel layer on the surface of titanium particles upon combustion of a mixture of Ti + C + 20 % Ni was previously shown in [8].

However, due to the low volume content of nickel in the mixture (≤ 8 wt%), only a portion of the titanium particles were covered by the nickel melt. The remaining titanium particles melt in the combustion wave and spread over the black, forming titanium carbide upon interaction. It was this reaction that was the leading one in the combustion front, because the combustion wave in a Ti + Ni mixture without preheating was not used [9]. Behind the combustion front, nickel carbon was displaced from its melt with titanium to form titanium carbide, accompanied by the release of heat, giving the afterglow effect, which was visually perceived as flaring. According to the X-ray phase analysis data, the final product, obtained both from powdered and granulated mixtures, contained titanium and nickel carbide phases (Fig. 3), which coincided with the results of thermodynamic calculations.

The experiments showed that in the combustion of granulated mixtures of Ti + C + 25 % Ni, the granules retained their dimensions and did not sinter. For powdered mixtures, the experiments showed that the combustion products of a mixture of Ti + C + 25 % Ni were sintered. This result is an argument in favor of the use of granulated mixtures instead of powdered mixtures for the production of ceramic materials with a metal bond, since in this case the energy consumption and time for further grinding of the synthesis products are significantly reduced and the contamination of the final product by the substance of the grinding bodies decreases.

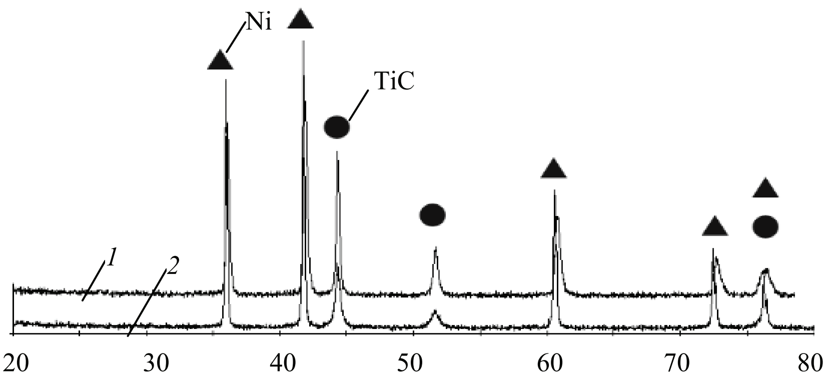


Fig. 3. Results of X-ray phase analysis of the combustion products of a Ti+C+25% Ni mixture from the PTM grade titanium granulate:
1 – without a gas flow, *2* – in a nitrogen flow (pressure drop of 1atm)

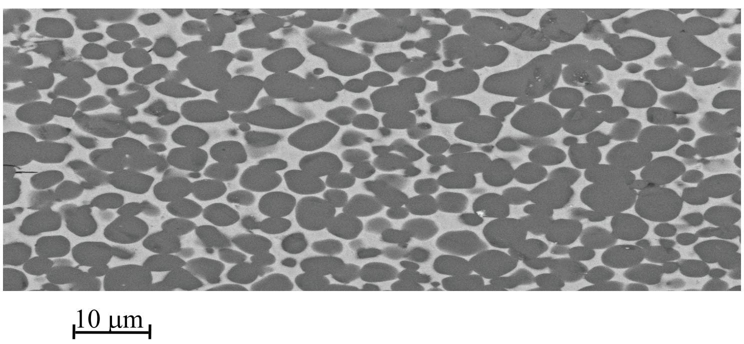


Fig. 4. Microstructure of the Ti + C + 25 % Ni granules after synthesis (light areas are nickel, dark areas are titanium carbide)

The microstructure of the condensed products (granules) obtained was studied by scanning electron microscopy (SEM) using the Ultra Plus microscope from Carl Zeiss. Fig. 4 shows a photograph of the microstructure of Ti + C + 25 % Ni granules after synthesis. As can be seen, the average grain size of titanium carbide was 2-4 μm, which was an order of magnitude smaller than the initial sizes of titanium particles (70 μm), i.e. in the combustion process, the titanium particles were dispersed, and the nickel binder prevented the growth of grains of titanium carbide after synthesis. Attention is drawn to the fact that, despite the small volume fraction in the charge, Ni was uniformly distributed over the granule after synthesis.

It is known that the gas co-flow is an effective controlling factor for the combustion of SHS mixtures [10], therefore the question naturally arose as to what effect the gas flow could have on the combustion characteristics, phase composition and structure of the synthesis products. The video recording of the combustion of a Ti + C + 25 % Ni granulated mixture in a co-flow of inert (argon) and active (nitrogen) gas showed that the afterglow effect associated with the presence of Ni retained. The velocity of the combustion front in the gas flow increased compared to the combustion without a gas flow from 27 to 36 mm/s for argon and up to 47 mm/s for nitrogen.

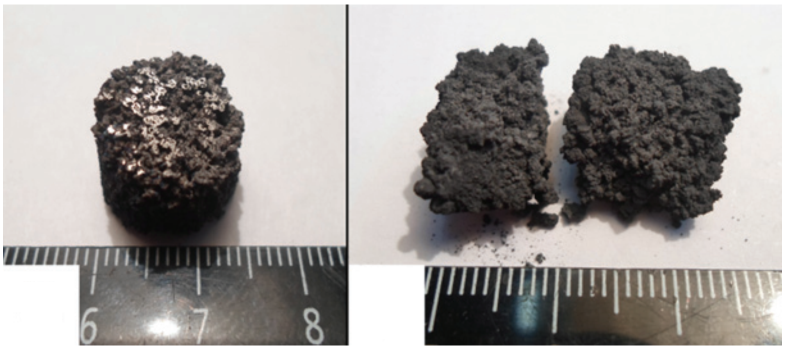
When the Ti + C +25 % Ni granulated charge was burned in the flow of argon, the batch shrank off by 30 %. The combustion product was a sintered mass that did not separate into individual granules and was not amenable to grinding under laboratory conditions. Fig. 5 *a* shows a photograph of the cross section of the sample after synthesis.

In accordance with the theory of filtration combustion, the cause of such an effect of an inert gas on the combustion characteristics and properties of products is an increase in the temperature in the combustion wave [5]. In turn, an increase in the combustion temperature leads to an increase in the fraction of the liquid phase in the products, an increase in their fluidity and, as a consequence, consolidation of the granules under the effect of a pressure drop.

In the combustion of the granulated mixture in a nitrogen flow, the shrinkage of the sample was smaller and amounted to 15–20 %, and the combustion rate was higher than that in the argon flow. The combustion product was a porous, weak sample from slightly sintered granules, which was crumbled during cutting. As a result, it was impossible to take a photograph of the cross-section of the sample. Fig. 5 *b* shows a photograph of the fracture of the burnt sample.

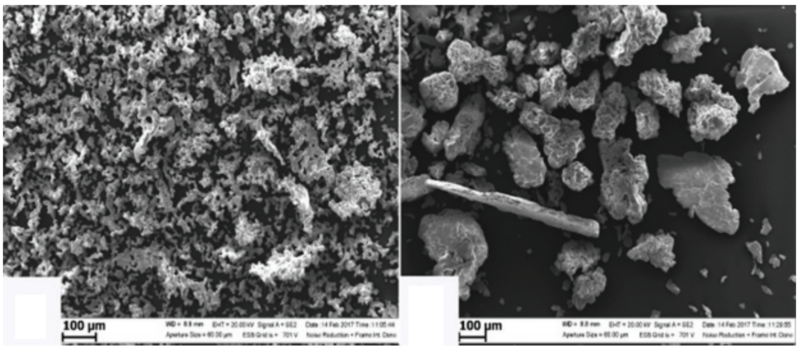
According to thermodynamic calculations in the THERMO program [4], in combustion of the Ti + C + 25 % Ni mixture, the products of the reaction should be only stoichiometric titanium carbide and nickel, i.e., nitrogen should behave like an inert gas, hence, as in the argon flow, should have a sintered mass. However, the experimental data obtained make it possible to conclude that nitrogen behaves differently than the inert gas. This result is in accordance with the conclusions of [5, 10], according to which the flow of nitrogen ignites from the surface of the granule, forming a refractory crust of titanium nitride on their surface. This crust prevents the solid granules from sintering under the influence of pressure drop and high temperature despite the presence of a nickel binder. Thus, additional evidence was obtained for the non-equilibrium combustion mechanism of granulated titanium-based mixtures in a nitrogen co-flow, when the sequence of chemical reactions in the combustion wave is determined by the kinetic features of the interaction of titanium with nitrogen and carbon [12]. We note that for the Ti + C + 25 % Ni powdered mixture, the conducted studies have shown that the combustion products, irrespective of the experimental conditions (in the flow or without the gas flow), are a sintered mass that has ductility and is practically unbreakable under laboratory conditions.

According to the chemical analysis, the combustion products of Ti + C + 25 % Ni mixtures in the nitrogen flow contained 2.5–3.0 % of nitrogen by weight. However, according to the results of the X-ray phase analysis, the phases of TiC (main phase) and Ni were observed in the synthesis products of the Ti + C + 25 % Ni mixture in a nitrogen flow and without a flow. A possible reason for this apparent contradiction is the presence of the $TiC_xN_{(1-x)}$ phase, whose angles are close to the angular position of the peaks in the X-ray diffraction pattern of titanium carbide [13].



a) *b*)

Fig 5. A cross section of the synthesis product of Ti + C + 25 % Ni granules in a gas flow:
a – argon flow, *b* – nitrogen flow



a) *b*)

Fig. 6. Microphotographs of titanium powders of PTM (*a*) and PTM-1 grades (*b*)

The presence of the $TiC_xN_{(1-x)}$ phase is manifested in the fact that in Fig. 3 peaks of the main phase on the roentgenogram of products obtained during combustion in a nitrogen flow are shifted to the right and broadened. The phase composition of the synthesis products of the Ti + C + 25 % Ni mixture in the argon flow was not obtained, since the product was not amenable to grinding under laboratory conditions.

Thus, in the combustion of the granulated Ti + C + 25 % Ni charge based on PTM titanium nickel-bound titanium carbide doped with nitrogen was produced in a nitrogen co-flow.

Long-term experience in studying SHS processes has shown that the grade of initial reagents can have a significant effect on the patterns of combustion and the phase composition of the products obtained. Therefore, studies of the patterns of synthesis and composition of the resulting products of the Ti + C + 25 % Ni mixture from the powdered titanium of another brand (PTM-1) were conducted. The chemical composition of titanium of these grades is practically the same, so attention was paid to the differences in the dimensions and shape of titanium particles. Fig. 6 shows microphotographs of titanium powders of different grades, made with scanning electron microscope Ultra Plus from Carl Zeiss.

As can be seen from the photographs, the particles of titanium powders of different grades differ in shape and size. The PTM-1 titanium particles were about 1.5 times larger, had a planar shape, with a less developed surface. The specific surface area of the PTM-1 titanium powder, which was determined on the Sorbi-M specific surface meter, was 0.35 m^2/g (0.59 m^2/g for PTM grade titanium). The particle size distribution was determined on a MicroSizer-201 particle analyzer.

First of all, it was verified whether the titanium grade affected the front propagation velocity and the composition of the product in the combustion of the Ti + C stoichiometric mixture. As shown by the results of the experiments, the combustion rate of the powdered mixture based on PTM-1 titanium decreased by a factor of 2 compared with the PTM titanium and was 8 mm/s. The combustion rate of the granulated mixture also fell from 75 to 22 mm/s. However, the phase composition of the products obtained from both the powdered and the granulated mixture based on PTM-1titanium, as well as for PTM titanium, according to the results of X-ray phase analysis, was stoichiometric titanium carbide.

It turned out that the addition of 25 % nickel to the Ti + C mixture for PTM-1 titanium resulted in a change in the combustion behavior and composition of the products compared to the PTM-based titanium blend. In the combustion of the granulated mixture the afterglow stage was not observed, and the combustion rate decreased from 27 mm/s for a PTM titanium mixture to 11 mm/s. According to the X-ray phase analysis, the combustion products had a more complex composition and included Ti_xNi_y intermetallides. Fig. 7 shows the results of X-ray phase analysis of the combustion products of Ti + C + 25 % Ni granulated mixtures based on titanium of different grades. It should be noted that according to thermodynamic calculations, the synthesis products of such a mixture must consist of titanium carbide with a nickel binder.

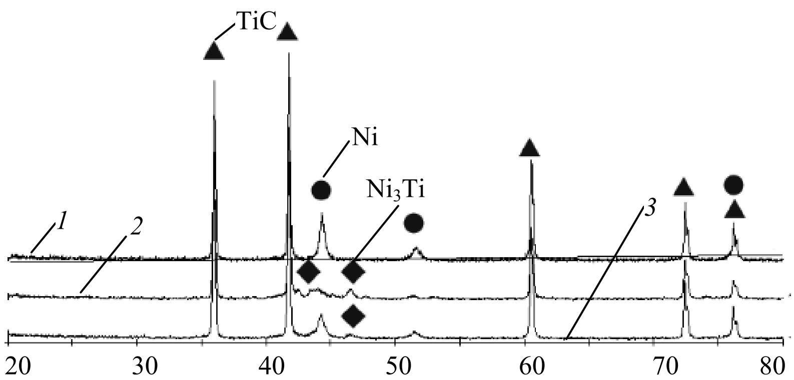


Fig. 7. Results of X-ray phase analysis of the combustion products of Ti + C + 25 % Ni granulated mixtures without gas flow from PTM titanium (*1*), PTM-1 titanium (*2*) and PTM and PTM-1 titanium in equal parts (*3*)

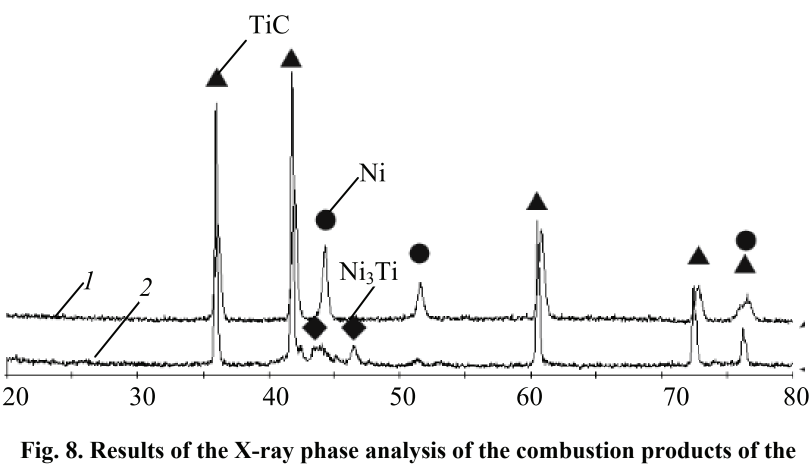


Fig. 8. Results of the X-ray phase analysis of the combustion products of the Ti + C + 25 % Ni granulated mixture from PTM-1/PTM titanium in equal parts without a gas flow (*1*) and in a nitrogen flow (*2*)

Table 2

Front velocity and phase composition of the combustion products of granulated mixtures from titanium of different grades

Gas flow	Titanium grade in the granulated mixture Ti + C + 25 % Ni					
	PTM		PTM-1		50 % PTM/50 % PTM-1	
	front velocity, mm/s	phase composition	front velocity, mm/s	phase composition	front velocity, mm/s	phase composition
Without gas flow	27	TiC, Ni	11	TiC, Ni, Ti_xNi_y	20	TiC, Ni, Ti_xNi_y
Argon	36	–	23	–	30	–
Nitrogen	47	TiC, Ni	30	TiC, Ni	42	TiC, Ni

The granules of Ti + C + 25 % Ni retain their dimensions after synthesis and do not sinter. To test the hypothesis that replacing part of PTM-1 titanium can lead to a decrease in the content of intermetallic compounds in products, the experiments were conducted to burn powdered and granulated mixtures of Ti + C + 25 % Ni, in which 50 % of PTM-1 titanium was replaced with PTM titanium. The studies showed that for this mixture the combustion process proceeded with an afterglow.

The combustion rate of such a granulated mixture (PTM/PTM-1 titanium) of 20 mm/s was intermediate between the combustion rates of compositions with titanium of individual grades (27 mm/s for a PTM titanium mixture and 11 mm/s for PTM-1 titanium mixture). The X-ray phase analysis showed the presence of intermetallides in products, but in a smaller amount than for a PTM-1 titanium mixture.

Then, the influence of the flow of inert and active gas on the combustion characteristics and the phase composition of the synthesis products for PTM-1 titanium mixture and PTM/PTM-1 titanium mixture in equal parts was studied. The velocity of the combustion front of the granulated mixture in the gas flow (pressure drop of 1 atm) increased compared to the combustion without a flow: in the argon flow from 11 to 23 mm/s for a PTM-1 titanium mixture, and from 20 to 30 mm/s for a PTM/PTM-1 titanium mixture, in a nitrogen flow from 11 to 30 mm/s for a PTM-1 titanium mixture and from 20 to 42 mm/s for a PTM/PTM-1 titanium mixture.

In the combustion in a nitrogen flow, the afterglow was observed for granulated PTM-1 titanium mixture and a PTM/PTM-1 titanium mixture, and the products had a small shrink-off. The synthesis product was a porous, weak sample from slightly sintered granules, which crumbled during cutting. It should be noted that by blowing nitrogen, it was possible to change the composition of the combustion products both of PTM-1 and PTM / PTM-1 titanium mixtures: they did not contain intermetallides according to the X-ray phase analysis (Fig. 8).

When burning in the argon flow, the PTM-1 titanium mixture and the PTM/PTM-1 titanium mixture, the synthesis products were a sintered mass with a noticeable shrink-off, fragmentation of the sinter in the laboratory was impossible (therefore, the X-ray diffraction data for the synthesis products in the argon flow are absent). The data on the effect of the gas flow on the propagation velocity of the combustion wave front of granulated titanium mixtures of different grades and the phase composition of the synthesis products are summarized in Table 2.

Thus, the conducted study showed that granulation of the mixture followed by combustion in a nitrogen flow made it possible to neutralize the influence of the titanium grade on the phase composition of the final products of synthesis.

Conclusions

The regularities and composition of the products of the synthesis of nickel-bound titanium carbide from powdered and granulated charge from the titanium of PTM and PTM-1 grades were studied.

It was found that the combustion of the Ti + C + 25 % Ni mixtures (except for the PTM-1 titanium-based granulated mixture) occurred in two stages: first, the combustion front occurred, then the afterglow followed. A two-stage mechanism for the formation of the final product to explains this effect was proposed. It was shown that in the combustion of the Ti + C + 25 % Ni granulated mixture in the absence of the gas blowing, the titanium granules after the synthesis retained their dimensions and did not sinter.

It was shown that when using PTM titanium, the final combustion product of a Ti + C + 25 % Ni granulated mixture was nickel-bound titanium carbide. It is shown that combustion of the Ti + C + 25 % Ni mixture from the PTM-1 titanium or PTM / PTM-1 titanium, the final product in the absence of gas flow consisted of TiC, Ni phases and Ti_xNi_y intermetallides. The SEM method for combustion products of these mixtures showed that during the synthesis, the so-called spontaneous dispersion of titanium particles occurred, while the nickel binder prevented the growth of titanium carbide grains.

It was shown that for the PTM-1 titanium mixture and the PTM / PTM-1 titanium mixture, the synthesis in a nitrogen flow made it possible to change the phase composition of combustion products, namely, to the disappearance of intermetallide phases according to the X-ray phase analysis data.

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