

INORGANIC SYNTHESIS
AND INDUSTRIAL INORGANIC CHEMISTRY

Synthesis of Composite Materials in the System Cr–Ti–B
by the Self-Propagating High-Temperature Synthesis
from Mixtures CaCrO₄/TiO₂/Al/B

P. A. Miloserdov^{a,*}, V. A. Gorshkov^a, N. V. Sachkova^a,
N. Yu. Khomenko^a, and O. M. Miloserdova^a

^a Merzhanov Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences,
Chernogolovka, 142432 Russia
*e-mail: yu_group@ism.ac.ru

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Abstract—Using the method of self-propagating high-temperature synthesis (SHS metallurgy), cast composite materials were produced in the Cr–Ti–B system. The experiments were carried out in universal SHS reactors with an initial argon pressure of $P_{in} = 5$ MPa. Mixtures of CaCrO₄, TiO₂, Al, and B powders were used as batch. It was shown that by varying the mass ratio α of CaCrO₄/2Al/2B and 3TiO₂/4Al/6B mixtures in a batch, it is possible to significantly affect the synthesis patterns, phase composition, and microstructure of the target products. The initial mixtures are capable of burning in the range of α 0–20%. The phase separation limit occurs at $\alpha = 15\%$. The introduction of a highly exothermic CaO₂ + Al additive into the mixture made it possible to expand the phase separation limit to $\alpha = 20\%$. As α increases, the amount of titanium boride in the final product increases. The resulting composite material consists of titanium-chromium boride distributed in a matrix of chromium boride. The synthesized materials were characterized by X-ray and local microstructural analysis. The structural phase states of the target products produced under various conditions were studied.

Keywords: SHS metallurgy; synthesis; composite materials; borides; titanium chromium boride; calcium chromate

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Titanium and chromium borides are used for the manufacture of heat-resistant, refractory and wear-resistant alloys and as a basis for cutting high-temperature materials, in cermets for nuclear technology, for the manufacture of immersion thermocouple covers, etc. AlB₂ borides exhibit significant mutual solubility, which leads to the formation of extensive high temperature solid solutions [1]. The Cr–Ti–B system has a hardness higher than individual compounds and has recently been intensively studied as a promising material for nuclear energy. Ceramic based on chromium borides, especially CrB₂, has unique properties: high hardness (20–22 GPa), high melting point (2200°C), good elasticity modulus (211 GPa), good oxidation resistance, high thermal conductivity, low thermal coefficient expansion, high wear resistance, and chemical inertness [2, 3]. These unique properties allow utilization of chromium boride

as a material for high-temperature structural products and hard coatings on cutting tools [4]. Compared to TiB₂ and CrB₂, titanium-chromium diboride has a higher hardness, oxidation resistance, and wear resistance. Titanium-chromium diboride has important advantages over popular tungsten carbide materials, such as lower specific gravity, high resistance at elevated temperatures, low cost, and readily available raw materials for its production. Despite the fact that (Ti, Cr)B₂ diboride has such properties as high hardness, oxidation resistance, wear resistance, thermal and electrical conductivity, its high fragility limits its use in its pure form [5].

To create these materials and their manufacturing, the most widely used methods are melting and high-temperature consolidation (sintering and hot pressing) from mixtures of metal powder and pure boron powders in vacuum at temperatures of 1800–2200°C. Titanium

and chromium borides are obtained by sintering without pressure with agglomeration additives (TiSi_2 , CrSi_2 , WSi_2) and without additives in the temperature range of 1450–1950°C in vacuum, as well as in argon atmosphere +5% hydrogen for 2–4 h [6]. Titanium-chromium borides are obtained by hot pressing from chromium oxide Cr_2O_3 , titanium oxide TiO_2 and boron at a temperature of 1800°C in a hydrogen medium [5].

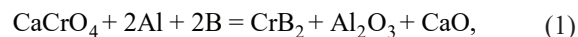
In [7], the preparation of titanium-chromium boride is described by high-temperature mechanochemical synthesis using titanium, chromium, and magnesium polyboride Mg_mB_n . Titanium-chromium borides are also produced by SHS metallurgy (one of the areas of self-propagating high-temperature synthesis) from mixtures based on chromium oxides (CrO_3 and Cr_2O_3), titanium (TiO_2), boron (B_2O_3) and aluminum [8], by SHS compaction (followed by pressing the hot end product) from mixtures based on Cr, Ti, B with the addition of TiN nanoparticles [9], by the SHS method in combination with *p*-HIP from mixtures of elemental powders of titanium, chromium, boron, and copper additives or niobium [10, 11]. In [12], the authors by intensification of combustion produced cast boride ceramics using a highly exothermic additive based on calcium peroxide, a mixture of elemental powders of Ti, Cr, and B. SHS metallurgy is one of the most promising methods for the synthesis of cast composite materials [13]. In this method, the temperature released during the reaction allows the products to be cast. It was decided to abandon chromium (VI) oxide CrO_3 because of its toxicity [14] and thermal instability. Previously, the authors conducted studies on the use of CaCrO_4 as a chromium-containing agent for the production of chromium carbides and borides [15, 16]. Studies of the $\text{CaCrO}_4 + \text{Al} + n\text{B} \rightarrow \text{Cr}_x\text{B}_y + \text{Al}_2\text{O}_3 + \text{CaO}$ system, where the amount of boron (*n*) was varied to synthesize Cr_2B , CrB , Cr_3B_4 , CrB_2 , showed that replacing CrO_3 in the initial mixture with a low-hygroscopic stable CaCrO_4 allows maintaining the high energy of the initial mixture and the ability of the mixture to burn, as well as to obtain refractory chromium borides in cast form. It was found that mixtures can burn in a wide range of B content; the final product consists of a mixture of chromium borides and free aluminum [15].

The aim of the work is to study the patterns of combustion of the $\text{CaCrO}_4 + \text{TiO}_2 + \text{Al} + \text{B}$ system to obtain a cast composite material based on titanium-chromium boride, and to synthesize this material by SHS metallurgy methods.

EXPERIMENTAL

Components with thermal stability and the ability to realize a high combustion temperature were selected for termite mixtures.

The calculation of the ratios of the reagents of the initial mixtures was carried out according to the following schemes of chemical conversion:



Thermodynamic calculation of the adiabatic temperature of combustion and the formation of gaseous products during combustion of the mixture based on schemes (1) and (2) depending on α , where $\alpha = [M_2/(M_1 + M_2)] \times 100\%$, M_1 is the mass of the mixture according to the scheme (1), M_2 is the mass of the mixture according to scheme (2), carried out on a personal computer using Thermo [17].

In the experiments, mixtures of powders CaCrO_4 (analytical grade), TiO_2 (extra pure grade), Al (ASD-1 brand) and B (SVS-M brand) with a particle size $d_{\text{Mg}} \leq 10 \mu\text{m}$ and a content of B = 85 wt % and Mg = 15 wt%. In preparing the mixtures for the experiments, the Al and B contents were adjusted taking into account the participation of Mg in the reduction of CaCrO_4 and TiO_2 and ensuring the calculated content of B. The initial gas pressure in the experiments was 5 MPa.

To increase the combustion temperature, a highly exothermic additive $3\text{CaO}_2 + 2\text{Al} = 3\text{CaO} + \text{Al}_2\text{O}_3$ was added to the mixture, the adiabatic combustion temperature of which at $P = 5 \text{ MPa}$ is 4290 K. As a result of combustion of the additive, oxides are formed that remain in the oxide ingot and do not enter the target product. This additive allows you to raise the synthesis temperature by more than 300°.

To study the combustion, the experiments were carried out in quartz glasses with a diameter of 20 mm and a height of 50 mm, the mass of the mixture was 20 g. The experiments were carried out in graphite forms with a diameter of 40 mm and a height of 100 mm for examining the technological parameters of the synthesis and final products, therewith mass of the mixture was 100 g. The studies were conducted in a 3 L reactor (Fig. 1) in an argon atmosphere with an initial gas pressure of 5 MPa. The mixture was initiated by a spiral of molybdenum

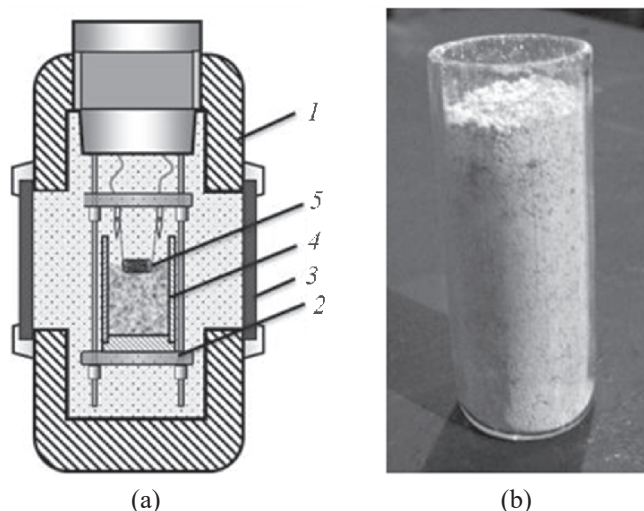


Fig. 1. Reactor with viewing windows ($V = 3$ L). (a) Scheme of the experimental setup: (1) reactor vessel, (2) substrate, (3) viewing window, (4) quartz glass with the mixture, (5) molybdenum spiral), (b) quartz glass with the mixture.

wire. The combustion process was investigated using a video camera.

In the experiments, the burning rate u_b , the pressure increase in the reactor ΔP , the mass loss of the mixture during combustion η_1 due to the spreading, the yield of the metal phase in the ingot η_2 , and the completeness of the chemical reaction η_3 were determined by the formulas

$$\begin{aligned} u_b &= h/t, \\ \Delta P &= P_{\text{fin}} - P_{\text{in}}, \\ \eta_1 &= (M_{\text{fin}} - M_{\text{in}})/M_{\text{in}} \times 100\%, \\ \eta_2 &= m_{\text{ingot}}/M_{\text{in}}, \\ \eta_3 &= m_{\text{ingot}}/m_{\text{ingot}\cdot\text{calc}}, \end{aligned}$$

where h is the height of the mixture layer in the quartz glass, t is the burning time, P_{in} and P_{fin} are the initial and final pressure in the reactor, M_{in} is the mass of the initial mixture, M_{fin} is the mass of the final products, m_{ingot} is the mass of the metal ingot, $m_{\text{ingot}\cdot\text{calc}}$ is the calculated mass of the metal ingot

The burning time of the mixture was measured in two ways: by stopwatch and video; pressure was recorded by a manometer. The mass fraction of mixture 2 in the initial charge α was calculated by the formula

$$\alpha = M_2/(M_1 + M_2) \times 100\%,$$

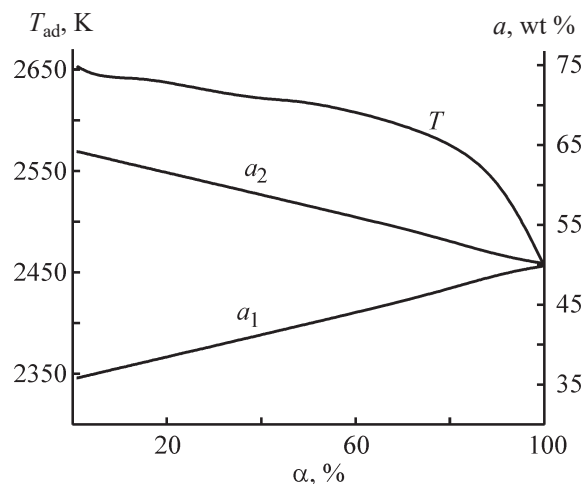


Fig. 2. The results of the thermodynamic calculation of mixtures according to schemes (1) and (2). T is the adiabatic combustion temperature, a_1 is the number of metal synthesis products, a_2 is the number of oxide synthesis products.

where M_1 is the mass of the mixture calculated according to the scheme (1), M_2 is the mass of the mixture calculated according to the scheme (2).

The phase composition of the structural components was identified based on the data of X-ray phase and local microstructural analysis. X-ray phase analysis was performed on a DRON-3M diffractometer using Cu radiation with a monochromator in a secondary beam. X-Ray patterns were recorded in a step-by-step scanning mode in the range of angles $2\theta = 20\text{--}80^\circ$ with a shooting step of 0.02° and an exposure of 2 s. The study of the microstructure and elemental analysis of the samples was carried out on an ultra-high resolution ULTRA plus Zeiss field emission scanning electron microscope with an INCA 350 Oxford Instruments microanalysis system.

According to thermodynamic calculations (Fig. 2), with an increase in α , the combustion temperature of mixtures decreases from 2660 to 2470 K. The products of chemical transformation of the mixture are “metallic” Cr–B–Ti–Al and oxide $\text{Al}_2\text{O}_3\text{--B}_2\text{Ca}_3\text{O}_6$ melts. With increasing α , the content of the “metallic” phase a_1 of the combustion products increases, while that of the oxide a_2 phase decreases (Fig. 2). The calculation showed the presence of $\text{B}_2\text{Ca}_3\text{O}_6$ in the oxide phase, which indicates the participation of boron in the reduction of CaCrO_4 and TiO_2 .

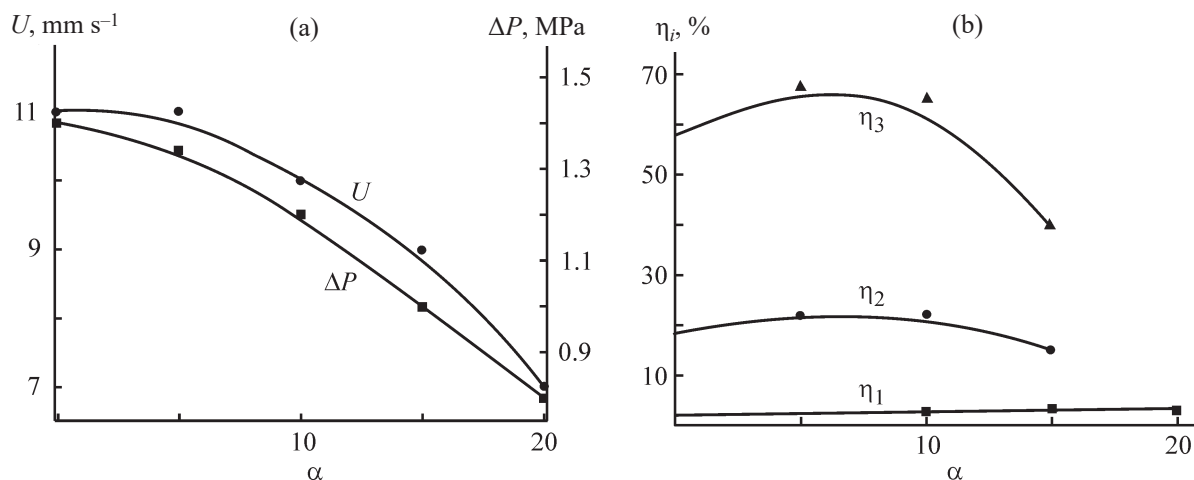


Fig. 3. The effect of α on (a) the burning rate U and the pressure increase ΔP in the reactor and (b) the yield of the target product η_2 , the spreading of the combustion products η_1 , and the completeness of the reaction η_3 .

RESULTS AND DISCUSSION

Visual observations showed that after ignition a combustion front forms, which moves through the mixture. The final products in the combustion wave are obtained in the liquid-phase state and, due to different specific gravities, are divided into two layers: the lower one is “metallic” Cr–Ti–B, and the upper one is oxide Al₂O₃–CaO. An increase in the amount of the mixture in the initial batch according to scheme (2) led to the fact that, due to the low calculated combustion temperature, the mixtures are capable of burning in the range of α 0–20% (Fig. 3). With an increase in α , the burning rate U decreases from 11 to 7 mm s⁻¹, and the pressure increase

ΔP in the reactor also decreases from 1.35 to 0.8 MPa. The yield of the target product (η_2) with increasing α passes through a maximum, and the phase separation limit occurs at $\alpha = 15\%$. The spreading of products (η_1) practically does not change and does not exceed 3%. The completeness of the reaction (η_3) also passes through a maximum at $\alpha = 5\%$ and then decreases to 40% at $\alpha = 15\%$.

To expand the phase separation limit, an experiment with a highly exothermic CaO₂ + Al additive was carried out. In the mixture calculated at $\alpha = 20\%$, the 20 wt % additive was introduced. As a result, phase separation was achieved, but the boride ingot in the form of droplets with a diameter of 1 to 5 mm was distributed in the oxide

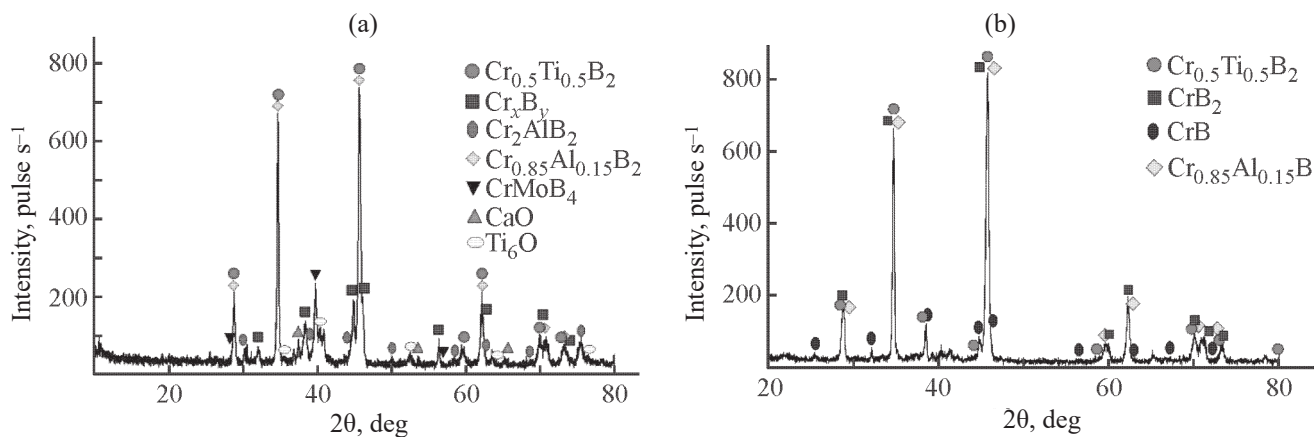


Fig. 4. X-ray diffraction patterns of samples obtained in the synthesis of thermite mixtures in the system CaCrO₄ + TiO₂ + Al + B at (a) $\alpha = 10\%$, (b) $\alpha = 20\%$.

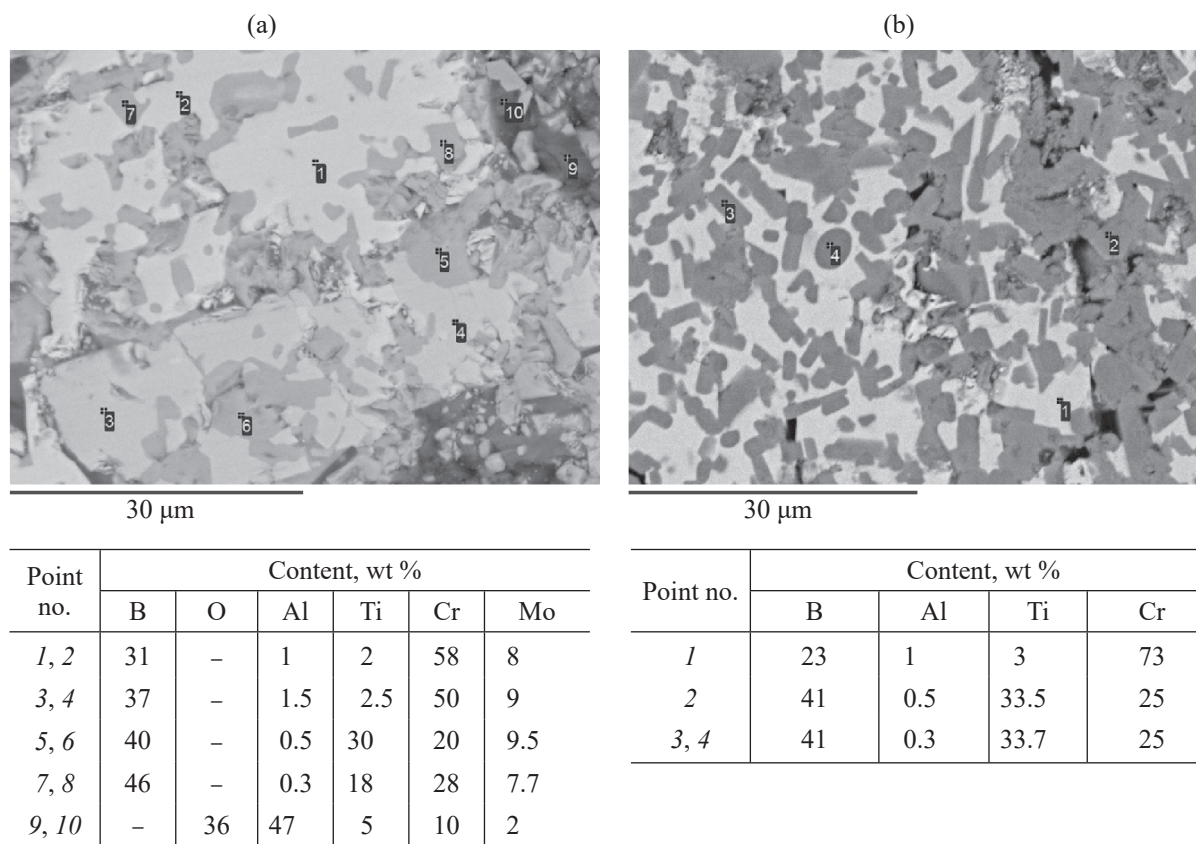


Fig. 5. Microstructures and elemental composition of structural components of samples obtained during the synthesis of thermite mixtures in the $\text{CaCrO}_4 + \text{TiO}_2 + \text{Al} + \text{B}$ system at (a) $\alpha = 10\%$, (b) $\alpha = 20\%$.

ingot and poorly separated from it.

X-ray analysis of the target products showed that at $\alpha = 10$ (Fig. 4a) the product consists of a large number of phases. The main phases are titanium-chromium boride $\text{Cr}_{0.5}\text{Ti}_{0.5}\text{B}_2$ and various chromium borides. Oxides of titanium and calcium, as well as phases Cr_2AlB_2 and $\text{Cr}_{0.85}\text{Al}_{0.15}\text{B}_2$ indicate incomplete chemical transformation. The CrMoB_4 phase was formed as a result of entering of initiation helix in the melt. At $\alpha = 20$ (Fig. 4b), the product consists of titanium-chromium boride, chromium borides, and the $\text{Cr}_{0.85}\text{Al}_{0.15}\text{B}_2$ phase. There are no oxide phases.

The results of electron microscopy are in good agreement with the results of X-ray phase analysis (Fig. 5). The tables below photographs of microstructures show the results of energy dispersive analysis of the structural components of the obtained product. On microsections of a metal product obtained from a mixture of $\text{CaCrO}_4 + \text{TiO}_2 + \text{Al} + \text{B}$ with $\alpha = 10\%$ (Fig. 5a), two main phases were revealed: the first phase (structural components 1–4) contains Cr, B, and Mo; the

second phase (structural components 5–8) contains Cr, Ti, B, and Mo. Structural components 9, 10 contain Cr, Al, O, and Ti. The microsection of the product obtained at $\alpha = 20\%$ (Fig. 5b) also shows that the product contains two phases: the first phase, the product base, contains Cr, B and a small amount of Al and Ti (structural component 1), the second phase contains Cr, Ti and B (structural components 2–4).

From the results of the thermodynamic calculation and experimental data, it follows that the change in the burning rate and the completeness of the metal phase in the ingot are in good agreement with the change in the calculated combustion temperature (Figs. 2, 3). Lowering the combustion temperature reduces the melt life time and results in diminishing the yield of the target product.

In the obtained materials, CrB_2 is the main phase, in which grains of titanium-chromium boride are uniformly distributed. At $\alpha = 10\%$ (Fig. 5a), Al_2O_3 oxide phase inclusions are present (structural components 9, 10). It can be seen on the microstructure of the sample at $\alpha = 20\%$ (Fig. 5b) that the grains of titanium-chromium boride are

more uniformly distributed over the sample and there are no inclusions of the oxide phase Al_2O_3 . This is explained by a higher combustion temperature due to the use (20%) of a highly exothermic CaO_2/Al additive. As a result, the life time of the melt and the completeness of the reaction of reduced titanium with boron increased, and the mutual solubility of chromium and titanium borides rose.

CONCLUSIONS

The foundations of a scientific approach for the synthesis of cast composite materials in the Cr–Ti–B system using calcium chromate as a chromium-containing agent have been developed by SHS metallurgy technique. Mixtures are capable of burning up to $\alpha = 20\%$, the phase separation limit occurs at $\alpha = 15\%$. With increasing α , the burning rate of the mixture decreases, and the yield of the metal (target) product passes through a maximum. The product of the autowave chemical transformation of the mixture is cast material, clearly divided into two layers: target and oxide. The introduction of a highly exothermic $CaO_2 + Al$ additive into the mixture made it possible to expand the phase separation limit to $\alpha = 20\%$. The structure and phase composition of the target products obtained at various contents of the starting components were studied. The resulting product is a composite material based on chromium diboride with uniformly distributed inclusions of titanium-chromium boride.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest requiring disclosure in this article.

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