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# Studies on the Macrokinetic Characteristics of Combustion Processes in Cr–B and Cr–Ti–B Reaction Mixtures after Preliminary Mechanical Activation

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## Abstract

Macrokinetic characteristics of the combustion process in Cr–B and Cr–Ti–B reaction mixtures after preliminary mechanical activation were investigated. It has been established that mechanical activation exerts a substantial effect on the composition and structure of the initial mixtures and therefore on temperature and rate of combustion of mechanically activated mixtures. It has been demonstrated that the interaction between the reagents at the combustion temperature occurs according to the solid-phase mechanism. The mechanisms of phase formation in the combustion wave have been studied with the help of a stopped-front method. With the increase in the concentration of oxygen in the mixture due to mechanical activation, the role of gas transport of boron to the surface of the metal increases thus the reaction diffusion becomes the limiting stage of the interaction between metal and boron. It has been established using X-ray structural analysis that the products of combustion of Cr–Ti–B mixture contain ternary compounds such as $Cr_4Ti_9B$ and $Ti_2CrB_2$ unknown earlier.

**Key words:** self-propagating high-temperature synthesis, mechanical activation, $CrB_2$, Ti–Cr–B

## INTRODUCTION

Transition metal borides are of especial interest due to a unique combination of mechanical, thermal, electrophysical and magnetic properties. They are used in chemical industry, in the manufacture of abrasives, protective coatings, wear resistant materials and for obtaining constructional ceramics [1].

In our work, ceramic materials based on chromium and titanium borides are made employing the method of self-propagating high-temperature synthesis (SPHTS) [1–9] from preliminary mechanically activated mixture. The use of mechanical activation (MA) allows one to carry out the SPHTS process in low-exothermic systems such as Mo–B, Cr–B [10–13]. The mechanical activation of the mixture results in a simultaneous increase in the absolute value of heat generation and rate of heat generation in the reaction of combustion, exerting a positive effect on the thermodynamics and kinetics of the process.

The purpose of the present work consists in obtaining new ceramic materials in Cr–B and Ti–Cr–B systems from preliminary activated mixture in the combustion mode, as well as in studying the structurization in the combustion wave of and the composition of compact synthesis products.

## MATERIALS AND METHODS

For the studies we have chosen a stoichiometric mixture of powders PH-1C chromium

TABLE 1

Sample composition for initial powders

| Samples | Content, mass % | | |
|---|---|---|---|
| | Cr | Ti | B |
| 1 | 70.6 | – | 29.4 |
| 2 | 30.0 | 60.2 | 9.8 |
| 3 | 40.0 | 51.6 | 8.4 |

powder and B-99A boron powder in the mass ratio Cr : B = 70.6 : 29.4 on the basis of the formation of compound $CrB_2$. The ratio of components Ti and B for Ti–B–Cr mixtures was constants amounting to 6.14. For the preparation of mixtures we used PTS titanium powder. The composition of samples under investigation is presented in Table 1.

The synthesis of compact samples was carried out to the technology of power SPHTS compacting. The mechanical activation of mixtures was performed within in AIR-0.015 planetary type mill at the following technological parameters: the operating drum volume being of 250 $cm^3$, centripetal acceleration at the axis of the drum amounting to 250 $m/s^2$, the ratio between the mass of balls and the mass of mixture for Cr–B mixture amounting to 20 : 1, for Ti–Cr–B mixture being equal to 10 : 1.

The preliminary pressing of initial briquettes from the mixture was carried out in cylindrical press moulds 78 mm in diameter. The pressure value for pressing was matched so that the relative density of the reaction briquettes amounted to 55–60 %. For obtaining compact products, the synthesis was carried out within a reaction press mould using DA-1532B hydraulic press with the maximal pressing force amounting to 1600 kN. Right after the completion of the process of combustion, hot synthesis products were loaded with a pressure of 6.86 MPa, optimizing in this case the pressing delay time of and the time of exposure under pressure.

The thermal effect of the reaction of boride formation was determined on a BKS-4 quick-response combustion calorimeter. The maximum error of the measurement amounted to 0.15 % within the range of measured heat values of $5 \cdot (10^2–10^4)$ J.

The influence of the initial warming temperature $T_0$ upon the temperature of combustion $T_c$ was studied employing a micro-thermocouple method with the use of tungsten-rhenium thermocouples with the diameter of wire amounting to 0.1 mm. The rate of combustion $U_c$ was determined according to video filming. In this case we used pressed briquettes with the cylindrical shape of 10 mm in diameter and relative density amounting to 58–60 %.

The content of oxygen in the initial and activated mixtures was measured with the help of a reductive melting technique in the flow of an inert gas (helium), from the amount of $CO_2$ formed employing the method of infrared absorption with the use of TC-600 oxygen and nitrogen analyzer (LECO Corp., USA).

In order to study the sequence of reactions within the wave of combustion we carried out the quenching of the combustion front with the use of a massive copper block. The reaction mixture of the compositions under investigation structures was pressed into a wedge-shaped cutout in the massive copper block which provided fast heat dissipation from a sample whereby the combustion reaction stopped.

The microstructure of samples was investigated using the method of scanning electron microscope employing a Jeol JSM-6480 LV electron microscope with the system of local XRD spectral microanalysis. The XRD phase analysis of synthesized products was performed employing DRON-3 X-ray diffractometer, nanometres carried out(spent) on installation, $CuK_\alpha$ radiation, the wavelength $\lambda = 15.4178$ nm, the registration range $2\theta = 10–120°$, with the increment of 0.1°, the exposition at the registration point being of 6 s.

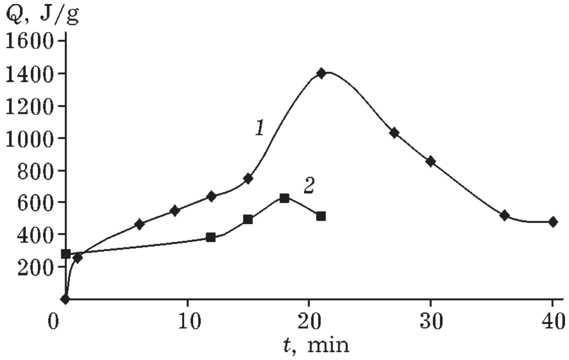

Fig. 1. Specific heat generation value (Q) depending on the duration of mechanical activation (t): *1* – Cr–29.4 % B, *2* – Ti–40 % Cr–8.4 % B.

## RESULTS AND DISCUSSION

### *Effect of mechanical activation on the structure of initial material and the parameters of combustion*

The experimental dependence of heat generation in the course of chemical reaction on the MA duration time is presented in Fig. 1. It is seen that the process of interaction is accompanied by a low heat generation. The SPHTS reaction was not possible to perform in non-activated Cr–B mixture under the conditions of the calorimeter at $T_0 = 311$ K. Owing to incomplete transformation, the measured quantity of heat generated under combustion appeared to be less than the expected value. According to XRD data, the products of Cr–B mixture combustion contain intermediate reaction products such as lower borides CrB and $Cr_3B_4$ with a lower value of the heat of formation. A similar picture is observed for three-component Ti–Cr–B mixtures. Besides lower chromium borides there are titanium boride TiB and unreacted titanium and chromium.

Thus, the absolute values of the reaction thermal effects appeared to be lower. Nevertheless, it is possible to trace changing in thermal effect depending on the duration of MA. So, with the increase in MA duration time, the amount of generated heat grows. To all appearance, it could be connected with the growth of the conversion level in the combustion reaction owing to the accumulation of macro- and microdefects within the initial powders, which results in the growth of the internal energy of the system, as well as the reduction of the heterogeneity scale. The increase in the thermal effect for Cr–29.4 % B mixture occurs up to 21 min of MA duration, whereas for Ti–40 % Cr–8.4 % B mixture this phenomenon occurs up to 18 min of MA. The further activation results in the reduction of the heat generation, which could be connected with the beginning of mechanochemical reactions of chromium boride formation in the process of MA. Thus, in order to obtain the greatest heat generation value, the optimum MA duration time should amount to 21 min for Cr–29.4 % B mixture, amounting to 18 min for Ti–40% Cr–8.4 % B mixture.

With machining, the energy density of particles is summarized from the energy of subgrain boundaries formed from mosaic blocks, new surfaces formed as the result of the destruction of particles, and the energy of elastic deformation. In turn, the energy of elastic deformation in a crystal is determined by the energy of dislocations and the energy of vacancies. Each dislocation, having a certain stock of energy and playing the role its accumulator in a crystal, represents an ultimate sublocal distortion of the crystal lattice. The introduction of dislocations into a crystal results in the increase of its energy, whereas with the increase in number of homogeneously distributed dislocations, the average value of the energy absorbed within the operation volume is observed to increase [11–14].

The optimum condition of the structure of reagents before the beginning of SPHTS corresponds to the certain dislocation structure of metal and the certain reaction surface of mixture. In order to estimate MA influence upon the structural state of initial reagents we have performed the analysis of processing time influence upon the structure of chromium

TABLE 2

Coherent scattering areas (CSA) size and the level of Cr lattice microdeformation for different duration of mechanical activation (MA)

| MA duration, min | CSA size, nm | | Microdeformation level, % | |
|---|---|---|---|---|
| | Cr–29.4 % B | Ti–40 % Cr–8.4 % B | Cr–29.4 % B | Ti–40 % Cr–8.4 % B |
| 1 | 130.9 | – | 0.14 | – |
| 12 | 73.1 | 41.7 | 0.18 | 0.150 |
| 15 | 51.6 | 40.8 | 0.19 | 0.211 |
| 18 | 25.6 | 31.5 | 0.23 | 0.267 |
| 21 | 16.0±2 | 25.9±3 | 0.27±0.01 | 0.343±0.05 |

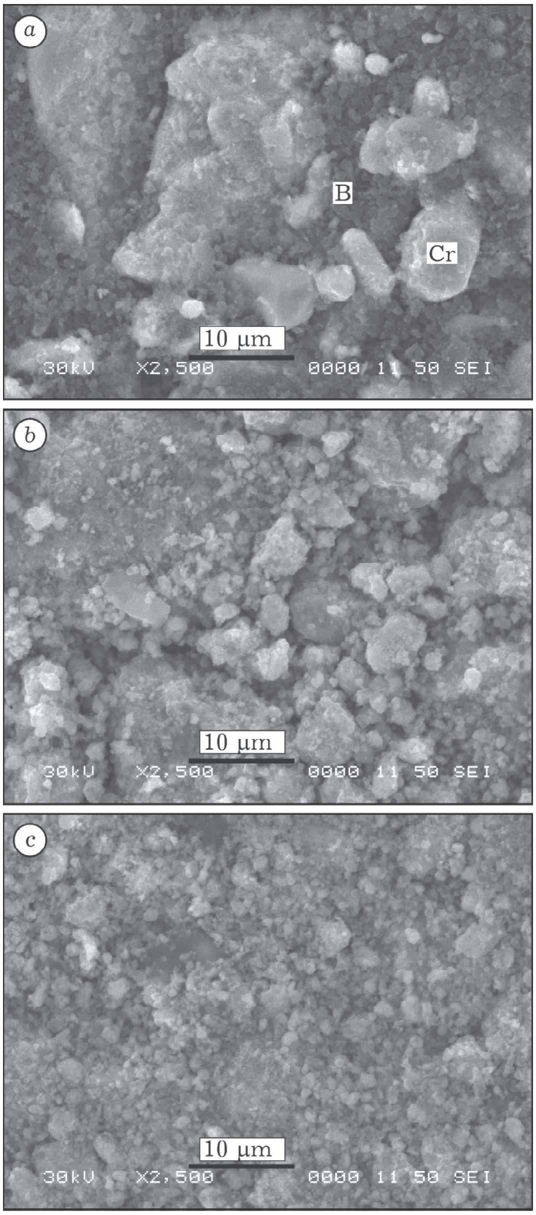

Fig. 2. Morphology of Cr–29.4 % B mixture after mechanical activation during 1 (*a*), 21 (*b*) and 40 min (*c*).

powder. From the broadening of XRD lines we calculated the size of coherent scattering areas (CSA). The physical broadening was determined using a technique presented in [17, 18]. The results of the investigation are presented in Table 2.

It is seen that the increase in the MA time results in a decrease in the CSA size, and in an increase in the size of microdeformation (MCD), which confirms the assumption that the energy stored increases. It should be noted that size of CSA in Cr–29.4 % B mixture is an order of magnitude decreased, whereas the MCD size is approximately twice decreased. From the data presented in Fig. 2 one can see that the mixture originally consists of chromium particles of 5–40 μm in size and boron particles about 0.1 μm in size. With the increase in the duration of MA an intense grinding of chromium occurs. The maximal size of particles does not exceed 5 μm. Owing to the uniform stirring and boron redistribution over the surface, the size scatter of chromium particles decreases to a considerable extent. This results in the growth of the reaction surface and the reduction of kinetic hindering in the SPHTS reaction process.

In the course of MA the specific surface of the mixture increases due to grinding the particles of powders, owing to the formation of cracks, as well as the accumulation of microstructural and surface defects. For the MA procedure with the duration longer than 21 min for Cr–B and 18 min for Ti–Cr–B, borides appear in the mixture, whose structure is not amenable to any quantitative interpretation *via* the method of local micro X-ray spectral analysis due to a small size of particles and low atomic number of boron.

The changes occurring in the structure of a mixture after MA procedure exert a considerable effect on the character of combustion wave propagation, its rate $U_c$ and temperature $T_c$. Figure 3 demonstrates a video image of the combustion process for activated Cr + 2B mixture. The wave of combustion is seen to propagate top-down along the axis of the sample. In the case under consideration the centre of combustion (picture *2*), in a similar manner to a “spin”, moves in the plane perpendicular with respect to the direction of the combustion wave propagation (picture *3*). After the centre passes all the plane of the sample (picture *4*) the combustion goes to the following layer (picture *5*). The phenomenon presented in the pictures is periodically repeated in regular time intervals every 0.16 s. This fact indicates that the combustion of an activated sample represents a non-steady-state process being near the stability limit.

The investigation of the macrostructure of burnt samples has demonstrated the presence of stratification in the products obtained from Cr–B mixture activated during 21 min. A periodical character of transverse cracks repeats the movement of the combustion front line.

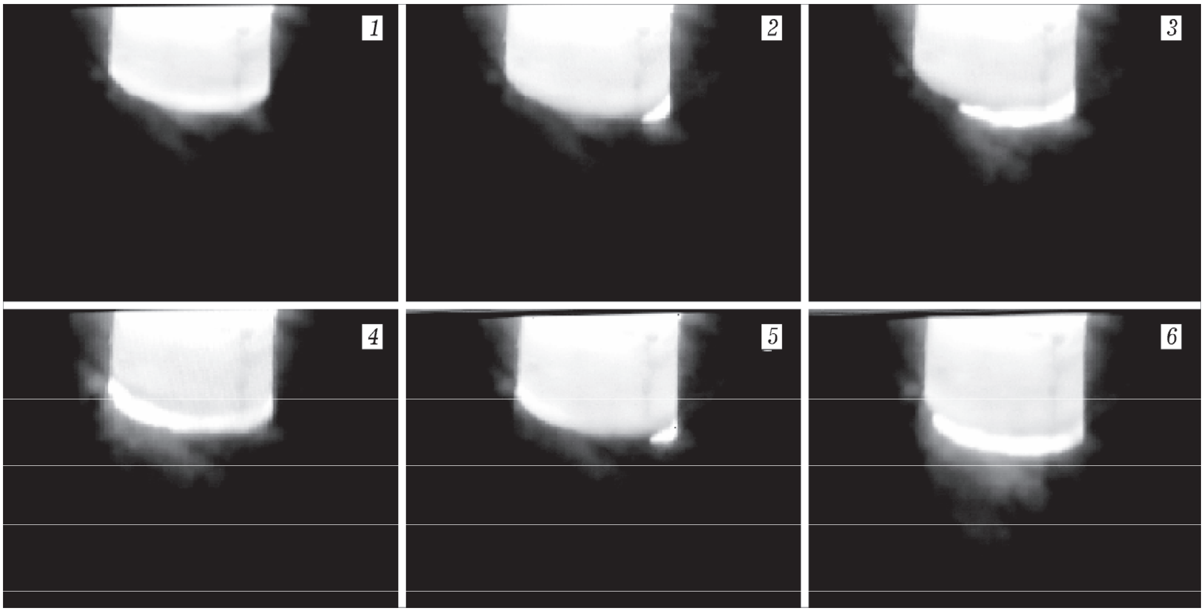

Fig. 3. Frame-by-frame video filming of the wave of combustion for Cr + 2B mixture after mechanical activation within 21 min. $T_0$ = 293 K, picture frequency being equal to 25 frames/s. Design. see text.

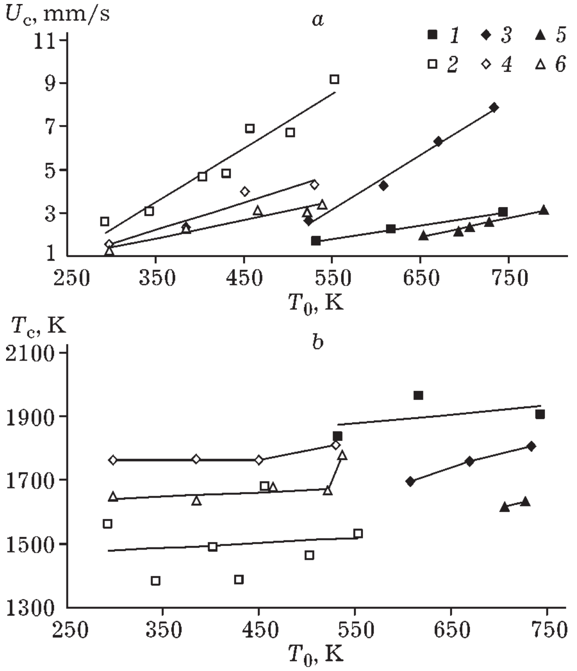

Fig. 4. Rate of combustion $U_c$ (*a*) and the temperatures of combustion $T_c$ (*b*) depending on the initial temperature ($T_0$) for mixtures such as Cr–29.4 % B (*1*, *2*), Ti–30 % Cr–B (*3*, *4*) and Ti–40 % Cr–B (*5*, *6*): *1*, *2* – mixtures mechanically activated during 1 and 21 min, respectively; *3*, *5* – non-activated mixtures; *4*, *6* – activated mixtures.

On the contrary, the structure of a burnt sample made of low-activated Cr–B mixture is homogeneous and does not contain any seen transverse cracks those determine the character of combustion front propagation.

The results of qualitative and quantitative XRD analysis of the structure of the samples synthesized according to the technology of SPHTS compacting have demonstrated, that in the case of highly activated Cr–29.4 % B mixture of combustion the fraction of higher chromium borides in the products increases with the increase in $T_0$, whereas the amount of boride phases decreases. It is connected with the fact that in the transition such as $CrB \rightarrow Cr_3B_4 \rightarrow CrB_2$ according to the mechanism of the solid-phase reaction diffusion, the stage $CrB \rightarrow Cr_3B_4$ runs almost up to the completion because of a great value energy saved. However, the subsequent stage ($Cr_3B_4 \rightarrow CrB_2$) has not time to be completed. The product of SPHTS compacting is two-phase and consists of $CrB_2$ and $Cr_3B_4$ with a small amount of fine pores.

Data concerning the analysis of the phase structure of samples after SPHTS compacting in the systems such as Ti–30 % Cr–9.8 % B and Ti–40 % Cr–8.4 % B indicate that the basis of ceramic materials (~75 %) is composed of phases unknown earlier with proposed formulas $Cr_4Ti_9B$ and $Ti_2CrB_2$, the fraction of TiB amounting to about 15 %, whereas the fraction of $TiCr_2$ is approximately equal to 10 %.

Figure 4, *a* demonstrates the results of measuring $U_c$ as a function of the initial temperature $T_0$. One succeeds in realizing the SPHTS process in mechanically activated mixtures already at $T_0$ = 300 K, whereas for a low-activated ($t_{MA}$ = 1 min) mixture Cr–29.4 % B the process could be realized only at $T_0$ = 525 K, and for non-activated Ti–30 % Cr–9.8 % B and Ti–40 % Cr–8.4 % B mixtures the corresponding temperature values are equal to 523 and 653 K, respectively. For all the compositions one can observe linear dependence of the combustion rate on the initial temperature. With the MA treatment of Cr–B mixture the formation of chromium boride occurs with a much higher rate depending on the initial temperature in a greater extent as compared to Ti–Cr–B system. It is interesting to note that for all the compositions after MA procedure the centres of combustion at $T_0$ > 530–540 K are formed all over the volume of a sample (the combustion proceeds in a thermal explosion mode), whereas their movement is of heterogeneous character. The rate of combustion in this case could not be determined.

From Fig. 4, *a* one can see that for activated Cr–B and Ti–Cr–B mixtures the rate of combustion at the same initial temperature is higher than for non-activated ones. So, the rate of combustion for Cr–29.8 % B mixture at $T_0$ = 525 K amounts to 1.8 mm/s in the case mixture activated during 1 min, and 8.7 mm/s for the mixture with $t_{MA}$ = 21 min. According to the data calorimetric analysis, the quantity of heat generated in the course combustion at $T_0$ = 311 K for these samples amounts to 0.3 and 1.4 kJ/g, respectively. Thus, the MA procedure exerts a considerable effect on the process of combustion. This effect is in a good agreement with the conclusions made by authors of [12–17] concerning the positive influence of MA upon the kinetics and mechanism of the combustion of various SPHTS systems.

The distinctive feature of Cr–B and Ti–Cr–B systems under investigation in contrast to others (studied earlier) systems consists in the fact that within a certain range of initial warming temperature values, the value of $T_c$ depends slightly on $T_0$. This phenomenon is exhibited both for a high-activated and for low-activated Cr–B mixture (see Fig. 4, *b*). In the case of Ti–Cr–B system this effect is observed only for activated mixtures.

It is experimentally established, that for a low-activated Cr–B mixture $T_c$= 1800–1900 K, which is close to the value of adiabatic temperature (1900–2200 K), calculated according to ISMAN-THERMO software package [9]. For a highly activated Cr–B mixture ($t_{MA}$ = 21 min) despite of a considerable growth of the combustion rate, the value of $T_c$ is lower in a considerable extent amounting to 1500 K.

It should be noted that the dependences for activated and non-activated Ti–Cr–B mixtures presented in Fig. 4 exhibit qualitatively different features. For mechanically activated mixtures within the range of temperature values from a room temperature up to 450 K, the increase of the initial temperature almost either does not affect the combustion temperature (for the mixture 30 % Cr–9.8 % B) or influences insignificantly (for Ti–40 % Cr–8.4 % B). Such a character of curves one usually connects with the processes those proceed with the absorption of heat. As the values of the initial temperature approached to 530–540 K the rate of combustion for activated mixtures exhibits an abrupt increase, which results in scattering of the material analyzed owing to the evolution of a significant amount of gases adsorbed under MA and the loss of the contact between a sample and a thermocouple. In this connection, it was not possible to measure the temperature of combustion at $T_0$ > 530–540 K for Ti–Cr–B activated. For non-activated Ti–Cr–B mixtures, a linear dependence between the temperature of combustion and the temperature of mixture warming is observed.

### *Studying the structurization mechanism for SPHTS products*

In order to reveal the mechanism of combustion and structurization of the products in Ti–Cr–B system we performed quenching the samples in a copper wedge. Figure 5 demonstrates the microstructure of the quenched combustion front. Near the line 1–1 there is a quenched zone of combustion, above this line there are end products of combustion formed

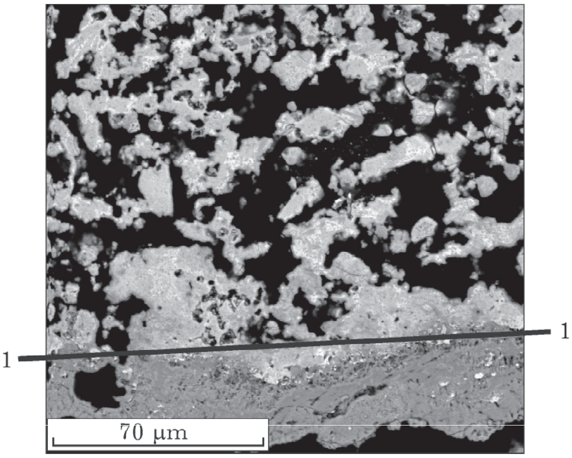

Fig. 5. Quenched combustion front for a sample of mechanically activated Ti–30 % Cr–B mixture.

as a result of completing the reaction, and below there are the warming zone and the initial reaction mixture located.

In the detailed analysis of phase composition within the zone of combustion and behind the front of combustion in the region of products formed, the following facts have been established. In the zone of combustion one can distinguish areas with different colour, which is caused by a different chemical composition. Light areas (Fig. 6, *a*, point 3a) are enriched with chromium, grey areas (points 2a, 4a) are enriched with titanium. At the separate sites of dark colour (point 1a) there are unreacted initial components containing oxygen. Behind the front of combustion, one can also distinguish the areas different both in colour, and in shape. In a similar manner to the above-stated, light areas (point 3a) are enriched with chromium, whereas light grey and dark grey areas are enriched with titanium. Morphological features of these areas such as needle-like or round shape allow us to make an assumption concerning their phase structure. To all appearance, the areas with a characteristic needle-like shape are corresponding to titanium and chromium borides, whereas round irregular-shaped areas are corresponding to initial components or solid solution on the base of metals.

In the mixtures with chromium concentration amounting to 30 and 40 %, immediately behind the front of combustion at the boundary with the area of the products formed there are light sites enriched with chromium observed.

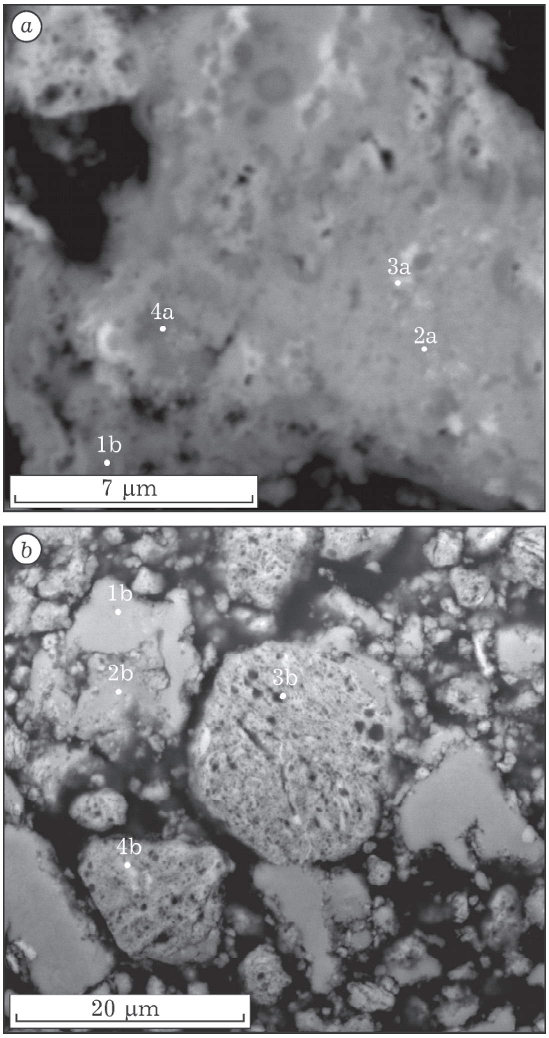

Fig. 6. Stopped combustion front (the area lower than line 1–1) for Ti–Cr–B mixtures: *a*, *b* – magn. 5000× and 1500×, respectively. Elemental composition in points:

| Points | Content, mass % | | | |
|---|---|---|---|---|
| | B | O | Ti | Cr |
| 1a | 16.16 | 20.58 | 57.58 | 5.68 |
| 2a | 15.42 | abs. | 72.62 | 11.45 |
| 3a | abs. | 22.02 | 65.20 | 12.42 |
| 4a | 11.57 | abs. | 82.72 | 5.55 |
| 1b | abs. | abs. | 99.50 | 0.50 |
| 2b | 17.89 | abs. | 80.64 | 1.37 |
| 3b | 56.00 | 3.66 | 10.12 | 29.26 |
| 4b | 48.15 | 3.05 | 15.15 | 21.63 |

The interaction between the reagents begins from the surface of particles (see Fig. 6, *b*). So, for example, point 1b corresponds to titanium, whereas point 2b corresponds to completed interaction between titanium, chromium and boron. Light needle-like formations correspond to titanium or chromium borides. However, one should indicate the complexity of an exact determination of the phase formation sequence in connection with their variety and similar elemental composition of intermediate phases.

The analysis for oxygen of Cr–B mixture has demonstrated that the initial chromium powder contains 0.4 % of oxygen, whereas in the initial boron there is the concentration of oxygen amounting to 3.7 %. From the recalculation for a preset composition of the mixture, it is seen that chromium contributes 0.28 %, and boron contributes 1.09 % of oxygen. The total content of oxygen in the mixture amounts to 1.37 %. For the mixture after the MA duration amounting to 1 min the total content of oxygen increases almost twice and reaches 2.6 %, whereas after 21 min of MA procedure the oxygen content is equal to 3.3 %. This excess oxygen makes the concentration of boron and chromium oxides to increase. To consider the total oxygen being factorized into the reagents of the mixture after 21 min, the content of oxygen in chromium should amount to 0.66 %, being 2.64 % in boron, which corresponds to 3.83 % of $B_2O_3$ in the mixture. Thus, the basic carrier of oxygen in the mixture is the boron: 80 % of total oxygen falls on boron and only 20 % of that falls on chromium. Such a distribution indicates that the contribution of chromium oxide in the mechanism and kinetics of the combustion process takes place, but it is not rate-determining. At the same time there is no oxide phases among the products of combustion observed.

By the analogy with the Mo–B system [10], within the zone of warming in the mixtures with the concentration chromium 30 and 40 % and in Cr–29.4 % B mixture there are following reactions to proceed:

$B_2O_3(s) + B \rightarrow 3/2B_2O_2(g) - Q$

$Me + 2B \rightarrow MeB_2 + Q$

The solid-phase interaction of chromium with boron within the zone of warming is improbable because of a rather low diffusion mobility of atoms at the given temperature values. At the same time, on the surface of reagents at the temperature values ranging within 1100–1250 K there proceeds a reversible gas-transport reaction to result in forming of volatile boron suboxide:

$B_2O_3 + B \rightarrow 3/2B_2O_2$ (g)

This reaction in the wave of combustion is preceded by melting boron oxide $B_2O_3$ at 723 K [9]. Gaseous suboxide is chemisorbed onto the surface of chromium and titanium particles with the formation of the most thermodynamically favourable boride phases according to the following reactions

$3B_2O_2(g) + 2Ti \rightarrow 2B_2O_3(l) + TiB_2 + Ti + Q$

$\rightarrow 2B_2O_3(l) + TiB + Ti$

$B_2O_2(g) + Cr \rightarrow B_2O_3(l) + Cr_xB_y + Cr + Q$

Thus, the saturation of the particles of a metal-reagent by boron occurs in the direction from the surface to the centre. In the after-burning zone of Ti–Cr–B mixtures, the products formed interact among themselves with the formation of ternary boride compounds, as well as solid solutions and compounds in Ti–Cr system:

$$TiB + Cr_xB_y \begin{array}{l} \rightarrow CrTi_2B_2 \\ \rightarrow Cr_4Ti_9B \end{array}$$

Concurrently to these reactions, within the warming zone ahead of the front of combustion there is endothermic reaction

$B_2O_3(l) + B \rightarrow 3/2B_2O_2(g) - Q$

occurring.

We have performed thermogravimetric analysis for boron and chromium powders within the temperature range of 300–1273 K, as well as for mixtures activated during 1 and 21 min. It has been established that chromium within the specified temperature range does not undergo any significant phase transformations accompanied with thermal effects and mass change. In the powder of boron there is an endothermic transformation proceeding with the energy of 2.0 kJ/g, within the temperature range of 1020–1250 K. Mixtures after MA also exhibit endothermic peaks within the temperature range of 1020–1230 K ($t_{MA} = 1$ min) with the thermal absorption of 0.18 kJ/g. For the mixtures exposed to MA during 21 min, the endothermic transformation is shifted towards lower temperature values (900–1020 K). The heat absorption in this case has amounted to 0.9 kJ/g.

## CONCLUSION

1. It is established that the MA exerts a considerable influence upon the composition and

structure of initial mixtures and, as a consequence, upon the temperature and combustion rate of mechanically activated mixtures in the process of SPHTS. The investigation of macrokinetic characteristics for combustion processes in preliminary mechanically activated Cr−B and Cr−Ti−B reaction mixtures has demonstrated that the interaction between reagents occurs according a solid-phase mechanism at the combustion temperature. With the increase in the content of oxygen in the mixture after the MA, the role of the gas-transport carrying of boron towards the surface of metal increases, and the reaction diffusion becomes a rate-determining stage of the interaction between the metal and boron.

2. With the help of a stopped-front method, we have established the mechanisms of phase formation in the combustion wave.

3. According to the results of the investigations, the samples of 125 mm in diameter with the following structure have been synthesized: Cr−29.4 % B, Ti−30 % Cr−9.8% B, Ti−40 % Cr−8.4 % B. The formation of ternary compounds such as $Cr_4Ti_9B$ and $Ti_2CrB_2$ unknown earlier has been established.

## REFERENCES

1 G. V. Sasonov, L. Ya. Markovskiy, A. F. Zhigach, M. G. Valyashko, Bor, Yego Soyedineniya i Splavy, Izd-vo AN USSR, Kiev, 1960.
2 K. Akasaka, H. Ohrui, H. Merugo, Sh. Okada, K. Kudou, K. Iizumi, K. Kudaka, I. Higashi, T. Lundstrom, *J. Crystal Growth.*, 166 (1996) 429.
3 E. L. Muetterties (Ed.), The Chemistry of Boron and Its Compounds, Wiley, New York, 1967.
4 G. V. Sasonov, T. I. Serebryakova, V. A. Neronov, Boridy, Atomizdat, Moscow, 1975.
5 Yu. B. Kuzma, Kristallokhimiya Boridov, Vishcha Shkola, L'vov, 1983.
6 T. Ya. Kosolapova (Ed.), Svoystva, Polucheniye i Primeneniye Tugoplavkikh Soyedineniy (Handbook), Metallurgiya, Moscow, 1986.
7 T. I. Serebryakova, V. A. Neronov, P. D. Peshev, Vysokotemperaturnye Boridy, Metallurgiya, Moscow, 1991.
8 A. L. Ivanovskiy, G. P. Shveykin, Kvantovaya Khimiya v Materialovedenii. Bor, Yego Splavy i Soyedineniya, Izd-vo UrO RAN, Yekaterinburg, 1998.
9 E. A. Levashov, A. S. Rogachev, V. I. Yukhvid, I. P. Borovinskaya, Fiziko-Khimicheskiye i Tekhnologicheskiye Osnovy Samorasprostranyayushchegosya Vysokotemperaturnogo Sinteza, Binom, Moscow, 1999.
10 E. N. Eremina, V. V. Kurbatkina, E. A. Levashov, A. S. Rogachev, N. A. Kochetov, *Chem. Sust. Dev.*, 13 (2005) 197.
11 V. V. Boldyrev, E. V. Boldyreva, Fundamentalnye Osnovy Mekhanicheskoy Aktivatsii, Mekhanosinteza i Mekhanokhimicheskikh Tekhnologiy, in E. G. Avvakumov (Ed.), Izd-vo SO RAN, Novosibirsk, 2009.
12 N. Z. Lyakhov, T. L. Talako, T. F. Grigorieva, Vliyaniye Mekhanoaktivatsii na Protsessy Fazo- i Strukturo-obrazovaniya pri Samorasprostranyayushchemsya Vysokotemperaturnom Sinteze, Parallel, Novosibirsk, 2008.
13 T. F. Grigorieva, A. P. Barinova, N. Z. Lyakhov, Mekhanokhimicheskiy Sintez v Metallicheskikh Sistemakh, in E. G. Avvakumov (Ed.), Parallel, Novosibirsk, 2008.
14 I. I. Novikov, K. M. Rozin, Kristallografiya i Defekty Kristallicheskoy Reshetki, Metallurgiya, Moscow, 1990.
15 V. V. Boldyrev, A. K. Tkacova, *J. Mat. Synth. Process.*, 8, 3−4 (2000) 121.
16 V. V. Kurbatkina, K. V. Kolesnichenko, E. A. Levashov, I. G. Rybin, *Izv. Vuzov. Tsv. Metallurgiya*, 4 (2002) 51.
17 E. V. Shelekhov, O. N. Pripisnov, S. I. Rupasov, *Izv. Vuzov. Tsv. Metallurgiya*, 1 (2001) 29.
18 S. S. Gorelik, L. N. Rastorguev, Yu. A. Skakov, Rentgenograficheskiy i Elektronno-Opticheskiy Analiz, MISiS, Moscow, 1999.