

## Features of Structural and Phase Transformations in Mo–Si–B and Cr–Al–Si–B Systems During Self-Propagating High-Temperature Synthesis

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### Abstract

This study is dedicated to investigation of the combustion mechanisms during the SHS of ceramic materials in multicomponent Mo–Si–B and Cr–Al–Si–B systems. It is concluded that the following processes are defined the SHS for Si-rich Mo–Si–B compositions: Si melting, its spreading over the surfaces of the solid Mo and B particles, followed by B dissolution in the melt, and formation of intermediate Mo<sub>3</sub>Si-phase film. The subsequent diffusion of Si into Mo results in the formation of MoSi<sub>2</sub> grains and MoB phase forms due to the diffusion of Mo into B-rich melt. The formation of MoB phase for B-rich compositions may occur via gas-phase mass transfer of MoO<sub>3</sub> gaseous species to B particles and B<sub>2</sub>O<sub>2</sub> to Mo particles. In Cr–Al–Si–B system firstly, the Al–Si eutectic mixture undergoes contact melting followed by formation of the reactionary surface as the eutectic melt spreads over the Cr and B particles surface. An increase in Al content increases the proportion of the Al–Si eutectic melt. The dissolution of Cr particles in this melt becomes the rate-limiting stage of the combustion process. The melt is saturated with these elements followed by crystallization of CrB and Cr(Si,Al)<sub>2</sub> grains. In the Cr- and B-rich areas and low melt concentration, the formation of CrB may occur via gas-phase mass transfer of B<sub>2</sub>O<sub>2</sub> gaseous species to Cr particles. Consecutive formation of chromium and molybdenum borides and silicides is established by means of dynamic X-ray diffraction analysis. Compact ceramic samples were produced using forced SHS pressing technique. Their structural investigations were conducted by XRD and SEM.

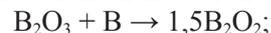
### Introduction

Borides and silicides of molybdenum and chromium are promising compounds because of their unique combination of mechanical, thermal and physical properties. The high melting point, heat resistance, low oxidation resistance at temperatures above 1200 °C, relatively high thermal and electrical conductivity, make these compounds attractive for the development of advanced materials. These materials also can be used as targets (cathodes) in the ion-plasma technologies for deposition of functional (heat-resistant and wear-resistant) nanostructured coatings, for example by magnetron sputtering (PVD).

During combustion of two-component Mo–B and Cr–B mixtures in [1, 2] was noted the leading role of the gas-transport reactions which determine the supply of reagent to the reaction surface. The au-

thors have shown that the gas-transport agent B<sub>2</sub>O<sub>2</sub>, providing interaction of metal with boron in powder mixture. The following reactions proceed on the reagents surface:

- a direct reaction on the boron surface



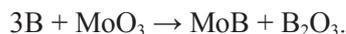
- a reverse reaction with borides formation on the metal particles surface



Gas-transport reactions have also been observed during the combustion of Ta–C mixtures, where carbon is transferred to the surface of tantalum particles via circulation of CO and CO<sub>2</sub> by the Buduar–Bell cycle [3]. In the case of combustion in Mo–B mixtures the gas-transport mechanism is also working by gas-phase transfer of the volatile suboxide MoO<sub>3</sub> to the spatially separated (or pointwise contacting) boron particles, where chemisorption occurs, giving

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rise to molybdenum boride by the following reaction [4, 5]:



In addition to reactions with the participation of the gas phase in the combustion wave of Mo–B and Cr–B systems also solid-phase interaction  $\text{Me} + \text{B} \rightarrow \text{MeB}$  may occur on the contacts between Me and B particles by the reaction diffusion of boron into metal.

For mixtures Mo–Si and Cr–Si the formation of intermediate silicides starts after melting and spreading of Si melt over the surface of metal particles, i.e. via the reaction diffusion mechanism [6, 7]. Depending on the combustion conditions and the size of refractory reagent particles the product can be formed as a layer on the surface of refractory particles if they are large enough or can be crystallized from the melt if refractory particles are very small because of their dissolution in it.

The purpose of this work was the investigation of the combustion mechanisms and stages of structural and phase transformations in the combustion wave of the SHS systems Mo–Si–B, Cr–Al–Si–B and obtaining of compact ceramic targets (cathodes).

## Experimental

Powders of chromium (PKh-1S grade), molybdenum (PM-99.95), aluminum (ASD-1 grade), black boron (B-99A grade), and silicon produced by grinding of KEF-4.5 monocrystals with the orientation (100) were used as initial reagents. Compositions of the reactionary mixtures with different ratio between initial elements were calculated under an assumption of complete chemical transformation with the formation of chromium and molybdenum borides, silicides and aluminides. These compositions provide the required elemental composition of the synthesis products for their further sputtering by PVD.

Table 1 lists the compositions of the green mixtures studied in the Mo–Si–B system, where composition Mo<sub>3</sub> corresponds to Mo<sub>5</sub>SiB<sub>2</sub> (T<sub>2</sub> phase). Table 2 lists the compositions of the green mixtures studied in the Cr–Al–Si–B system.

**Table 1**

Compositions of the green mixtures in the Mo–Si–B system

Composition	Content of the reagents, wt%		
	Mo	Si	B
Mo <sub>1</sub>	90.49	4.41	5.10
Mo <sub>2</sub>	74.12	21.70	4.18
Mo <sub>3</sub>	90.61	5.31	4.08

**Table 2**

Compositions of the green mixtures in the Cr–Al–Si–B system

Composition	Content of the reagents, wt%			
	Cr	Al	Si	B
Cr <sub>1</sub>	69.4	8.1	12.0	10.5
Cr <sub>2</sub>	65.8	16.2	12.0	6.0
Cr <sub>3</sub>	63.4	21.6	12.0	3.0

To study the dynamics of structural transformations in the combustion wave, we used method of quenching the combustion front in a copper wedge (the vertex angle of 5°), followed by scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) of the characteristic areas of the stopped combustion front (SCF). Hitachi S-3400N scanning electron microscope equipped with a NORAN energy-dispersive X-ray spectrometer was used. This microscope was also used to analyze the microstructure of the compact samples, obtained by forced SHS-pressing.

The stages of the phase transformations in the combustion wave were studied by dynamic X-ray analysis (Time resolved X-ray diffraction – TRXRD). One-coordinate position-sensitive detector was used for frame-by-frame recording of the X-ray diffraction patterns. The XRD patterns were recorded in the 2θ range of 25–60°, since the initial reagents, expected intermediate, and final products have strong diffraction maxima in this range.

The optimization of technological parameters of forced SHS pressing [8] was carried out for obtaining of high quality composite materials with a given level of residual porosity. As a result the optimal values of pressing delay time after the end of combustion process (required for completion of the degassing process) and holding time of hot synthesis products under pressure were established. The main criteria of optimization were minimal residual porosity and quality of compact synthesis products, notably the absence of cracks and delaminations. Complex investigations of the phase composition, structure and properties of compact synthesis products were carried out.

## Results and Discussion

### *Investigation of Structural and Phase Transformations in the Combustion Wave of SHS Systems*

The quenching method of the combustion front in a copper wedge was carried out for investigation of combustion mechanisms and structure formation. For Mo–Si–B system (comp. Mo<sub>2</sub>) a detailed analy-

sis of the composition of the different phases formed in the combustion zone, after-combustion zone and in the final products area, it was found that in the combustion front (Fig. 1a) the silicon particles are melting and this melt spreading over the surface of molybdenum particles with simultaneous chemical interaction, yielding the intermediate product in the form of an underlayer close to composition of the silicide  $\text{Mo}_3\text{Si}$ . Grains of disilicide  $\text{MoSi}_2$  formed in the outer layer due to mutual reaction diffusion of molybdenum and silicon. Further the molybdenum

boride  $\text{MoB}$  grains formed mostly in the after-combustion zone (Fig. 1b). The boride phase emerges after the formation of  $\text{MoSi}_2$ . This sequence of structure and phase conversions confirms that interaction between molybdenum and boron occurs in the silicon melt followed by releasing of molybdenum boride crystallites from the melt. The two-phase microstructure of the final synthesis products is shown in Fig. 1c. The products consist of light-coloured grains and interlayers of boride  $\text{MoB}$  1–5  $\mu\text{m}$  in size in a light grey molybdenum disilicide  $\text{MoSi}_2$  matrix.

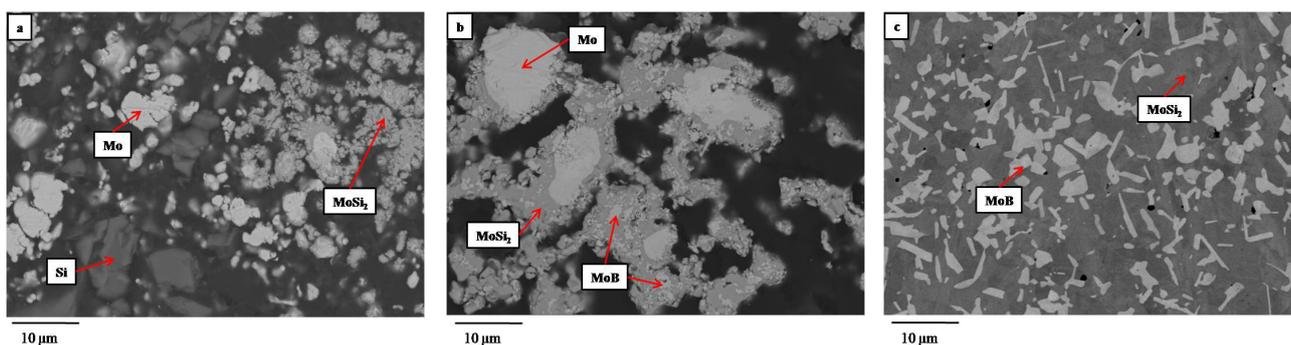


Fig. 1. Microstructures of SCF of the Mo–Si–B mixture with composition  $\text{Mo}_2$  recorded in different areas of the quenched sample: combustion front (a); after-combustion zone (b); final product (c).

Method of dynamic TRXRD analysis (Fig. 2) also confirm the fact, that in the Mo–Si–B system (comp.  $\text{Mo}_2$ ) the molybdenum disilicide  $\text{MoSi}_2$  is the first phase to be formed, and only 1,25 s later the molybdenum boride phase  $\text{MoB}$  emerges.

Thus, the stages of chemical transformations in the reactionary mixtures in Mo–Si–B system determining the combustion mechanism were ascertained using two independent methods. For the other mixture compositions (Table 1) with low silicon content, and therefore with less melt amount (comp.  $\text{Mo}_1$ ,  $\text{Mo}_3$ ), a solid-state interaction of Mo with B becomes a defining. The reactions with the participation of solid boron and molybdenum particles with volatile suboxides  $\text{MoO}_3$  and  $\text{B}_2\text{O}_2$ , respectively (gas-transport mechanism) also can occur.

The study of the SCF sample in Cr–Al–Si–B system (comp.  $\text{Cr}_1$ ) allowed to establish the following stages of chemical transformations and structure formation. Initially, contact melting of the Al–Si eutectic occurs in preheating zone (Fig. 3a) with the following formation of a reactionary surface as the melt spreads over chromium and boron particles. Then the melt is saturated with chromium and boron with subsequent crystallization of  $\text{Cr}(\text{Si},\text{Al})_2$  and  $\text{CrB}$  grains from the melt. In silicon-rich regions,  $\text{Cr}_5\text{Si}_3$  grains are formed in the combustion zone (Fig. 3b). Figure 3c shows that the final combustion product consists of chromium boride  $\text{CrB}$  grains nearly

1  $\mu\text{m}$  in size, which are uniformly distributed over the gray matrix of chromium aluminosilicide  $\text{Cr}(\text{Si},\text{Al})_2$ , and a small amount of the light gray chromium silicide phase  $\text{Cr}_5\text{Si}_3$ .

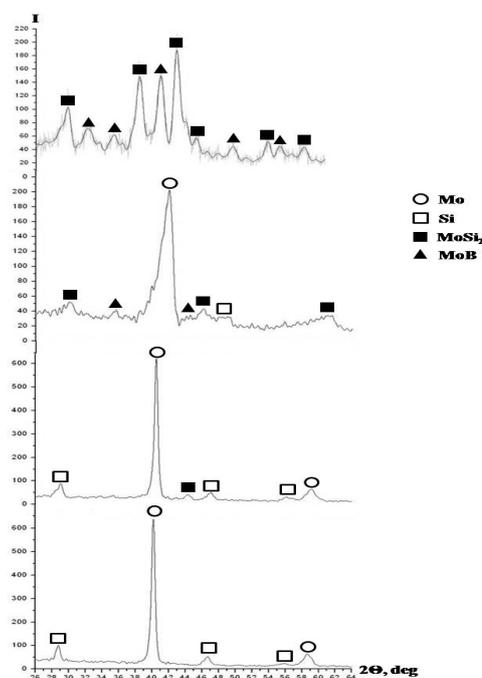


Fig. 2. Sampling sequence of TRXRD patterns for the combustion process for composition  $\text{Mo}_2$ .

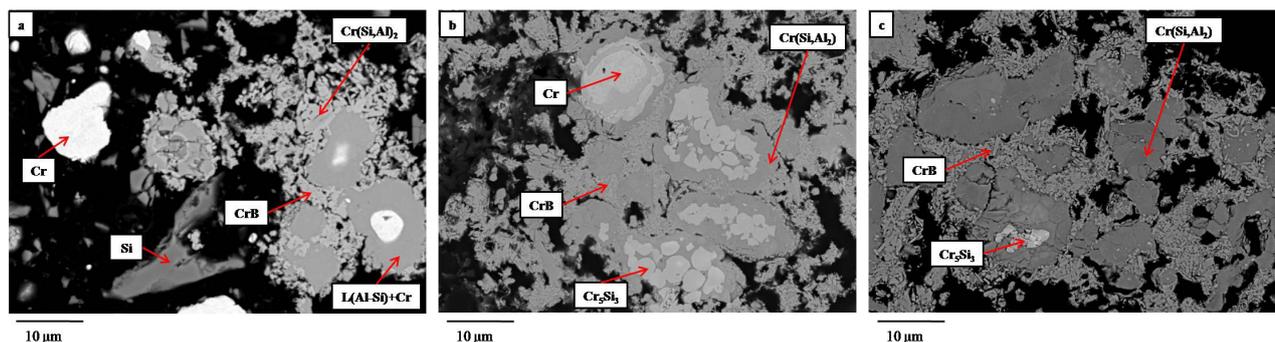


Fig. 3. Microstructures of SCF in the Cr–Al–Si–B mixture with composition  $Cr_1$  recorded in different areas of the quenched sample: combustion front (a); after-combustion zone (b); final product (c).

Dynamic diffraction TRXRD analysis (Fig. 4) in the Cr–Al–Si–B system (comp.  $Cr_1$ ) also confirmed the sequential chemical transformations in the combustion wave. First of all in the combustion wave the CrB phase is formed and the phase based on chromium silicide and aluminide  $Cr(Si,Al)_2$  emerged  $\sim 1$  s later.

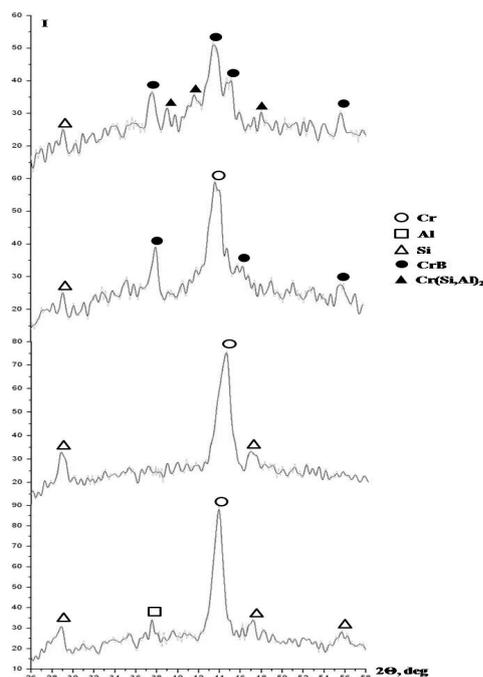


Fig. 4. Sampling sequence of TRXRD patterns for the combustion process for composition  $Cr_1$ .

Thus, it can be assumed that for the composition  $Cr_1$  with a minimal concentration of aluminum combustion process is controlled by solid-state and gas-transport reactions of Cr with B and  $B_2O_3$ , that yield chromium borides formation. With increasing the concentration of aluminum (comp.  $Cr_3$ ) the proportion of the melt increase in the combustion zone, and the combustion process, in this case, controlled

by the interaction of Cr particles with melted Al or the eutectic melt  $L \rightarrow (Al) + (Si)$ . In the latter case chemical interaction of chromium with aluminum, silicon and boron occurs with less kinetic difficulties: the values of the effective activation energy of the combustion process will be reduced.

#### Investigation of the Compact Synthesis Products

Analysis of the phase composition and microstructure of the samples after forced SHS pressing in the Mo–Si–B system (Fig. 5) revealed that the main phases in the sample with composition  $Mo_1$  are  $Mo_2B$  and ternary compound  $Mo_5SiB_2$  ( $T_2$  phase) contained in an amount of 51 and 47%, respectively. The main phase components of the synthesis product of composition  $Mo_2$  are monoboride  $MoB$  and molybdenum disilicide  $MoSi_2$  with the content of 41 and 59%, respectively. The compact sample with composition  $Mo_3$  contains 98% of  $T_2$  phase, which is attractive for ultrahigh-temperature applications [9]. The main phases of SHS ceramics in the Cr–Al–Si–B system (Fig. 6), fabricated using forced SHS pressing technology, are CrB,  $Cr_5Si_3$ ,  $Cr(Si,Al)_2$  and  $Cr_4Al_{11}$ . The ternary compound  $Cr(Si,Al)_2$  was identified in the SHS product with  $Cr_1$  composition. The formation of this compound is the result of the dissolution of Al in chromium disilicide  $CrSi_2$  (the maximum solubility is  $\sim 25$  at. %) when aluminum displaces silicon in crystalline lattice.

Furthermore, the samples  $Cr_1$  and  $Cr_3$  contain a small amount of the ternary chromium borosilicide  $Cr_5Si_3B_{(x)}$ . Probably, this compound was formed in after-combustion zone as a result of interaction between chromium boride and silicide, because at high temperatures B and Si atoms exhibit mutual substitution ability [10]. The increase in Al content (decrease in Cr and B content) leads to decrease in chromium boride concentration and to increase in chromium aluminide content (comp.  $Cr_3$ ). Also the average size of the boride grains decreases significantly.

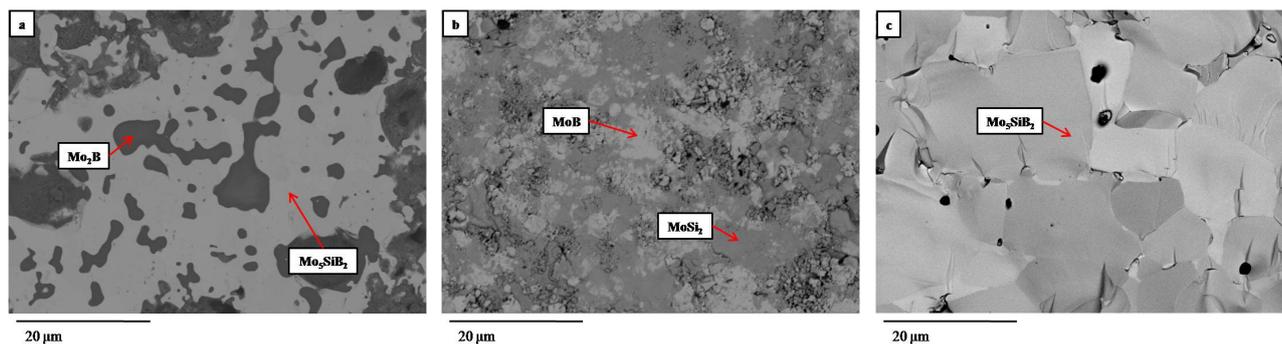


Fig. 5. Microstructure of compact ceramics in Mo–Si–B system with compositions Mo<sub>1</sub> (a), Mo<sub>2</sub> (b), Mo<sub>3</sub> (c).

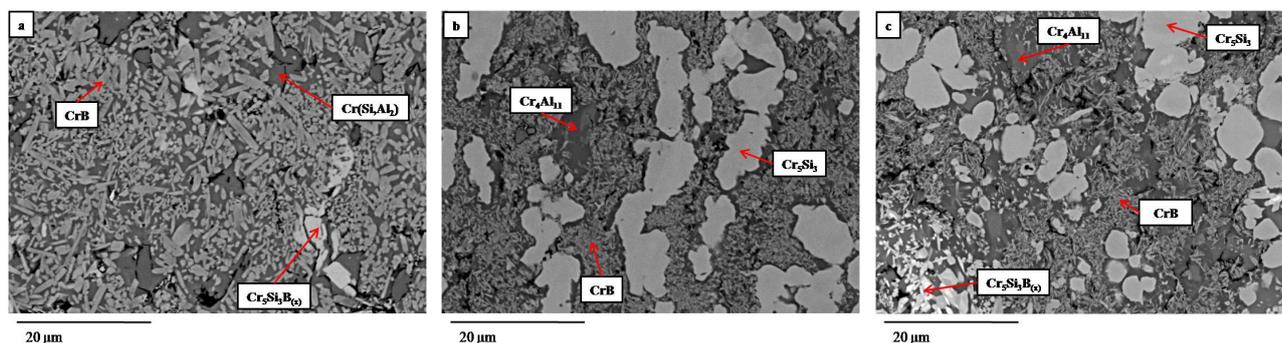


Fig. 6. Microstructure of compact ceramics in Cr–Al–Si–B system with compositions Cr<sub>1</sub> (a), Cr<sub>2</sub> (b), Cr<sub>3</sub> (c).

Some properties of compact SHS ceramics were also studied in this work. So in the Mo–Si–B system for compositions Mo<sub>1</sub>, Mo<sub>2</sub> and Mo<sub>3</sub> the porosity was about 12.7, 14.4 and 9.1%, Vickers hardness was about 9.1, 14.9 and 13.4 GPa, respectively. For the Cr–Al–Si–B system for compositions Cr<sub>1</sub>, Cr<sub>2</sub> and Cr<sub>3</sub> the porosity was about 12.6, 7.6 and 3.6%, Vickers hardness was about 9.8, 10.6 and 9.1 GPa, respectively.

## Conclusions

1. It was shown that the driving force of SHS process for silicon-rich Mo–Si–B mixtures is the formation of the silicon melt and its spreading over the surface of molybdenum and boron particles followed by the dissolution of boron and chemical interaction with molybdenum, forming a layer of the intermediate silicide Mo<sub>3</sub>Si. Next, the diffusion of silicon in to molybdenum at the film–melt interface results the formation of MoSi<sub>2</sub> grains, while the diffusion of molybdenum in the melt yields MoB grains. In compositions with high boron and low silicon contents, MoB can be formed by the gas-phase mass transfer of MoO<sub>3</sub> suboxide to boron particles and B<sub>2</sub>O<sub>2</sub> to molybdenum particles.

2. Depending on the mixture composition, the dispersibility of powders, the heterogeneity of the

mixture, and the initial temperature chemical reactions in the combustion wave can occur in sequential and the merging modes. For the Cr–Al–Si–B system, as an example for Cr<sub>1</sub> composition, it was found that chemical transformations occur sequentially: chromium monobomide CrB is the first compound to be formed, followed by formation of chromium silicide Cr<sub>5</sub>Si<sub>3</sub> or aluminosilicide Cr(Si,Al)<sub>2</sub>. As the Al content increases (comp. Cr<sub>3</sub>), dissolution of chromium particles in the Al–Si eutectic melt becomes the limiting stage of SHS process.

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