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The features of combustion and structure formation of ceramic materials in the Cr–Al–Si–B system

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Abstract

Kinetics of the SHS process, stages of chemical transformations and structure formation of ceramic materials in the Cr–Al–Si–B multicomponent system were investigated. The effect of reaction mixtures composition and initial temperature on the combustion rate U_c and combustion temperature T_c, which reduce with increasing Al content, was studied. An increase in the initial temperature of the SHS process causes a linear increase of U_c and T_c in the range of T_0=290–750 K. This is evidence to the fact that each composition is characterized by the similar combustion mechanism, when the stages of chemical reactions of product formation remain unchanged. However, an increase in T_0 above 750 K, probably, may lead to exponential character of U_c growth. Furthermore, 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, thus reducing the effective activation energy approximately from ~290 to ~110 kJ/mol. The stages of chemical transformations in the combustion wave were studied; the mechanism of structure formation was proposed. Firstly, the Al–Si eutectic mixture undergoes contact melting followed by formation of the reactionary surface as the melt spreads over the Cr and B particles surface. The melt is saturated with these elements followed by crystallization of CrB and $Cr(Si,Al)_2$ grains. In the Cr- and B-rich areas and low melt concentration, the formation of CrB may occur by solid-phase interaction supported via gas-transport reaction. Dynamic X-ray diffraction confirmed the sequential formation of chromium monoboride CrB and after chromium silicide Cr_5Si_3 or chromium alumosilicide $Cr(Si,Al)_2$. Force SHS–pressing was used to fabricate ceramic targets for magnetron sputtering of multicomponent coatings.

Keywords: SHS; Mechanism; Phase formation; Ceramic materials; Chromium borides and silicides

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1. Introduction

An intensive research aimed at designing of novel multifunctional coatings [1–3] to be used in various branches of industry (engineering, aircraft and space engine building, tool-making industry, etc.) has recently been conducted all over the world. The use of protective coatings simultaneously characterized by high hardness, abrasive wear resistance [4], heat and corrosion resistance, high thermal stability [5], and a relatively low friction coefficient [6] will significantly improve the performance of various products and increase their service life. Multicomponent coatings based on borides, silicides, aluminides, and nitrides of transition metals, which exhibits excellent chemical, mechanical, and tribological properties, are widely used as a protective layers on the surface of responsible machine parts and assemblies. Doping with Cr, Al, and Si allows one to attain a combination of high thermal stability and oxidation resistance at elevated temperatures [5,7]. Ensuring high hardness and wear resistance at a relatively low friction coefficient is a crucial factor for increasing the durability of products. Therefore, the development of synthesis fundamental bases of hard ware-resistant coatings characterized by high thermal stability at temperatures above 1000 °C, as well as heat and corrosion resistance, is extremely urgent task nowadays.

One of the common methods for ion-plasma deposition of such multicomponent coatings is magnetron sputtering [8].

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Application of a novel composite ceramics based on chromium borides, silicides, and aluminides as multicomponent targets (cathodes), which already contain all required elements, will make the magnetron sputtering procedure much simpler, enhance coating homogeneity, improve reproducibility of results, and reduce deposition time. The powder metallurgy techniques [9] often cannot ensure fabrication of such complicated multicomponent ceramic compositions, therefore we resorted to the method of self-propagating high-temperature synthesis (SHS) [10–13], namely, to forced SHS-–pressing technology, used in this case. Studying the combustion regularities and mechanisms, processes of phase and structure formation in a combustion wave are among the most relevant problems in SHS of composite ceramic materials, since this knowledge makes it possible to effectively control the structure and properties of materials.

This work was aimed at studying the features of the SHS process in the Cr–Al–Si–B system, the stages of chemical transformations and the structure formation of synthesis products, which have a great potential as a target materials for magnetron sputtering of quasi-amorphous heat-resistant coatings.

2. Materials and methods

Powders of chromium (PKh-1S grade), aluminum (ASD-1 grade), black boron (B-99A grade), and silicon produced by grinding of KEF-4.5 monocrystals with the orientation (1 0 0) were used as initial reagents. Compositions of the reactionary mixtures with different ratio between Al and B content (Table 1) were calculated under an assumption of complete chemical transformation with the formation of chromium borides, silicides and aluminides. These compositions provide the required elemental composition of the synthesis products for their further sputtering by PVD.

In the Cr–Si and Cr–Al systems, Cr_5Si_3 and Cr_4Al_9 compounds are characterized by the greatest enthalpies of formation ($-\Delta H^0_{298}=326.6$ and 135.7 kJ/mol, respectively [13]), which is rather important for the SHS process. The enthalpy of formation of chromium diboride CrB_2 ($-\Delta H^0_{298}=126.4$ kJ/mol) somewhat higher as compared with that of chromium monoboride CrB ($-\Delta H^0_{298}=105.2$ kJ/mol) [14]. In addition, chromium diboride is characterized by the maximum melting point and the best thermal resistance and stability among the components of the Cr–B system [15].

Table 1 lists the compositions of green powder mixtures and their adiabatic combustion temperatures (T_c^{ad}), calculated using the THERMO software package [16]. The adiabatic combustion temperature decreases with increasing of aluminum content.

Table 1
Compositions of the green mixtures.

Composition	T_c^{ad}, K	Content of the reagents, wt %			
		Cr	Al	Si	B
1	1596	69.4	8.1	12.0	10.5
2	1342	65.8	16.2	12.0	6.0
3	1151	63.4	21.6	12.0	3.0

Before mixing the initial powders were dried at a temperature of 90 °C. The reactionary mixtures were prepared in a ball mill equipped with steel drums with using of hard alloy balls as milling agents. Wet milling in isopropanol was used to prevent adhesion of aluminum onto the balls and drum walls; the mixture was subsequently dried in a sealed cyclone equipped with a condensate collector.

The effect of the initial temperature (T_0) of the reactionary mixture on combustion temperature (T_c) and combustion rate (U_c) was studied experimentally using a laboratory-scale SHS reactor according to the conventional procedure [11,17,18]. Cylindrical samples with 10 mm in diameter and 15 mm height with relative density equal to 60% were pressed from the reactionary mixtures. The combustion temperature (T_c) was measured using W–Re thermocouples; a hole (~4 mm deep and 2 mm in diameter) was drilled in the sample in order to mount the thermocouple. The combustion rate (U_c) was measured by high-speed video recording using a Panasonic WV-BL600 camera at 15-fold magnification.

The stages of the phase transformations in the combustion wave were studied by dynamic X-ray analysis. An LKD-41 one-coordinate position-sensitive detector was used for frame-by-frame recording of the X-ray diffraction patterns [19]. The XRD patterns were recorded in the 2θ range of 25–60° [18], since the initial reagents, expected intermediate, and final products have strong diffraction maxima in this range.

To study the dynamics of structural transformations in the combustion wave, we used the well-known method of quenching the combustion front in a copper wedge (the vertex angle of 5°) [20], followed by scanning electron microscopy (SEM) and energy- dispersive spectroscopy (EDS) of the characteristic areas of the stopped combustion front (SCF) using a Hitachi S-3400N scanning electron microscope equipped with a NORAN energy-dispersive X-ray spectrometer. This microscope was also used to analyze the microstructure of the compacted samples.

The phase composition of the combustion products was studied by X-ray diffraction analysis (XRD) using monochromatic CuK_α radiation in the mode of step-by-step scanning in the 2θ range of 10–110° with the scan increment of 0.1°; the exposure time 4 s per point. The spectra were processed using the JCPDS database [21].

The technological parameters of force SHS-pressing (pressing delay time after the combustion was finished; time of exposure of hot synthesis products under pressure; and molding pressure) were optimized to produce porous less and defects free ceramic samples [10,17,18].

3. Results and discussion

3.1. Investigation of the macrokinetic parameters of the combustion process

The resulting experimental dependences of T_c and U_c from the initial temperature T_0 in the Cr–Al–Si–B system with