Structure and properties of ZrB2, ZrSiB and ZrAlSiB cathode materials and coatings obtained by their magnetron sputtering

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Abstract. The ceramic ZrB2, ZrSiB, and ZrAlSiB cathodes were manufactured by means of self-propagating high-temperature synthesis (SHS). The parameters of SHS process including dependence of the combustion temperature and rate on the initial temperature of the reaction mixtures, as well as values of effective activation energy were estimated. Cathodes were subjected to the magnetron sputtering in the argon atmosphere. The structure and properties of cathodes and coatings were studied by means of X-ray diffraction, scanning electron microscopy, energy-dispersive and glow discharge optical emission spectroscopy. Bulk ceramic samples and coatings were characterised in terms of their hardness, elastic modulus, elastic recovery, density, and residual porosity. Results obtained shows that cathodes possess homogeneous structure with low porosity level in range 2-6% and hardness between 10 and 17 GPa. Coatings demonstrate dense defect-free structure and contain nanocrystallites of h-ZrB2 phase. The grain size and hardness decrease from 8 down to 2 nm and from 37 down to 16 GPa with the addition of the silicon and aluminum dopes.

1. Introduction

Recently, ultra-high-temperature ceramics (UHTC) is of great interest in various branches of science and technology. Among the UHTC, the leading material is zirconium diboride due to its high melting point of 3245°C, high thermal conductivity of 57.9 W/(m·K), low thermal expansion coefficient of 5.9×10^-6 °C^-1 [1], hardness up to 22 GPa [2] and strength up to 565 MPa [3], high heat resistance up to 2000°C [4]. As a result, ceramics based on ZrB2 are used as materials for heaters, crucibles, covers and electrodes of high-temperature thermocouples, refractory components, high-speed bearing, as well as for functional coatings deposited onto cutting tools, parts of hypersonic aerospace vehicles, high-temperature sensors etc. Bulk ZrB2 can be used also as a cathode material for the magnetron sputtering and deposition of protective coatings. Addition of Si and Al is expected to improve the oxidation resistance and thermal stability of the bulk metal borides and coatings [5-8].

The bulk ZrB2-based ceramics can be manufactured by powder metallurgy methods, such as spark-plasma sintering [9-11] or hot pressing [10]. However these processes are not economically advantageous, because for their implementation the large expenditures of electricity and expensive equipment (furnaces) are required. In connection with this, self-propagating high-temperature synthesis (SHS) for the production of boride ceramics has become increasingly widespread [9,12]. One of the important advantages of the SHS method is the self-cleaning effect of the combustion products during the synthesis process [13,14].

The magnetron sputtering is one of the most common methods of coating deposition in vacuum. The main advantage of magnetron sputtering is that a coating of the desired composition can easily be deposited onto the surface of different substrates [15-19]. Coatings deposited by magnetron...
sputtering do not significantly change the substrate geometry [20,21], posses low defect density, and a dense homogeneous structure with uniform elemental distribution through the coating thickness [22]. Method is useful in the deposition of multicomponent coatings [23,24].

This work is devoted to the study of the ZrB₂, ZrSiB, and ZrAlSiB bulk ceramic electrodes and coatings produced by their sputtering in the magnetron deposition system. Special attention was paid to the investigation of kinetics and mechanism of the combustion during SHS, mechanical properties of the deposited coatings.

2. Experimental part
Cathodes were manufactured by SHS technology using powders of zirconium (grade PTsrK-1) with an average particle size in range of 10-15 μm, aluminium (grade ASD-1) with a dispersion of about 50 microns, amorphous boron (grade B-99A) with an average particle size ~ 0.1 μm, and silicon (powder was prepared by grinding KEF-4.5 (100) monocrystals) with grain size < 45 μm. The powders were mixed in a stainless steel ball mill using the hard-alloy grinding bodies. To prevent self-ignition of zirconium powder, mixing was performed in isopropyl alcohol medium. Drying of the finished mixtures was carried out in a vacuum oven at a temperature of 50 °C. Table 1 shows the test compositions of powder mixtures.

| Composition | Concentration |
|-------------|---------------|
|             | Zr   | Si   | B    | Al   |
|             | Weit.% | At.% | Weit.% | At.% | Weit.% | At.% | Weit.% | At.% |
| 1           | 81.0  | 33.3 | -     | -    | 19.0   | 66.7 | -     | -    |
| 2           | 64.7  | 20.4 | 20.0  | 38.7 | 15.3   | 40.9 | -     | -    |
| 3           | 75.9  | 40.0 | 11.7  | 20.0 | 6.8    | 30.0 | 5.6   | 10   |

Composition №1 was calculated to form a 100% ZrB₂ phase. Composition №2 was calculated assuming complete chemical interaction of zirconium with boron and the formation of 80% ZrB₂, as well as 20% of free silicon. Composition №3 was calculated assuming the formation of ZrB₂ diboride and ZrSi silicide in the 1:1 ratio and the addition of aluminium (10 at.%) in analogy to [23]. Calculation of the adiabatic combustion temperatures T₀ ad of these mixtures and the equilibrium phase compositions of the combustion products at the initial temperature T₀ = Tₐ (293 K) was carried out using "THERMO" software under the assumption of adiabatic process [14]. The macrokinetic characteristics of the combustion process were studied in a home-made SHS reactor using the methods described in [25,26]. Cylindrical briquettes with a diameter of 10 mm and a height of 18 mm with a relative density of 55-60% were formed from the powder mixtures. The combustion temperature Tc was measured with W-Re thermocouples installed in the holes of a cylindrical sample. The combustion rate Uc was measured by the method of high-speed video recording using a "Panasonic" WV-BL600 video camera at a 15-fold magnification of the image. Based on the experimental dependences Tc vs T₀ and Uc vs T₀, the values of the effective activation energy Eₐ of self-sustained reactions were calculated by the method described in [15], which allowed us to assume the limiting stage of the combustion process. Bulk ceramic were obtained by forced SHS-pressing technology [14]. Hydraulic press DA-1532B and "sand" reaction mold were used. Synthesized samples were subjected to polishing and electroerosion cutting to get cathodes 120 mm in diameter and 8-10 mm in height.

The phase composition of the SHS products was determined by X-ray diffraction (XRD) analysis using monochrome Cu-Kα radiation. Vickers hardness of bulk ceramic samples was measured on an HVS-50 instrument at a load of 10 kg. The density was evaluated by the hydrostatic weighing method on the "AND1 GR-202" analytical balance. The true density of the compact samples was determined using "AccuPyc 1340" Micromeritics helium pycnometer. The residual porosity was calculated from the relative density values, which was found to be the ratio of the hydrostatic (experimental) to the true density of the bulk material.
The ceramic ZrB$_2$, ZrSiB, and ZrAlSiB cathodes were subjected to the DC magnetron sputtering (current 2 A, voltage 500 V) in pure argon (99.993 %) using a UVN-2M vacuum unit. The principal scheme of the vacuum chamber configuration has been shown elsewhere [27]. Polished plates of polycrystalline alumina (VK-100-1 trademark, JSC Polykor), 2x3 cm$^2$ in size, were used as a substrate material. Samples were mounted on a 2-axis rotating table equipped with bias voltage supply system, heater, and thermo-couple for temperature control. Before coating, the substrates were ultrasonically cleaned in isopropyl alcohol for 5 min using an UZDN-2T machine operating at a power of about 100 W and a frequency of 22 kHz, after which they were etched for 20 min in a vacuum chamber by Ar$^+$ ions with an average energy of about 2 keV using slit-type ion source, 180 mm in length. The distances form the target and ion source to substrate were 9 and 13 cm, respectively. The total pressure was maintained at 0.1-0.2 Pa. During deposition, the negative substrate bias voltage was kept constant at -250 V, the temperature was controlled in the range of 350-400 °C, and the deposition time was kept constant at 40 min.

The coating elemental compositions were determined from the elemental depth profiles obtained by glow discharge optical emission spectroscopy (GDOES) using a PROFILER 2 instrument (Horiba Jobin Yvon) [28]. The microstructure of coatings was examined by a S-3400N Hitachi scanning electron microscope equipped with a Noran 7 Thermo energy dispersive X-ray spectrometer, X-ray diffraction (XRD) patterns were recorded using a D8 Advance X-ray diffractometer (Bruker) using CuK$\alpha$ monochromatic radiation. The coatings were characterized in terms of their hardness (H), Young's Modulus (E) and elastic recovery (W) using a Nano-Hardness Tester (CSM Instruments) equipped with a Berkovich diamond indenter tip under an applied load of 5 mN. The detail description of method is presented in [27].

3. Results and Discussion

$T_0$ study of kinetics and mechanism of combustion the experimental dependences of $T_c$ and $U_c$ on the $T_0$ were obtained (Figure 1). While the graphs for compositions №2 and №3 were successfully constructed the data for compound №1 was not obtained because the value of $T_c$ at $T_0=298$ K was 2900 K, which exceeds the recommended measuring range of the W-Re thermocouple (2773 K). According to the literature data the values a $T_{ad}$ of ZrB$_2$ formation are in the range 3200-3300 K [14, 29]. It is worth considering that often the experimental $T_c$ values are below the calculated values of $T_{ad}$ in average 150 $T_0$ [14], which is associated with thermal losses the heating of the environment and the local heterogeneity of the starting mixture. Thus experimental values of $T_c$ can be in the range 3000-3200 K.

An increase in the initial temperature $T_0$ for compositions №2 and №3 leads to linear growth of $T_c$ and $U_c$. This indicates that the stage of chemical transformations in the combustion wave does not change with increasing $T_0$. For composition №2, an increase in $T_0$ by 300 K leads to an insignificant increase in $T_c$ of about 100 K (Figure 1a). In this case, the most sensitive characteristic to the change in $T_0$ is $U_c$ [15], the values increase by an order of magnitude (Figure 1b). This is probably due to the largest amount of liquid phase due to the melting of all the initial reagents (Zr, Si and B) in the temperature range 2268÷2403 K. Therefore, it can be assumed that the motive power of the combustion process in this multicomponent reaction mixture is the formation of the Zr-Si-B melt.

For composition №3, an increase in $T_0$ by 400 K leads to a linear growth of $T_c$ by approximately 200 K (Figure 1a), and $U_c$ increases by a factor of three. In this case, like the driving force of the combustion process is the formation of the melt, while all the initial reactants (Zr, Si, B and Al) also melt, liquid-phase interaction occurs. According to the calculation results, the $E_{eff}$ were 63 and 225 kJ/mol for compositions №2 and №3, respectively. The values obtained indicate the limiting role of liquid-phase interaction processes. Note that according to the literature data the $E_{eff}$ value for ZrB$_2$ is 150 kJ/mol [14] in the temperature range of 2600-2800 K or 300 kJ/mol for 2100-3100 K [14].

The results of XRD analysis of compact ceramic samples are presented in Table 2.
Figure 1. Dependences of the combustion temperature $T_c$ (a) and rate $U_c$ (b) of compositions №2 and №3 on the initial process temperature $T_0$

Table 2. Results of XRD analysis of the bulk samples

| Composition | Concentration, Weit.% |
|-------------|-----------------------|
|             | ZrB$_2$ | Si | ZrSi$_2$ | ZrO$_2$ | ZrSi | ZrSiAl$_2$ | Al | ZrB$_{12}$ |
| 1           | 94      | -  | -        | 3       | -    | -          | -  | 3          |
| 2           | 66      | 6  | 26       | 2       | -    | -          | -  | -          |
| 3           | 39      | -  | 5        | -       | 46   | 7          | 3  | -          |

The sample №1 contains 94 Weit.% of ZrB$_2$ phase. Formation of ZrB$_{12}$ can be due to the presence of a fraction bound to ZrO$_2$ in the initial Zr powder, i.e. locally zirconium interacts with an excess of boron to form ZrB$_{12}$. In sample №2 the stable ZrSi$_2$ phase is formed, whereas metastable ZrSi phases are not detected. The phase composition of sample №3 includes ZrB$_2$, ZrSi, ZrSi$_2$ and the ternary compound ZrSiAl$_2$. At the same time, their concentrations are 39, 46, 5 and 7%, respectively. Also in the structure there is 3% free Al. The presence of zirconium silicide ZrSi$_2$ is probably associated with a high conversion depth. When the sample is cooled slowly after synthesis, the monosilicide ZrSi is saturated with silicon from the zirconium depleted melt.

The SEM and EDS data correlate well with the XRD results (Figure 2). The main structural component in sample №1 is ZrB$_2$ phase, represented by rounded grains of the order of 10-20 μm in size (Figure 2a). On the microstructures of the sample №2 (Figure 2b), light faceted ZrB$_2$ grains 1-5 μm in size and a gray matrix of ZrSi$_2$ and silicon are distinguishable. Zirconium oxide ZrO$_2$ is presumably concentrated mainly in the pores. Figure 2c shows the microstructure of sample №3. The ZrB$_2$ grains with an average size of 2-3 μm are distributed in a matrix of monosilicide ZrSi. Additional ZrSi$_2$ and ZrSiAl$_2$ phases were detected.

Table 3 presents some of the physical and mechanical properties of synthesized bulk ceramic samples.

Table 3. The physical and mechanical properties of the bulk samples

| Composition | Density, g/cm$^3$ | Residual porosity, % | Hardness, GPa |
|-------------|------------------|----------------------|---------------|
| 1           | 4,5              | 5,8                  | 9,6           |
| 2           | 4,6              | 2,7                  | 14,2          |
| 3           | 5,3              | 3,0                  | 17,1          |
Samples have low residual porosity and are characterized by a sufficiently high hardness comparable to the hardness of structural ceramics. Note that in early work [30] the 100 %ZrB$_2$ cathodes were obtained by cold isostatic pressing with subsequent sintering at a temperature of 1500°C. Density of products was limited by 3.96 g/cm$^3$, and a residual porosity was about 35 %. In [31] compact ceramics ZrB$_2$-ZrSi$_2$ obtained by hot pressing (30 MPa, 1850 °C) showed a residual porosity in range 1-6 %.

The SEM-images of microstructure of coatings is shown in Figure 3. It’s possible to note a formation of very dense structure without coarse columnar elements. The coating thicknesses estimated from the SEM-images are 3, 5, and 4 μm for ZrB$_2$, ZrSi, and ZrAlSiB, respectively.

**Figure 2.** Microstructure of the bulk samples №1 (a), №2 (b), №3 (c)

**Figure 3.** Microstructure of coatings №1 (a), №2 (b) and №3 (c)
The main structural component of ZrB$_2$, ZrSiB and ZrAlSiB coatings is the hexagonal phase of ZrB$_2$ (Figure 4). Some lines of ZrB$_2$ phase coincide with the lines from the Al$_2$O$_3$ substrate, but the positions at angles 20: 25.2; 32.5; 41.5, 51.5 (JCPDS 89-3930), accurately indicate the presence of the h-ZrB$_2$ phase in these coatings. The preferrent orientation of ZrB$_2$ grains corresponds to the crystallographic direction (101), which is typical for coatings of similar systems [32]. In the ZrB$_2$ coating, the crystallite size of h-ZrB$_2$, calculated by the Debye-Scherrer formula, is 8 nm. It is known that silicon is a strong amorphizer. As a result of silicon doping, the size of crystallites of the h-ZrB$_2$ phase in the ZrSiB and ZrAlSiB coating decreases down to 2 nm.

The hardness of the ZrB$_2$ coating is 37.4 GPa (Table 4), which exceeds the previously known values from the literature data [2,33,34]. Also, the resistance to elastic and plastic deformation of fracture in the ZrB$_2$ coating proved to be the highest. The hardness of ZrSiB and ZrAlSiB coatings is almost 2 times lower than that of ZrB$_2$ (see Table 4). Usually the addition of silicon to the coatings increases their hardness [35], but there is some value of the silicon content in the coating, after exceeding which the reverse effect is observed. Reduction of hardness with increasing content of silicon in the coating can be explained by a reduction in the size of the grains. There is a critical grain size $d_c$ of 10 nm, at which the maximum hardness of the material is achieved, and any deviations in either direction ($d<d_c$ or $d>d_c$) lead to a decrease. This fact is called the Hall-Petch effect, which explains the low hardness, in comparison with ZrB$_2$, silicon containing coatings. Decreasing of the mechanical properties after Al-alloying was described in [23] dedicated to the MoSiB and MoAlSiB coatings. Calculation of H/E and $H^3/E^2$ values (Table 4) may be useful for predicting the behavior of coatings under conditions of tribological contact and establishing inclination to inhomogeneous deformation 36-38].

![Figure 4. X-ray diffraction pattern of coatings №1 (a), №2 (b), and №3(c)](image)
Table 4. Mechanical properties of coatings.

| Composition | Mechanical properties |
|-------------|-----------------------|
|             | H, GPa | E, GPa | W, % | H/E | H^2/E^2, GPa |
| 1           | 37.4   | 399.4  | 73   | 0.094 | 0.33 |
| 2           | 22.2   | 255.8  | 60   | 0.090 | 0.17 |
| 3           | 16.0   | 227.0  | 47   | 0.070 | 0.08 |

4. Conclusion
The kinetics and mechanisms of the combustion process in the Zr+B, Zr+Si+B, and Zr+Al+Si+B powder mixtures have been studied. The dependence of the combustion temperature and rate on the initial temperature of the reaction mixtures, as well as values of effective activation energy were determined.

The main structural components of the bulk ceramic sample №1 are ZrB2 and an insignificant amount of ZrB12 boride. The sample №2 contains the phases of ZrB2, ZrSi2 and Si. The ZrB2, ZrSi, ZrSi2; and the ternary ZrSiAl2 compound were detected in the sample №3. The obtained bulk ceramic samples have a low residual porosity (2.7-5.8%) and high hardness (10-17 GPa).

The ceramic ZrB2, ZrSiB, and ZrAlSiB cathodes obtained using force SHS-compacting technology were successfully used for the magnetron sputtering. The main component of the deposited coating was hexagonal ZrB2 phase. The addition of silicon or silicon and aluminum to the coatings resulted in a decrease in the crystallite size of the ZrB2 phase from 8 to 2 nm. All coatings had a dense and homogeneous structure. The greatest mechanical properties (hardness of 37.4 GPa) were shown by the ZrB2 coating.

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