Self-propagating high-temperature synthesis of ceramic composite material based on Al$_2$O$_3$ - SiO$_2$ - ZrB$_2$

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Abstract. The present work is devoted to the production of a ceramic composite material in the mode of self-propagating high-temperature synthesis from a mixture of powder reagents: ZrO$_2$, Al, SiO$_2$, B, and Zr. The adiabatic combustion temperature was calculated for the stoichiometric composition of ZrO$_2$-Al$_2$SiO$_4$ and for compositions with the addition of an energy additive from powders x(Zr + 2B), where x Є [10-30] wt. %. It was found that an increase in the fraction of Zr + 2B leads to the refinement of structural elements. An increase in its content to 30 wt. % leads to the formation of nanoscale structural components in the material. As a result of varying the initial composition, a ceramic composite material based on Al$_2$O$_3$-SiO$_2$-ZrB$_2$ was obtained containing an oxide matrix with particles of zirconium diboride distributed from 61 to 77 wt. %. It is shown that as a result of the SHS of the selected compositions, mullite is formed. Using SEM, EDS and XRD methods, we studied the structural features and phase composition of the materials obtained.

1. Introduction

Ceramic materials today are widely used in various industries [1-6]. One of the most common classes of ceramic materials is oxide ceramics. Oxide ceramic materials are widely used due to their high hardness, chemical inertness, ability to work at high temperatures and relative availability [7-10]. The most common type of oxide ceramic is aluminum oxide ceramic. Composite materials based on various oxides are also of great interest today. There are various types of such composites, for example, Al$_2$O$_3$-ZrO$_2$ [11, 12], Al$_2$O$_3$-SiO$_2$ [13, 14], Al$_2$O$_3$-SiC [15, 16], etc. The creation of composite materials makes it possible to compensate for some of the shortcomings of individual oxides, such as low ability of aluminum oxide to resist thermal shock. As a result, oxide ceramic composite materials are promising for various fields of application. For instance, refractory materials [17], cutting [18] ceramics, ceramic filters [19], etc.

Due to the great interest in the class of composite materials based on oxide ceramics, today there are a number of methods for the synthesis of such materials. In recent years, the sol-gel method [20], its variation Pechini method [21], hydrothermal synthesis method [22], solution combustion method [23], mechanochemical synthesis [24], and a number of other methods have become widespread. However, among all the methods used, it is possible to single out the method of self-propagating high-temperature synthesis (SHS), which is the process of an exothermic chemical reaction through a mixture of reagents with the formation of solid products [25, 26]. The reaction is initiated locally by rapidly heating a small portion of the sample. After local reaction initiation due to heat transfer, heating and initiation of a
chemical reaction in the adjacent layer of the starting components occurs. Thus, a chemical reaction localized in the layer spontaneously propagates through the sample in the form of a combustion wave. This mode of synthesis allows to avoid the need for external heating, provides refining of the starting reagents during the combustion process, and also allows to reduce the synthesis time to several seconds.

Today, SHS has established itself as a promising method for producing a large number of materials, including composite oxide ceramics [27, 28].

This work is devoted to the preparation of a composite ceramic material based on Al₂O₃-SiO₂-ZrB₂ by the SHS method, as well as to the study of the influence of the initial composition on its phase composition and microstructure.

2. Materials and methods

In this work, the synthesis of the material was carried out in the mode of self-propagating high-temperature synthesis. Powders of zirconium oxide ZrO₂ (<50 μm, ≥ 98.5), aluminum (<5 μm, ≥ 99.5), silicon oxide SiO₂ (<1 μm, ≥ 99.3), boron (<10 μm, ≥ 99.5) and zirconium (<100 μm, ≥ 99.9). The listed powders were previously aged in an oven and then mixed in a ball mill for 4 hours. Then, cylindrical billets weighing 50 grams and a relative density of 0.65 were pressed from the resulting powder mixture. The SHS process was initiated by a tungsten helix. The proposed reaction scheme during SHS in the studied compounds:

\[
\text{ZrO}_2 + \text{Al} + \text{SiO}_2 + \text{B} + x (\text{Zr} + 2\text{B}) \rightarrow \text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{ZrB}_2
\]

where \(x \in [0, 30]\) wt. %.

The percentage of the starting powder reagents is given in table 1. The percentage of the phases of the synthesized materials was determined by the corundum number method.

Table 1. Percentage of starting reagents, wt. %.

| №  | ZrO₂ | Al | SiO₂ | B  | Zr |
|----|------|----|------|----|----|
| 1  | 55,8 | 16,3| 18,1 | 9,8| -  |
| 2  | 50,2 | 14,7| 16,3 | 9,7| 8,1|
| 3  | 44,6 | 13  | 14,5 | 11,6| 16,2|
| 4  | 39,1 | 11,4| 12,7 | 12,6| 24,3|

3. Results and discussion

Firstly, the initial mixture was proposed, corresponding to composition No. 1 in table 1. The synthesis of the material in the selected mixture was planned to be carried out in the SHS mode due to the reduction of zirconium oxide by aluminum and the subsequent formation of zirconium diboride from reduced zirconium and boron. However, the reduction reaction of zirconium oxide with aluminum is weakly exothermic relative to other aluminothermic reactions; moreover, an inert component of silicon oxide is present in the system. The calculation of the adiabatic combustion temperature (table 2) showed that in such a system the SHS process cannot be initiated. The experiment also showed that in a system corresponding to composition 1, the SHS reaction could not be initiated without additional heating of the workpiece.

Table 2. Adiabatic combustion temperature of the studied compounds.

| №  | 1    | 2    | 3    | 4    |
|----|------|------|------|------|
| Tad, °C | 1195 | 1866 | 1995 | 2054 |

To increase the thermal effect, it was decided to add to the composition 1 a mixture of powders \(x (\text{Zr} + 2\text{B})\), where \(x \in [10-30]\) wt. % as an energy additive. The reaction of formation of zirconium diboride has a sufficiently high exotherm (\(\Delta H^0_{298} = -76\) kcal / mol, for comparison, \(\Delta H^0_{298} (\text{TiB}_2) = -70\) kcal / mol). As can be seen from table 2, the introduction of such an additive significantly increases the
adiabatic combustion temperature and allows for SHS in this system. Thus, further results are presented for the starting mixtures corresponding to compositions 2-4 in table 1.

As a result of synthesis, multiphase products were obtained, the results of x-ray phase analysis (XRD) of which are shown in figure 1. As can be seen from the figure, the obtained materials consisted of four phases: aluminum oxide, silicon oxide, zirconium diboride and zirconium oxide. The percentage of these phases are shown in table 3.

![Figure 1. Results of XRD of synthesized materials.](image)

**Table 3.** The percentage phase of the obtained materials, wt. %.

| №  | ZrB₂  | Al₂O₃ | SiO₂ | ZrO₂ |
|----|-------|-------|------|------|
| 2  | 61    | 30    | 5    | 4    |
| 3  | 71    | 23    | 2    | 4    |
| 4  | 77    | 19    | 2    | 2    |

According to the obtained results, the main phase in the synthesized materials was zirconium diboride, while in its composition 4 its share reaches 77 wt. %, which indicates the inappropriateness of increasing the proportion of additives (Zr + 2B) to 40 wt. % in the original charge. An increase in the proportion of zirconium diboride leads to a decrease in oxide components in the resulting materials, while the proportion of aluminum oxide decreases from 30 to 19 wt. %. Figure 1 shows that the diffraction patterns contain weak peaks of silicon dioxide, the intensity of which decreases with increasing proportion of zirconium diboride. This is due, firstly, to the amorphous state of the initial silica powder, and, secondly, to the formation of mullite.

Confirm the presence of mullite in the resulting materials allows several factors. First, in the diffractograms in figure 1, in the region of the angle 2θ = 16.3 °, there is a confirming mullite peak, as well as a number of peaks of aluminum oxide and silicon oxide coincide with the peaks characteristic
of mullite. It is difficult to quantify the fraction of mullite in products; most likely, this phase was in the process of nucleation, which did not manage to occur until the end due to the fleeting nature of the SHS process. Mullite is characterized by the formation of a lamellar structure. Figure 2 shows the results of SEM and EMF analysis of the material obtained on the basis of composition 2. In this figure, the formation of two phases is clearly visible, one of which has a pronounced plate structure (spectra S1 and S2) and consists of three elements: aluminum, silicon and oxygen. Thus, based on the foregoing, it can be concluded that mullite is formed in the synthesized materials. The presence of the described lamellar structure can also be seen in Figure 3b (spectrum S1) in the material based on composition 3.

!!!Table!!!

| Spectrum | B   | O   | Al  | Si  | Zr  |
|----------|-----|-----|-----|-----|-----|
| S1       | 49.15 | 34.16 | 14.77 | 1.92 |
| S2       | 58.00 | 21.00 | 17.46 | 3.54 |
| S3       | 4.46  | 6.21 | 0.74 | 1.36 | 87.24 |
| S4       | 4.13  | 6.02 | 1.78 | 88.07 |

Figure 2. Microstructure and elemental analysis of the material based on composition 2.

A general examination of the microstructure shown in figure 3 shows that the materials obtained had a composite structure. The dark regions corresponding to the oxide component were the matrix of the composite material. In figure 3a, the S1 spectrum corresponds to a large agglomerate of zirconium oxide particles, whose size was about 2-5 μm. This is unreacted zirconium oxide contained in the initial charge, the presence of which is also confirmed by the XRD results shown in figure 1. Table 3 indicates that the content in the obtained materials of the initial zirconium oxide was 2-4 wt. %. However, taking into account the error of the corundum number method used in calculating the percentage of phases, as well as the fact that no zirconium oxide deposits similar to composition 1 were found in the structure of materials based on compositions 3 and 4, we can say that with an increase in the proportion of diboride zirconium in materials decreases the amount of unreacted starting components. Thus, the completeness of the reaction of the studied compounds with increasing energy additives of zirconium diboride increases.

In addition to zirconium oxide agglomerates, the formation of a eutectic structure can be seen in figure 3a. Such a structure is characteristic of the Al₂O₃-ZrO₂ eutectic, which, most likely, was formed during SHS as a result of the interaction of unreacted initial zirconium oxide and the formed alumina.

As mentioned earlier, the oxide component was a matrix over the volume of which zirconium diboride particles were distributed, corresponding to the light regions in figure 3. When comparing the structures of the obtained materials, it can be noted that with an increase in the proportion of zirconium diboride in the materials, the particle size of ZrB₂ decreases. On the one hand, an increase in the combustion temperature of the system should promote particle growth. However, if we assume that the formation of ZrB₂ particles proceeds according to the diffusion mechanism as a result of the spreading of the zirconium melt along boron particles, then an increase in the content of zirconium diboride leads to an increase in the number of crystallization nuclei, the growth of which is hampered by the formation of the product layer. Further recrystallization is hindered due to the fleeting nature of SHS processes.
### Table 1: Elemental Composition of the Materials

| Spectrum | B   | O   | Al  | Si  | Z   |
|----------|-----|-----|-----|-----|-----|
| S1       | 23.06 | 76.94 |
| S2       | 10.56 | 23.13 | 11.44 | 47.41 | 7.46 |
| S3       | 2.49  | 36.05 | 2.87  | 2.12  | 56.47 |
| S4       | 58.10 | 14.09 | 20.05 | 7.74  |
| S5       | 37.42 | 6.16  | 13.19 | 43.24 |
| S6       | 47.76 | 23.69 | 19.52 | 9.03  |

### Table 2: Elemental Composition of the Materials

| Spectrum | B   | O   | Al  | Si  | Z   |
|----------|-----|-----|-----|-----|-----|
| S1       | 60.49 | 16.87 | 20.45 | 2.19 |
| S2       | 55.61 | 27.90 | 4.12  | 12.37 |
| S3       | 4.30  | 30.30 | 65.40 |
| S4       | 5.13  | 10.70 | 1.14  | 83.04 |
| S5       | 53.81 | 30.17 | 12.88 | 3.14  |
| S6       | 3.10  | 15.18 | 0.95  | 79.96 |
| S7       | 2.96  | 8.80  | 0.95  | 84.04 |

### Table 3: Elemental Composition of the Materials

| Spectrum | B   | O   | Al  | Si  | Z   |
|----------|-----|-----|-----|-----|-----|
| S1       | 4.69 | 11.00 | 0.58  | 83.73 |
| S2       | 4.91 | 6.20  | 0.69  | 4.36  | 83.84 |
| S3       | 3.98 | 7.69  | 0.60  | 1.12  | 86.60 |
| S4       | 54.03 | 19.13 | 26.84 |
| S5       | 50.95 | 7.57  | 19.58 | 21.90 |
| S6       | 4.59 | 32.09 | 3.15  | 9.02  | 51.16 |

Figure 3. SEM results of the materials obtained based on the compositions: a) No. 2 b) No. 3 c) No. 4.

In the structure of the material based on composition 2, zirconium diboride is mainly represented by particles of 1–3 μm in size, as shown in figure 4a. Smaller particles are also found, but their minority. When moving to a material based on composition 3, the thickness of the particles of zirconium diboride, which have a rectangular shape, becomes about 500 nm, as can be seen in figure 4b. When considering a material based on composition 4, it can be seen that the particles of zirconium diboride are agglomerates of rectangular grains, with the size of these grains not exceeding 100 nm. Thus, we can conclude that the increase in the proportion of energy additives (Zr + 2B) of the studied materials up to 30 wt. % leads to the formation of nanoscale grains of zirconium diboride.
Figure 4. Morphology of ZrB₂ particles of the materials obtained based on the compositions:
   a) No. 2 b) No. 3 c) No. 4.

4. Conclusions
It was shown that for the implementation of the SHS process in the initial ZrO₂-Al-SiO₂-B system, the introduction of an energy additive x (Zr + 2B), where x ε [10, 30] wt. %, is necessary. The introduction of such an additive makes it possible to increase the adiabatic combustion temperature from 1866 °C to 2054 °C, respectively. It was found that as a result of the synthesis of the studied compositions, a composite material is formed based on Al₂O₃-SiO₂-ZrB₂ containing an oxide matrix with particles of zirconium diboride distributed from 61 to 77 wt. %. It was shown that in the synthesized material during the SHS of aluminum and silicon oxides, mullite is formed. It was shown that an increase in the fraction of the energy additive (Zr + 2B) leads to the refinement of structural elements, while an increase in the proportion of the energy additive in the materials under study is up to 30 wt. % leads to the formation of nanoscale grains of zirconium diboride.

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