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Production of ceramic composite materials based on the ZrO_2-Y_2O_3-SiO_2-TiB_2 system by the free SHS compression method

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Abstract: The objective of this paper is to study the process of free SHS compression of composite materials in the ZrO_2-Y_2O_3-SiO_2-TiB_2 system. The content of Y_2O_3 stabilizing additive varied in the ratio $(x–1)ZrO_2$-xY_2O_3 from 0 to 9 mol %. The influence of such technological parameters as the delay time, the strain rate, the pressing pressure, on the process of molding the selected materials, as well as the processes of phase and structure formation were studied. To establish the influence of the specified technological parameters on the process of selected materials molding, their formability was assessed. It was found that the nature of the dependences of the combustion characteristics of the studied materials on the content of the stabilizing additive correlates with the nature of the curves of the dependences of the degree of deformation on the delay time and the rate of deformation. It was shown that on the curve of the dependence of the degree of deformation on the pressing pressure, there is a limiting value, above which an increase in pressure does not affect the formability of the materials. It was shown that at a Y_2O_3 content of 0 to 4 mol %, the monoclinic and cubic modification of ZrO_2 is predominantly observed. A further increase in the Y_2O_3 content leads to the formation of a tetragonal modification of ZrO_2 in the obtained compact blanks. It was also found that in the studied materials the texture formation was observed in the direction perpendicular to the direction of pressure application.

Keywords: self-propagating high-temperature synthesis; free SHS compression; high-temperature deformation; zirconium oxide; yttrium oxide; composite material; titanium diboride; YSZ.

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Получение керамических композиционных материалов на основе системы ZrO_2-Y_2O_3-SiO_2-TiB_2 методом свободного СВС-сжатия

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Аннотация: Настоящая работа посвящена изучению процесса свободного СВС-сжатия керамических композиционных материалов в системе ZrO_2-Y_2O_3-SiO_2-TiB_2. В качестве объекта исследования выбрана исходная порошковая система B_2O_3-Zr-SiO_2-Ti-B-Y_2O_3. Содержание оксида иттрия, выступавшего в качестве стабилизирующей добавки, варьировалось в соотношении $(x–1)ZrO_2$-xY_2O_3 от 0 до 9 % моль. В работе изучено влияние таких технологических параметров свободного СВС-сжатия, как время задержки между инициированием реакции и приложением давления, скорость деформации, давление прессования на процесс формования выбранных объектов исследования, а также процессы фазо- и структурообразования. Для установления влияния указанных технологических параметров на процесс формования выбранных объектов исследования в работе проводилась оценка их формуемости. Установлено, что характер зависимостей характеристик горения исследованных материалов от содержания стабилизирующей добавки коррелирует с характером кривых

зависимостей степени деформации от времени задержки между инициированием реакции и приложением давления и скоростью деформирования. Показано, что на кривой зависимости степени деформации от давления прессования существует предельное значение, выше которого увеличение давления не оказывает влияния на формуемость материалов. Показано, что содержание Y_2O_3 от 0 до 4 % моль в полученных материалах преимущественно наблюдается моноклинная и кубическая модификация ZrO_2. Дальнейшее увеличение содержания Y_2O_3 приводит к формированию тетрагональной модификации оксида циркония в полученных компактных заготовках. Также установлено, что в исследованных материалах после свободного СВС-сжатия наблюдалось образование текстуры в направлении, перпендикулярном направлению приложения давления.

Ключевые слова: самораспространяющийся высокотемпературный синтез; свободное СВС-сжатие; высокотемпературное деформирование; оксид циркония; оксид иттрия; композиционный материал; диборид титана; YSZ.

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1. Introduction

One of the urgent tasks of modern materials science is the development and creation of new materials with improved physical, mechanical and operational properties. One of the areas experiencing the need for such materials is the industry associated with high-temperature production, where materials are required that can operate under conditions of high thermal and mechanical loads [1–3]. To solve this problem, a promising solution is the use of composite materials based on zirconium dioxide [4, 5]. Due to its outstanding properties, such as high melting point, high hardness, fire resistance and chemical inertness, as well as a fairly low density [6], zirconium dioxide is the subject of a large number of research studies. In addition, by creating composite materials based on ZrO_2, it is possible to improve its mechanical and operational properties. Today, a large number of different composite materials have been developed based on zirconium oxide with additives of aluminum oxide [7–9], magnesium oxide [10], silicon carbide [11], boron nitride [12, 13], molybdenum disilicide [14, 15], etc. It is known that the introduction of silicon oxide into a matrix based on ZrO_2 increases the refractory properties of the latter [16, 17]. In addition, the introduction of TiB_2 improves the tribological properties of materials based on zirconium dioxide [18, 19].

When making materials and products from zirconium dioxide-based ceramics, it is necessary to take into account that ZrO_2 undergoes a number of polymorphic transformations when heated [20, 21]. Namely, when heated to a temperature of 1170 °C, a transition from the monoclinic modification to the tetragonal one occurs, and when heated to 2370 °C, from the tetragonal to the cubic one. When cooling, the reverse transition occurs, and the monoclinic modification is stable at room temperature. At the same time, the tetragonal modification is promising for high-temperature application. To prevent the transition from the tetragonal modification of ZrO_2 to the monoclinic one, various stabilizing additives are used. For example, CaO [22], MgO [23], CeO_2 [24], while Y_2O_3 is one of the most frequently used stabilizing additives [25].

Various methods are used to synthesize materials based on stabilized zirconium dioxide, including, the sol-gel method [26, 27], hydrothermal [28, 29], mechanochemical [30, 31], carbothermal synthesis [32], etc. To produce compact blanks, the materials produced by the listed methods are subsequently consolidated. For this purpose, sintering and various methods of force compaction are used, for example, hot isostatic pressing [33] or spark plasma sintering [34]. A common feature of this approach is a large number of technological operations, the need to use complex technological equipment, as well as high energy costs due to the need for long-term high-temperature processing. From this point of view, a combination of self-propagating high-temperature synthesis (SHS) [35] and subsequent high-temperature shear deformation is promising for obtaining composite materials based on stabilized ZrO_2. Based on the specified combination, the free SHS compression method was developed [36–39]. Among the advantages of this method, it is possible to note the absence of complex technological equipment, the absence of the need to use external heating, and short process times. To date, compact blanks from various ceramic and metal-ceramic materials have been obtained using the free SHS compression method.

This paper seeks to investigate the effects of various process parameters in free SHS compression on the molding, phase, and structural formation

Table 1. Ratio of initial materials of the B_2O_3-Zr-SiO_2-Ti-B-Y_2O_3 composition

Composition No	Initial materials ratio, wt. %					Expected composition of synthesis products, wt. %					Y_2O_3 content, mol %
	B_2O_3	Zr	SiO_2	Ti	B	Y_2O_3	ZrO_2	Y_2O_3	SiO_2	TiB_2	
0	24.4	48.1	10.6	16.9	0	0	65	0	10.6	24.4	0
1	24.1	47.2	10.6	16.9	0	1.2	63.8	1.2	10.6	24.4	1
2	23.6	46.4	10.6	16.9	0.2	2.3	62.7	2.3	10.6	24.4	2
3	23.2	45.5	10.6	16.9	0.3	3.5	61.5	3.5	10.6	24.4	3
4	22.8	44.7	10.6	16.9	0.4	4.6	60.4	4.6	10.6	24.4	4
5	22.4	44	10.6	16.9	0.5	5.6	59.4	5.6	10.6	24.4	5
6	22	43.1	10.6	16.9	0.6	6.8	58.2	6.8	10.6	24.4	6
7	21.5	42.3	10.6	16.9	0.8	7.9	57.1	7.9	10.6	24.4	7
8	21.1	41.4	10.6	16.9	1	9	56	9	10.6	24.4	8
9	20.7	40.7	10.6	16.9	1.1	10	55	10	10.6	24.4	9

of ceramic plates derived from stabilized zirconium oxide materials. Specifically, we will examine the influence of delay time between the initiation of the reaction and the application of pressure, the rate of deformation, and the pressing pressure.

2. Materials and Methods

2.1. Initial materials and their ratio

The following powders were used as initial materials: boron oxide (> 99 %, < 2 μm), titanium (99.1 %, < 50 μm), silicon oxide (< 1 μm, > 99.3 %), zirconium (> 99 %, < 50 μm), boron (99.5 %, 10 μm), and yttrium oxide (99.95 %, < 10 μm). These powders were kept in a drying oven for 12 hours at a temperature of 50 °C to remove adsorbed moisture. Then, these raw materials were mixed in a ball mill for 12 hours in the ratios shown in Table 1.

2.2. SHS compression method

To study the dependencies of the process parameters of free SHS compression, the formability of the selected objects of study was assessed under conditions of a combination of SHS and high-temperature shear deformation processes. To conduct experiments to assess the formability, cylindrical blanks with a diameter of 30 mm and a height of 35 mm were prepared from the obtained mixtures of the initial reagents by the method of cold uniaxial pressing. The resulting blanks had a relative density of 0.65–0.70. These values of relative density correspond to the optimal range in which the maximum values of the combustion characteristics of the selected objects of study are realized. Then, the resulting blanks were installed in a press; SHS was initiated by a tungsten spiral with a diameter of 1 mm, after which, after a certain delay time, external pressure was applied. Then, the degree of deformation Ψ was calculated for the deformed sample, which is taken as a criterion for the formability of the synthesized material. This value is expressed through the relative change in the cross section of the sample after deformation. The formula for calculating the degree of deformation is as follows:

$$\Psi = 1 - \frac{S_i}{S_f},$$

where S_i is cross-sectional area of the original sample before deformation, mm^2; S_f is cross-sectional area of the synthesized material after deformation, mm^2.

Since the cross-section of the synthesized material after deformation is close to a circle, the average value is taken to calculate S_f:

$$S_f = \pi(d_{\max} + d_{\min})^2 / 16,$$

where $d_{\max}, d_{\min}$ are maximum and minimum diameters of the synthesized material after deformation. The process diagram is shown in Fig.1.

To study the influence of the combination of SHS and high-temperature shear deformation processes on the processes of phase and structure formation, compact ceramic materials based on the ZrO_2-Y_2O_3-SiO_2-TiB_2 system were obtained by the free SHS compression method. The scheme of the experiments on free SHS compression is shown in Fig. 2.

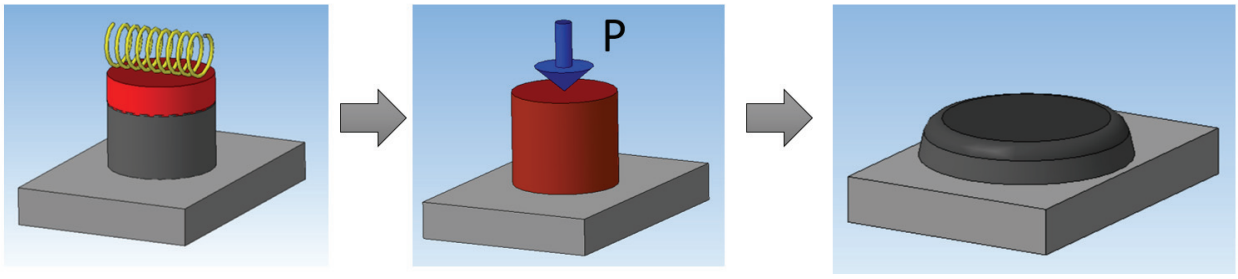

Fig. 1. Scheme of experiments to study formability

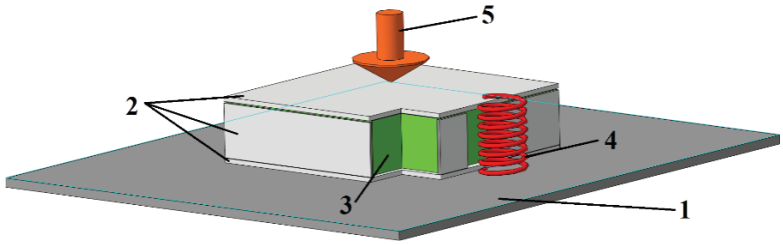

Fig. 2. Scheme of the free SHS compression process: *1* – substrate; *2* – asbestos insulation; *3* – original sample; *4* – tungsten spiral; *5* – direction of pressure application

The initial blank *3*, made by cold uniaxial pressing, was installed on the metal substrate *1*. The height was determined by the previously obtained value of the optimal relative density for each studied composition. The initial blanks were covered with thermal insulation *2* on each side. Synthesis was initiated by a tungsten spiral *4*. After the combustion wave passed through the volume of the blank, after a certain delay time, external pressure was applied in the direction *5*, perpendicular to the direction of front propagation.

2.3. Analytical methods

X-ray diffraction analysis (XRD) was performed on a DRON-3 diffractometer with a graphite monochromator on a secondary beam (CuKα radiation). The diffraction patterns were recorded in the step-by-step scanning mode in the angle range of $2\theta = 20–80°$ with a step of 0.025° and an exposure of 4 s per point. The obtained diffraction patterns were analyzed using the ICDD PDF2 powder diffraction database (2022). The microstructure of the obtained materials was studied by scanning electron microscopy (SEM) using a Carl Zeiss LEO 1450 VP electron microscope.

3. Results and Discussion

3.1. Combustion characteristics in SHS mode

In this paper, a ceramic composite material based on yttrium oxide-stabilized zirconium oxide (YSZ) ZrO_2-Y_2O_3-SiO_2-TiB_2 was chosen as the object of study was. The proportion of the stabilizing additive Y_2O_3 was from 0 to 9 mol %. The synthesis of materials in the SHS mode proceeded due to the reduction of boron oxide by zirconium with the formation of zirconium oxide and the release of free boron, which interacted with titanium to form titanium diboride. Silicon dioxide did not participate in the reaction in this case. When the stabilizing additive Y_2O_3 was introduced into the initial system, the total amount of oxygen increased. To reduce it, the proportion of boron oxide was reduced in compositions 1–9, which also led to a decrease in the amount of boron in the system. To compensate for this decrease, additional free boron was introduced into compositions 2–9. The use of boron oxide in this work is due to the fact that it is a cheap and readily available compound, the reduction reaction of which has a high thermal effect, which made it possible to obtain refractory zirconium oxide without significant energy costs. In addition, boron oxide is a cheap source of boron for the synthesis of titanium diboride. Below are the equations of the expected chemical reactions occurring during SHS:

$$2B_2O_3 + 3Zr \rightarrow 3ZrO_2 + 4B;$$

$$4B + 2Ti \rightarrow 2TiB_2;$$

$$ZrO_2 + Y_2O_3 \rightarrow (ZrO_2)_{1-x}(Y_2O_3)_x\,.$$

It is also worth noting that, according to the XRD results, zirconium diboride phase was obtained in some samples. This means that part of the boron

was spent on interaction with zirconium and did not interact with titanium. At the same time, the reaction of ZrB_2 formation has a high thermal effect (–76 kcal·moL^{-1}), the value of which is close to the thermal effect of TiB_2 formation (–70 kcal·moL^{-1}). Thus, it can be assumed that the total thermal effect of the synthesis process did not change.

It was previously shown [69] that a change in the content of the stabilizing additive Y_2O_3 can affect the combustion characteristics of SHS systems. Thus, in the initial B_2O_3-Zr-SiO_2-Ti system for the material without a stabilizing additive, the values of the temperature and combustion rate were 1808 °C and 5.1 mm·s^{-1}, respectively. Further, with the introduction of Y_2O_3, a monotonic increase in the temperature and combustion rate to values of 1836 °C and 8 mm·s^{-1} was observed at a Y_2O_3 content of 5 mol %. With a further increase in the Y_2O_3 content, a monotonic decrease in the combustion characteristics to 1784 °C and 5.1 mm·s^{-1} was observed at a Y_2O_3 content of 9 mol %. The dependences of the temperature and combustion rate of the studied materials on the Y_2O_3 content are shown in Fig. 3. Such behavior of the combustion characteristics can be explained by the fact that during the transition from the high-temperature tetragonal to the low-temperature monoclinic modification of ZrO_2, a significant (up to 6 %) increase in volume is observed, the sample of composition 0 experiences more significant heat losses than the samples in which ZrO_2 is stabilized. Thus, increased heat losses lead to the fact that the samples of composition 0 have a lower combustion temperature than the samples with the addition of Y_2O_3. According to the XRD results, zirconium diboride was observed in the synthesis products of samples of compositions 0–4, while its amount monotonically decreased correlating with an increase in the combustion temperature of these samples. Zirconium diboride was not observed in the synthesis products of the sample of composition 5, thus the reaction of boron oxide reduction proceeded completely, and this sample had the highest combustion temperature. Further, with an increase in the Y_2O_3 content in the studied samples, a decrease in the combustion temperature was observed due to the dilution of the original system with yttrium oxide. The stabilizing additive Y_2O_3 was inert, did not participate in the reaction of product synthesis, but interacted with zirconium oxide to form a solid solution upon cooling.

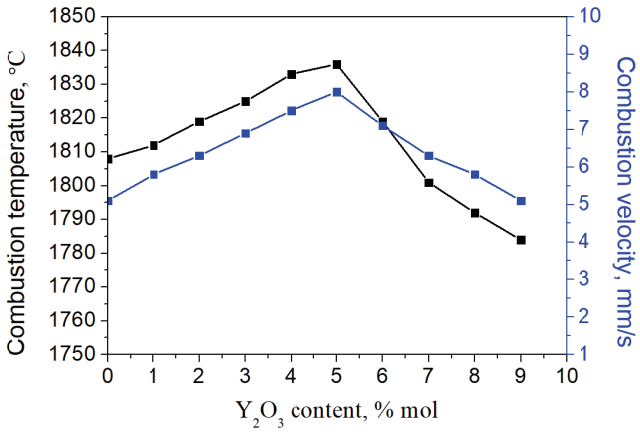

Fig. 3. Dependences of temperature and combustion rate of the studied materials on the Y_2O_3 content

3.2. High-temperature shear deformation of research objects

One of the important process parameters influencing the process of producing compact blanks by the free SHS compression method is the delay time. Ceramic materials are difficult to deform due to their mechanical properties and high melting point. Producing such materials in the SHS mode leads to the fact that the synthesis products are in a state heated to high temperatures (characteristic SHS temperatures are 1800–2500 °C). As a result, ceramic materials acquire the ability to high-temperature deformation. In addition, the SHS process is not only the synthesis of materials in the combustion wave, but also the processes of phase and structure formation occurring behind the combustion front. This leads to the fact that for ceramic materials obtained in the SHS mode, there is an optimal temperature-time interval of processing, within which, under the action of high-temperature shear deformation, it is possible to obtain compact blanks with minimal porosity. When leaving this interval, structural defects and pores will form in the obtained samples. Thus, at small values of the delay time, due to the low completeness of the reaction of the initial components, the processes of phase and structure formation in the deformed samples may not be completed. In addition, since the characteristic temperatures of SHS often exceed the melting temperatures of most of the initial components, as well as some synthesis products, an excess amount of liquid phase may form in the deformed samples. The presence of a liquid phase has a positive effect on the ability of ceramic materials to high-temperature deformation. However, if there is an excess of it during deformation, the liquid phase will be squeezed out of the blank, causing deterioration of the phase composition, structure and an increase in

porosity. If the delay time is excessive, the materials lose their ability to plastically deform due to cooling, which also leads to the occurrence of defects and cracks in the resulting blanks. Figure 4 shows the results of studying the effect of the delay time before applying pressure on the formability of the studied materials of compositions 0–9. As can be seen from Figure 4, for composition 0 without a stabilizing additive, the maximum value of the degree of deformation was 0.6. Further, with an increase in the proportion of Y_2O_3, the maximum value of the degree of deformation monotonically increases to 0.75 (composition 5), after which it monotonically decreases to a value of 0.53 for composition 9. This type of dependence of the degree of deformation on the delay time correlates with the behavior of the dependences of the temperature and combustion rate on the proportion of Y_2O_3, shown in Fig. 3. Namely, an increase in the content of yttrium oxide to 5 mol % leads to an increase in the combustion temperature and an improvement in the formability of the studied materials (compositions 0–5), and then to a decrease in both the combustion characteristics and the formability of the materials (compositions 6–9).

Figure 5 shows the curves of the dependences of the degree of deformation of the studied materials on the deformation rate. This process parameter has a significant effect on the production of compact ceramic blanks by the free SHS compression method. This effect is due to the fact that it was previously shown that SHS products containing a sufficient amount of liquid phase can have viscoelastic properties. Since the combustion temperature of the studied compositions exceeds the melting temperatures of the initial components (T_m of titanium is 1668 °C, T_m of boron oxide is 450 °C), including silicon oxide (T_m is 1713 °C), which is an inert additive and is retained in the synthesis products, a sufficient amount of liquid phase is formed during SHS. As a result, the synthesis products are a solid-liquid suspension with viscoelastic properties, consisting of molten and partially unreacted initial components, as well as crystalline particles of the synthesis products. This leads to the fact that the viscosity of the synthesis products increases with the growth of the deformation rate. Thus, at high values of the deformation rate, due to the increase in the viscosity of the synthesized materials, the degree of deformation decreases, the formability of the materials worsens and macro and micro defects are formed. At low values of this parameter, the time of the SHS compression process increases, leading to cooling of the material, a decrease in its formability and the formation of defects.

As can be seen from Fig. 5, the dependence of the degree of deformation of the studied materials on the deformation rate also correlates with the dependences of the combustion characteristics shown in Fig. 3. With an increase in the proportion of the stabilizing additive and with an increase in the combustion temperature, the value of the deformation rate at which the maximum value of the degree of deformation is achieved decreases. The maximum value of the degree of deformation of 0.75 was obtained for composition 5 at the minimum value of the deformation rate among all the studied materials, namely 75 mm·s^{-1}. This is due to the fact that composition 5 has the highest melting point, and, as a result, as a result of SHS of this composition, the largest amount of solid-liquid suspension is formed, the viscosity of which increases with an increase in the deformation rate.

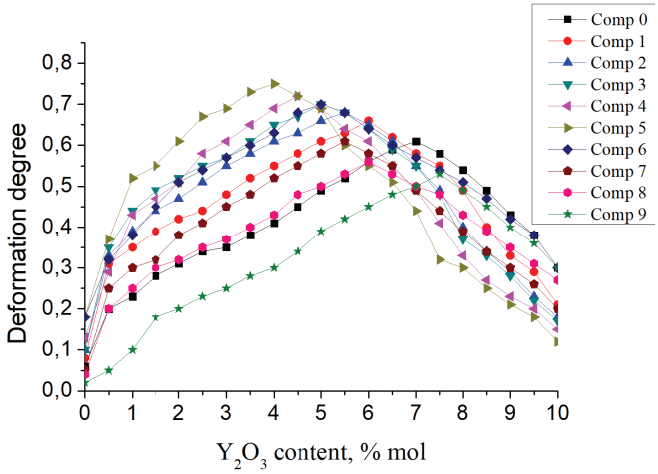

Fig. 4. Dependence of the degree of deformation of the materials under study on the delay time

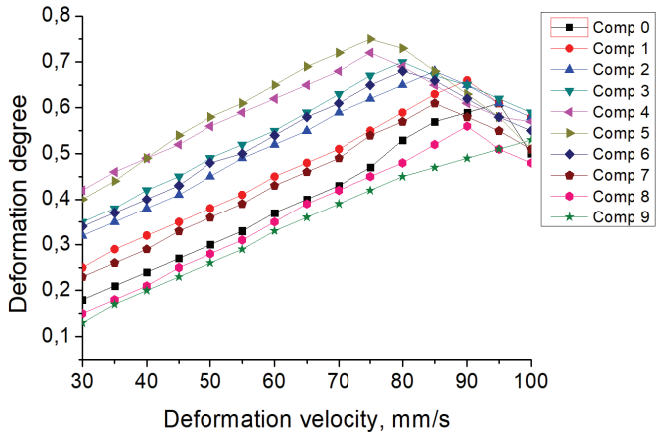

Fig. 5. Dependence of the degree of deformation of the materials under study on the deformation rate

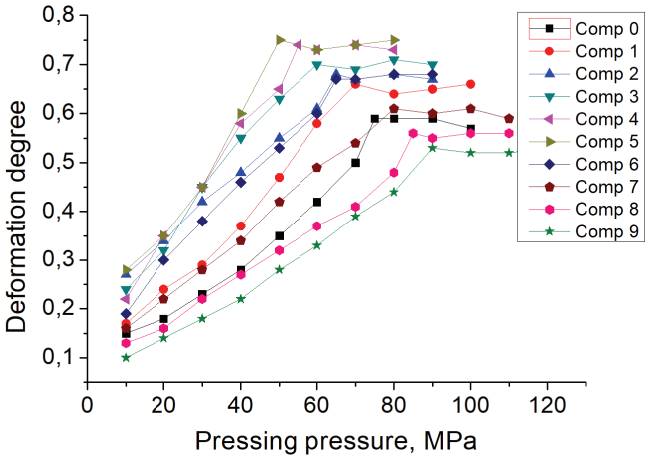

Fig. 6. Dependence of the degree of deformation of the materials under study on the value of pressing pressure

When studying the effect of pressing pressure on the process of molding ceramic blanks from the studied materials, it was found that there is a limiting value of this parameter, exceeding which does not further affect the molding process. Figure 6 shows the curves of the dependences of the degree of deformation of the studied materials on the pressing pressure. It is evident from the figure that the lowest value of pressing pressure required to achieve the maximum degree of deformation corresponds to composition 5 and is 50 MPa. Since this composition has the highest combustion temperature and, accordingly, has the greatest capacity for high-temperature deformation.

3.3. Phase composition and microstructure of the objects of study

When studying the effect of high-temperature shear deformation on the processes of phase and structure formation in the B_2O_3-Zr-SiO_2-Ti-B-Y_2O_3 system, it was found that in materials 0–4 after deformation, the formation of four phases was observed, namely monoclinic and cubic zirconium dioxide, as well as titanium and zirconium borides, Fig. 7. At the same time, silicon dioxide, which is part of the initial reagents, is not displayed on the X-ray diffraction pattern, since it has an amorphous structure. However, the X-ray diffraction results do not show any compounds with silicon, thus, it can be concluded that silicon dioxide is retained in the synthesis products. At the same time, in similar materials obtained without applying pressure, the cubic modification of zirconium dioxide was absent, and tetragonal and monoclinic ZrO_2 were formed. With increasing Y_2O_3 content in the starting materials (compositions 5–9), the samples obtained under free SHS compression conditions exhibited the formation of titanium diboride and tetragonal zirconium dioxide in the form of a solid solution $(Zr_{0.875}Y_{0.125})O_{1.938}$ (ICDD PDF2 cardNo 10-81-8290). At the same time, in similar materials obtained without applying pressure, the formation of tetragonal ZrO_2 in the form of a solid solution $(Zr_{0.75}Y_{0.25})O_{1.875}$ (ICDD PDF2 cardNo 10-81-8292) was observed.

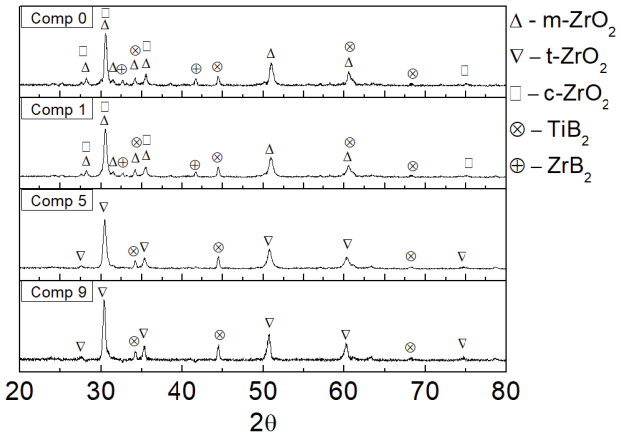

Fig. 7. Results of X-ray diffraction analysis of the materials under study produced by free SHS compression

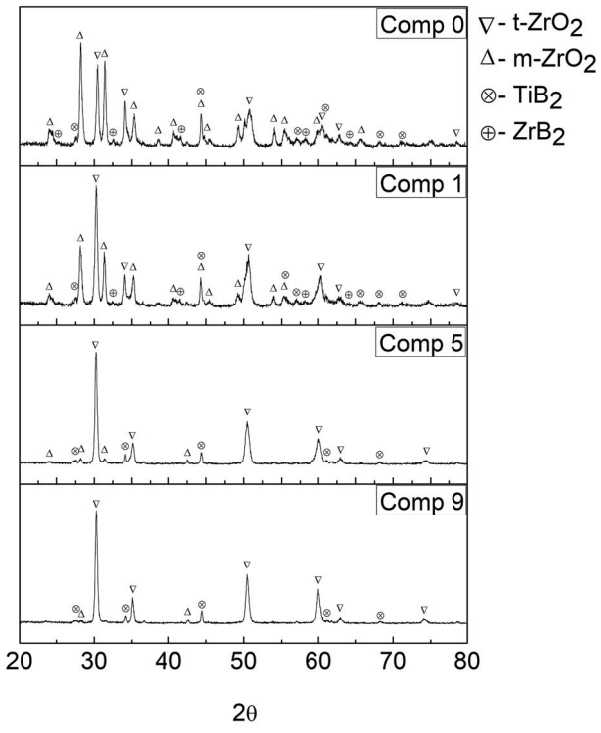

Fig. 8. SHS results of the produced materials without applying pressure

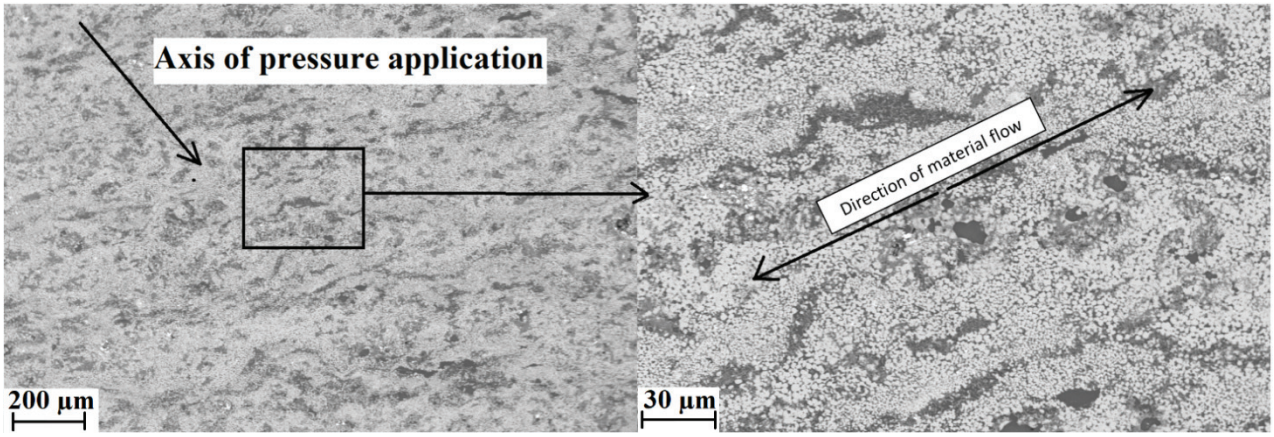

Fig. 9. SEM-images of the material based on composition 5 produced by the free SHS compression method

As the SEM-images of the produced compact ceramic materials showed, the formation of texture was observed in the structure of the samples obtained by the free SHS compression method. As shown in Fig. 9, during high-temperature shear deformation, the material is deformed in the direction perpendicular to the axis of pressure application, which promotes the healing of pores and cracks that may arise due to the nonequilibrium nature of the synthesis of materials in the SHS mode, as well as the formation of the corresponding texture.

In addition, it was found that for materials obtained in the B_2O_3-Zr-SiO_2-Ti-B-Y_2O_3 system, high-temperature shear deformation does not lead to a significant increase in particle size compared to materials obtained without applying pressure. Thus, the size of zirconium dioxide in materials obtained under free SHS compression conditions was 5–6 μm, while in materials obtained without applying pressure, the average particle size of ZrO_2 was 2–4.

4. Conclusion

Compact ceramic materials based on stabilized zirconium oxide in the initial B_2O_3-Zr-SiO_2-Ti-B-Y_2O_3 powder system were produced using the free SHS compression method. The proportion of the stabilizing additive in the $(1–x)ZrO_2$-xY_2O_3 ratio was from 0 to 9 mol %. The influence of such process parameters of free SHS compression as the delay time between reaction initiation and pressure application, deformation rate, pressing pressure on the molding process, as well as on the processes of phase and structure formation of compact materials based on the above materials was studied. It was found that the dependences of the deformation degree of the studied materials on the delay time between reaction initiation and pressure application, deformation rate and pressing pressure correlate with the dependences of the combustion characteristics of the studied materials on the Y_2O_3 content. The dependences of the deformation degree on the delay time of all the studied materials have a maximum, after which their ability to plastic deformation decreases. Thus, there is an optimal time interval for processing the studied materials by the free SHS compression method. It is shown that with an increase in the content of the stabilizing additive from 0 to 5 mol %, the maximum degree of deformation increases from 0.6 to 0.75. It was also found that an increase in the Y_2O_3 content to 5 mol % makes it possible to achieve the maximum value of the degree of deformation of 0.75 for the studied materials at a deformation rate of 75 $mm \cdot s^{-1}$. An increase in the Y_2O_3 content makes it possible to achieve the maximum value of the degree of deformation for the studied materials at a minimum pressing pressure of 50 MPa. With a content of the stabilizing additive from 0 to 4 mol %, the obtained materials predominantly contain monoclinic and cubic modifications of ZrO_2. A further increase in the Y_2O_3 content leads to the formation of a tetragonal modification of zirconium oxide in the obtained compact blanks. It was also found that in the studied materials after free SHS compression, texture formation was observed in the direction perpendicular to the direction of pressure application.

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6. Conflict of interest

The authors declare no conflict of interest.

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