Influence of electron-beam heating modes on the structure of composite ZrO$_2$-Al$_2$O$_3$ ceramics

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Abstract. The article presents the results of electron beam sintering of composite ceramics based on Al$_2$O$_3$ and ZrO$_2$ powders. Samples were made with different contents of Al$_2$O$_3$ and ZrO$_2$ components and different pressing pressures. Sintering was carried out in vacuum at a helium pressure of 30 Pa. An electron beam generated by a forevacuum plasma electron source was used for sintering. It is shown that the sintering result depends on the pressing pressure and the percentage of components. The influence of the geometry of the samples and their composition on the temperature drop over their volume during sintering has been determined.

1. Introduction

Scientific advances in the field of materials science and the constant need for modern materials capable of satisfying the necessary properties and qualities have led to the emergence of a new class of materials called functional-gradient materials (FGM). They represent the second generation of composite materials and usually consist of them [1].

The main advantage of FGM, consisting of similar components as composites, is the spatial change in physical and chemical properties, structure, grain size, density, and much more from layer to layer [2]. These properties in a functionally gradient material change smoothly, which makes them more reliable and preferred in many fields of science and technology.

The FGM composition usually includes at least one metallic phase. However, in recent years, much attention has been paid to ceramic-ceramic and glass-ceramic systems due to their extensive properties. Ceramic materials are designed for various operating conditions in aggressive liquids and gases, and also tolerate mechanical and thermal effects well. Functional ceramics is a modern material with unique properties and characteristics, which is capable of combining several properties that were not previously combined with each other [3, 4]. Due to its ability to withstand high temperature gradients, it is used in the aerospace industry. This material is used to construct aircraft bodies, rocket engine components and many other elements used in space [5]. Functional ceramic can also be used in the field of optoelectronics, due to the gradient refractive index for these materials [6]. The production process is one of the most important areas of functional ceramic research. Most of the functional ceramic manufacturing processes are based on variations of traditional processing methods that are already well known.

Techniques that are capable of performing the gradation step include powder metallurgy [7], sheet lamination, chemical vapor deposition, and coating processes. Typically, the molding methods used
include centrifugal casting [8], strip casting, and thermal spraying [9, 10]. The choice of method mainly depends on the combination of materials, the required functionality and the geometry of the required component.

The work [11] presents successes in the use of a forevacuum plasma electron source to create FGM ceramic materials based on aluminum oxide and zinc oxide. Forevacuum plasma electronic sources are successfully used for sintering ceramics, electron-beam welding of cermet units, processing of quartz glass and other technologies for processing dielectrics [12, 13]. The electron beam generated by such sources is capable of rapidly heating the sample surface to a temperature of about 1400 degrees Celsius. Plasma formed during the propagation of the beam in the gas neutralizes the negative charge of the surface irradiated by the electron beam [14]. The purpose of this study is to determine the influence of the pressing pressure and the composition of the samples on the possibility of electron-beam sintering of materials based on aluminum and zirconium oxides in the forevacuum pressure range.

2. Experimental setup
Experiments on electron beam sintering were carried out using a forevacuum plasma electron source 1 located on a vacuum chamber 2, figure 1. The electron beam 3 with a diameter of 1 mm, current of up to 50 mA and electron energy of up to 10 kV was directed to a sintered sample 4 located in a graphite crucible 5.

![Figure 1. Experimental setup: 1 - forevacuum plasma source of electrons; 2 - vacuum chamber; 3 - electron beam; 4 - compressed sample; 5 - graphite crucible; 6 - pyrometer; 7 - thermocouple; 8 - multimeter.](image)

The crucible was located at 45 cm from the electronic source. The choice of the crucible material is due to its high temperature resistance and ease of processing. To measure the temperature during heating and sintering, we used a RAYTEK1NM infrared pyrometer 6 located on the same flange as the electronic source. To measure the temperature of the sample not exposed to irradiation, we used a platinum – platinum-rhodium thermocouple 7 and a voltmeter 8. To ensure a close thermal contact of the thermocouple junction with the sample surface, a 0.5 mm depression was made in it. The thermocouple junction was placed in this depression. The sample was heated for twenty minutes. During heating, the power of the electron beam was increased from 20 to 200 W while the heating rate was 70 K/ min. When the surface temperature of the sample reached 1400°C, heating was stopped and the sample was kept at a constant temperature for 5 min. After exposure, the power of the electron beam gradually decreased to 20 W. After switching off the plasma source, the sample was cooled for some time (10–15 min) in vacuum.

Samples for sintering were made from fine-grained powders of aluminum and zirconium oxides. Cold static pressing in a closed mold was used [15]. The pressing pressure was 50, 100, 150 kgf / cm².
The sample either delaminated during removal from the mold, or collapsed further upon electron-beam heating. The density of the samples pressed at pressures of 100 kgf/cm$^2$ and 150 kgf/cm$^2$ did not differ significantly, so a pressure of 100 kgf/cm$^2$ was chosen.

Since the types of ceramics used (aluminum oxide and zirconium oxide) differ in thermophysical properties, in particular in the thermal conductivity coefficient, and the sintering temperature, two batches of 5 samples were made. Each batch had the same samples, the difference was in the thickness of the layers of materials. The first batch of samples consisted of four layers with the same thickness - 0.75 mm. The thickness of the layers in the second batch varied from layer to layer. The thickest was the material with higher thermal conductivity - aluminum oxide. According to our assumptions, a higher thermal conductivity will make it possible to reduce the total temperature difference over the thickness of the irradiated sample. The composition of the samples and the modes of pressing are presented in table 1.

| Layer No. | Layer composition (wt.%) | Sample type 1 | Sample type 2 |
|-----------|---------------------------|---------------|---------------|
| 1         | ZrO$_2$ (100)             | 0.75          | 0.4           |
| 2         | ZrO$_2$ - Al$_2$O$_3$ (70/30) | 0.75          | 0.6           |
| 3         | ZrO$_2$ - Al$_2$O$_3$ (30/70) | 0.75          | 0.8           |
| 4         | Al$_2$O$_3$ (100)         | 0.75          | 1.2           |

### 3. Experimental results and discussion

As a result of electron-beam sintering, samples were obtained, the parameters of which before and after sintering are given in table 2. The designations in the table and below are $d$ – diameter, $h$ – height, $m$ – mass, $\rho$ – sample density, $\Delta \rho$ – relative change in density.

| Sample type 1 | Sample type 2 |
|---------------|---------------|
| before        | after         | before        | after         |
| $m$ (g)       | 10.17         | 9.69          | 10.2          | 9.4           |
| $d$ (mm)      | 3.43          | 3.27          | 3.35          | 3.3           |
| $h$ (mm)      | 0.622         | 0.597         | 0.562         | 0.537         |
| $\rho$ (g/cm$^3$) | 2.2335       | 2.4769        | 2.0541        | 2.346         |
| $\Delta \rho$ (%) | 10.9         | 14.2          |               |               |

As can be seen from table 2, the volume and weight of all samples after sintering decreased, and the density increased. The highest density of 2.346 g/cm$^3$ was found for a sample consisting of layers of various thicknesses. Such an increase in density may be associated with a difference in the shrinkage coefficient of the sample components. Sample 2 contains a larger amount of alumina than sample 1, the shrinkage coefficient of which is higher than that of zirconium oxide.

The time dependence of the temperature of the irradiated side $T_1$ (curve 1), the non-irradiated side $T_2$ (curve 2), and their difference $\Delta T$ (curve 3) for samples of the first type are shown in figure 2.

As can be seen from figure 2, when the samples are heated, the irradiated side is heated more strongly. Even after holding for 10 minutes, the temperature of the non-irradiated side remains significantly lower than the temperature of the irradiated one. The maximum temperature difference between the irradiated side and the unirradiated side was $\Delta T = 670^\circ$C. Such a temperature difference is undesirable in the case of sintering a sample consisting of one material - aluminum oxide or zirconium oxide. However, in the case of compact sintering, the effect of the drop can be leveled by the selection of components with different sintering temperatures and thermophysical properties, as well as different layer thicknesses.
Figure 2. The time dependence of temperature for the sample type 1.

Figure 3. The time dependence of temperature for the sample type 2.

Figure 3 shows the time dependence of temperature during heating for sample type 2.

As can be seen from figure 3, a decrease in the thickness of the zirconium oxide layer having a lower thermal conductivity coefficient led to a decrease in the temperature drop across the sample thickness. The temperature of the non-irradiated side reached the mark \( T_2 = 1052^\circ\text{C} \). The maximum temperature difference for the entire time was \( \Delta T = 352^\circ\text{C} \).

4. Conclusion
The results of electron-beam sintering of composite ceramics based on aluminum and zirconium oxide are presented. It is shown that the result of sintering depends on the pressing pressure of the samples when preparing them from powders, as well as on the thickness of the layers of aluminum and zirconium oxides. The most optimal for sintering was the pressing pressure of 100 kgf / cm². The use of alumina and zirconium oxide layers for sintering samples with different thicknesses makes it possible to reduce the temperature drop from 670 to 350 degrees, which ensures more uniform heating and sintering of composite ceramics.

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