Influence of the composition of Al$_2$O$_3$-ZrO$_2$ ceramics on the distribution of thermal fields during its electron beam sintering

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Abstract. The article presents the results of sintering a composite graded ceramic based on Al$_2$O$_3$ / ZrO$_2$ using a focused electron beam. To prevent surface charging, sintering was carried out in the forevacuum pressure range. It was demonstrated that under electron beam exposure, the surface temperature reaches 1600 degrees within 20 minutes. The distribution of elements over the depth of sintered specimens is presented. The dependence of the temperature difference over the sample as a function of the number of layers in the sample is shown. The value of the temperature drop along the depth of the sintered sample is calculated and recommendations are given for reducing the temperature drop.

1. Introduction
The acceleration of the dynamics of using ceramic-ceramic composites [1] in various branches of modern industry is associated primarily with the unique properties of such materials. Ceramic composites are distinguished by high resistance to corrosion in aggressive environments and temperatures, high values of mechanical and thermal resistance in a wide temperature range. Composites are used for the manufacture of critical structural parts in aircraft or automobile factories [2] or in nuclear power plants and in the aerospace industry [3], [4], medical instruments and implants [5-7]. Among ceramic composites, materials based on ZrO$_2$ and Al$_2$O$_3$ stand out. The high flexural strength and fracture toughness of zirconium oxide, combined with the chemical inertness and hardness of Al$_2$O$_3$, make them widely used as structural and functional ceramics. At present, various methods have been developed for preparing ZrO$_2$ and Al$_2$O$_3$ ceramic-ceramic composites: pressureless sintering [8], hot or cold uniaxial pressing, hot isostatic pressing, spark plasma sintering, microwave sintering, layer-by-layer laser sintering [9–11]. Sintering of ZrO$_2$ and Al$_2$O$_3$ ceramic-ceramic composites by traditional methods requires heating to a high temperature of 1600-1750 °C and maintaining it for a long time, which leads to undesirable grain growth [12].

Earlier we described in [13-14] a decrease in the sintering time while maintaining a relatively low temperature during isothermal holding. An electron beam propagating at a pressure of 10 Pa in a vacuum chamber was used to influence a pre-compressed ceramic sample consisting of several layers of ceramics of various compositions. A flux of high-energy electrons was directed to the sample, and due to the kinetic energy of electrons entering its surface, the ceramic sample was heated to the required temperature. In this case, the beam plasma neutralizes to a high degree the processes of charging the irradiated surface [15]. Due to this property, this type of sources can be used for...
processing of ceramic materials and glasses, in particular, sintering, welding of cermets, making holes in quartz glass [16-17]. The advantage of this method is the direct transfer of energy to the surface of the sample, without the need to warm up the crucibles and holders in which the sample is fixed with other methods. In addition, heating of the compact under beam irradiation also occurs due to the flow of current through its volume [18].

When a ceramic composite is irradiated with an electron beam, it is impossible to ensure that accelerated electrons hit all sides of the sample, since, as a rule, the sample is located on a stationary crucible. In this connection, a temperature gradient inevitably arises along the depth of the sample during sintering. The magnitude of this difference can be several hundred degrees, which will lead to a decrease in the sintering rate or to the impossibility of its implementation. The temperature drop depends on the thermophysical properties of the materials, the thickness and the number of layers of materials from which the ceramic-ceramic composite is made.

This work presents the results of studying the effect of electron-beam irradiation modes, as well as composition on the temperature distribution over the volume of a sintered ceramic-ceramic composite based on ZrO₂ and Al₂O₃.

2. Materials and methods
The experiment was carried out in a vacuum installation using a source of a narrowly focused electron beam. The electron source formed an electron beam. The energy of electrons was up to 10 keV, the current of up to 100 mA [19]. The experimental setup is shown in Figure 1.

![Figure 1. Schematic of the setup for electron beam sintering in the forevacuum pressure region: 1 - forevacuum plasma electronic source; 2 - vacuum chamber; 3 - magnetic focusing system; 4 - electron beam; 5 - processed compact; 6 - crucible; 7 - source of discharge voltage; 8 - source of accelerating voltage; 9 - pyrometer.](image)

An electron beam with 1 mm in the diameter was directed to a crucible and a sintered ceramic sample. The magnetic scanning system made it possible to scan the beam in a square, thereby providing a more uniform heating of the sample surface. The scanning frequency was 100 Hz. The scanned area was the same size as the crucible, i.e. was 2-3 mm larger than the sample diameter. Sintering was carried out in an atmosphere of grade A helium (the volume fraction of pure helium is 99.995%) at a pressure in the vacuum chamber of 30 Pa. The working pressure was controlled by letting gas. By smoothly increasing the power of the beam, the sample was heated to a sintering temperature of 1600 °C for 20 minutes. The holding time at a given temperature value was 10 min.
After exposure, the power of the electron beam was reduced. The surface temperature was measured using a RAYTEK 1MH infrared pyrometer.

Samples were made from ZrO$_2$ and Al$_2$O$_3$ powders. The samples were cylindrical (diameter $- 10 \pm 0.05$ mm, thickness $- 3 \pm 0.1$ mm). The number of layers with different percentages of ZrO$_2$ and Al$_2$O$_3$ in each layer varied. Three batches of samples were made with 3, 6 and 11 layers. The first and last layers in each sample consisted only of pure alumina or zirconia. The sample of the first batch consisted of three layers: aluminum oxide, aluminum oxide 50% and zirconium oxide 50% (mass), zirconium dioxide. The samples in the second batch consisted of 6 layers. The Al$_2$O$_3$ content in the second sample differed by 20% from layer to layer. Samples from the third batch contained 11 layers. The change in the Al$_2$O$_3$ ratio between the layers was 10%. The sintered samples were studied on a Hitachi S-3400N microscope.

3. Experimental results and discussion

Three samples were obtained during sintering process, differing in composition and parameters. Analysis of the results showed that their average density was from 18 to 45%, depending on the number of layers, which is associated with shrinkage due to a decrease in pore size during sintering. The highest density value was obtained for a sample containing 6 layers. The density reached 81% of the theoretical (the theoretical density of such a composite is 5 g / cm$^3$), which is high enough for a sample sintered without applying pressure. The study of the distribution of elements over the volume of samples obtained on a Hitachi S-3400N microscope showed that the most uniform distribution is obtained for samples from the third batch, Figure 2.

![Figure 2](image.png)

**Figure 2.** Depth distribution of elements for a sample from the first batch - a, the second - b and the third - c.

The sample with 3 layers has abrupt changes in the concentration of elements between layers, Fig. 2 a. The second and third samples are characterized by the most gradual change in concentration associated with a large number of layers. A smoother distribution of particles in the samples should lead to an increase in its strength characteristics.

To obtain homogeneous sintering, the issue of the temperature distribution over the depth of the sintered sample during heating and holding is of no small importance. And if the temperature of the irradiated surface can be measured in a non-contact way using a pyrometer, then it is rather difficult to measure the temperature of the non-irradiated surface and in the depth of the sample. The temperature of the back side can be roughly estimated using a thermocouple, but its reading will greatly depend on the quality of contact with the sample surface. To estimate the temperature distribution over the sample depth, a computational model was used. A simplified schematic model of the compact and the crucible on which it is located is shown in Figure 3. The compact consisted of two layers with a total height of 3 mm and a diameter of 10 mm. Materials for the compact were selected from the extensive library provided in this program. The upper layer of the compact consisted of pure alumina, and the lower layer of pure zirconia. The thermophysical parameters of the oxides are presented in Table 1.
Table 1. Thermophysical parameters of pure \( \text{Al}_2\text{O}_3 \) and \( \text{ZrO}_2 \) used in the calculation model

| Parameter                  | Value for \( \text{Al}_2\text{O}_3 \) | Value for \( \text{ZrO}_2 \) |
|----------------------------|----------------------------------------|-----------------------------|
| Density, g/cm\(^3\)        | 3.9                                    | 6                           |
| Heat capacity, kJ/(kg·K)   | \(0.79 + 0.42 \times 10^{-3} \cdot T\) | \(0.54 + 0.13 \times 10^{-3} \cdot T\) |
| Thermal conductivity, W/(m·K) | \(2.1 + 1.9 \times 10^{-3} \cdot T\) | \(1.3 – 0.64 \times 10^{-3} \cdot T\) |

*Note: T – temperature of the material*

For the calculation, the parameters of the beam were set according to experiments. The beam power was set as a function of time based on the values from the mode for the third sample. The beam diameter was set equal to 10 mm, the beam power density distribution was chosen to be rectangular to simplify the calculations, i.e. uniform over the entire irradiated surface. The environmental parameters were also taken into account, the sample was in a helium environment at an ambient temperature of \( T_{\text{amb}} = 293 \) K and an absolute pressure of \( P_{\text{amb}} = 30 \) Pa.

Since, at an electron beam energy of 10 keV, the electron range in the irradiated material does not exceed several micrometers, the heating source was considered to be surface. The impact surface is the area of the base of the compact, from the side of the aluminum oxide. The heating time was 20 minutes, the holding time at constant temperature was 10 minutes and the cooling time was 10 minutes according to the experiment.

The calculation of the temperature field upon irradiation of the sample were carried out according to the model described in [20]. The values of the material parameters were taken as a function of temperature, according to Table 1.

The temperature in the bulk of the sintered sample and crucible was estimated from the solution of the heat conduction equation:

\[
\frac{\partial T}{\partial t} - \frac{\lambda}{c_p \cdot \rho} \Delta T = P_h(x, y, z, t) + P_{th}(x, y, z, t),
\]

where \( \lambda \) – coefficient of thermal conductivity; \( c_p \) – heat capacity coefficient; \( \rho \) – density; \( P_h(x, y, z, t) \) – the power density transmitted by the electron beam to the irradiated surface of the sample (during the irradiation time it was set equal to the power density of the electron beam \( P_h(x, y, z, t) = 4 \cdot U_a \cdot I_b / (\pi \cdot d_b^2) \)); \( P_{th}(x, y, z, t) \) – power density lost by surfaces due to thermal radiation \( P_{th}(x, y, z, t) = \varepsilon \cdot \sigma \cdot T^4 \), \( \varepsilon \) – emissivity, \( \sigma \) – Stefan-Boltzmann constant.

When replacing their derivatives with a difference approximation, the expression for calculating the temperature of a cell with indices \( i, j, k \) along the \( x, y, z \) axes, respectively, after the expiration of the time step \( \Delta t \), has the form:

\[
T_{i,j,k}^{t+\Delta t} = T_{i,j,k}^t + \Delta t \cdot \frac{\lambda}{c_p \cdot \rho} \left[ \frac{T_{i,j,k-1}^t + T_{i,j,k+1}^t + 2T_{i,j,k}^t}{\Delta x} + \frac{T_{i-1,j,k}^t + T_{i+1,j,k}^t}{\Delta y} + \frac{T_{i,j,k-1}^t + T_{i,j,k+1}^t}{\Delta z} \right] + P_h(x, y, z, t) + P_{th}(x, y, z, t),
\]

where the superscript \( t \) is the designation of the temperature at the previous moment in time, the superscript \( t + \Delta t \) is the temperature after the time step \( \Delta t \).

Setting all of the above parameters made it possible to calculate the distribution of the thermal field during the irradiation of the compact. As a result of calculations, within 1200 seconds or 20 minutes, the irradiated surface of the compact heats up to \( 1650 \) °C. Let us present a graph of the temperature
drop over the depth of the compact in order to determine the temperature of the back side. The temperature difference over the depth of the compact $x$ is shown in Figure 3.

![Figure 3. Temperature difference over the depth of a compact consisting of two layers](image)

The temperature of the back side of the compact increased to $1380 \, ^\circ\text{C}$, and it is also noticeable that the temperature varies linearly within the same material. Different thermophysical properties of sintered materials lead to differences in the value of the slope of the temperature dependence. The obtained temperature values from the processing side of the compact are in good agreement with the experimental values. The temperature of the compact from the side of its contact with the graphite crucible is difficult to measure experimentally, due to the difficulty of ensuring contact between thermocouple and compact.

To assess the effect of the thickness of the samples on the temperature difference between the irradiated and non-irradiated sides, heating calculations were carried out for various sample thicknesses from 1 to 10 mm, with the electron beam parameters unchanged at 210 W. The temperature difference was determined at the points of their greatest divergence. The results obtained showed that, as the sample thickness increases, it is quite expected that the temperature difference also increases. In this case, the temperature of the treated surface decreases by an average of 30 degrees with an increase in the thickness of the sample by 1 mm. The minimum temperature difference $\Delta T_{\text{min}}$ is 120 degrees, and this is with a sample thickness of 1 millimeter. For comparison, $\Delta T_{\text{min}}$ for a steel sample with a thickness of 1 mm is about 33 degrees and is explained by the low thermal conductivity of ceramics compared to metals, the thermal conductivity for alumina ceramics is 25 W / (m $\cdot$ °C) and for steel 45 W / (m $\cdot$ °C).

To reduce the temperature difference, one can use the technology of two-sided irradiation, as mentioned in [21]. Calculations have shown that in the case of using two-sided heating of the samples, the temperature difference decreases to 100 degrees, Figure 4.
As you can see from Figure 5, the minimum temperature value of the sample is shifted towards its side containing a larger amount of zirconium oxide. The minimum falls on the boundary of layers with 80 and 70% zirconium oxide. A decrease in the number of layers leads to a displacement of the region of minimum temperature towards the side with a high content of alumina. So, for a sample with three layers, the minimum temperature is located at the boundary of layers with pure zirconium oxide and a layer with 50% zirconium oxide, i.e. at the border of the first and second layers. The shift in the position of the temperature minimum is most likely due to the difference in the thermal conductivity coefficients of Al_2O_3 and ZrO_2. The higher thermal conductivity of zirconium oxide leads to greater heat removal from the irradiated surface, and since the irradiated surface is kept at a constant temperature, the magnitude of the temperature difference across the zirconium oxide is set at a high value. Aluminum oxide, having a lower value of the thermal conductivity coefficient, heats up under the same conditions to a greater depth, which leads to a shift of the temperature minimum region towards the side containing zirconium oxide. Such heating features should be taken into account when sintering composite ceramics when choosing materials with similar thermal conductivity for sintering, using thin specimens or applying the technology of double-sided irradiation.

4. Conclusion
Samples with a varying composition in depth were obtained. It is shown that the number of layers in a gradient composite ceramic does not affect the temperature drop across the sample depth. The calculated value of the temperature difference over the depth of the sample with a thickness of 3 mm was 100 degrees and did not change significantly when the number of layers changed from three to 11. In the case of double-sided heating, the region with the minimum temperature value in the depth of the sample is located at the boundary of layers with a predominant content of zirconium oxide. With an increase in the number of layers, this region shifts into the bulk of the sample. Such heating features should be taken into account when sintering composite ceramics when choosing materials with similar thermal conductivity coefficients for sintering or using thin specimens.

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