Electron-beam synthesis of graded metal-ceramic materials in the forevacuum pressure range

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Abstract. The results of using a forevacuum plasma electron source for obtaining gradient metal-ceramic materials are presented. The sintered material was located in a graphite crucible, which was heated by a wide electron beam to the temperature of 100 degrees lower sintering temperature for a given material. The sintering was carried out using a narrow-focused beam directed to the surface of the cermet powder. It is shown that when a coarse-grained aluminum oxide powder and fine-dispersed titanium powder are used, quite brittle samples are obtained. In the same time using of fine powder of aluminum and titanium, as well as their mixtures, allow to create a multilayer metal-ceramic sample with a variable composition, from titanium to aluminum.

1. Introduction
At present time, due to the intensive development of science and technology, it is required to obtain new promising materials which can be useful for the creation of wear-resistant coatings, the design of new microelectronic devices and devices for optoelectronics, as well as bioimplants, prosthetics, etc. It is known that abrupt changes in the composition and properties of materials often lead to abrupt surface tension [1]. However, if the transition from one material to another is smooth, then the surface tension is much lower. This concept is in the basis of functional gradient materials [2].

Functional gradient materials (FGMs) are a combination of various components, such as ceramics, metal, glass and so on, forming a strong continuous frame and metal binders, the content of which continuously varies in the volume of the material [3]. The main feature of functional graded metal-ceramic material is the presence of continuously changing properties from one surface of the material to another, such as chemical composition and crystal structure. In such cases, functionally graded metal-ceramic materials can possess properties of both ceramics (high hardness) and metal (high impact strength) [4].

Due to unique properties of FGMs, this kind of materials has become widely used in such industries as: military equipment for production of armored plates (protection from fragmentation shells); mining industry and metallurgy (creation of strong incisors for mining rocks and processing of complex metal alloys) [5]; medicine (manufacturing of dental crowns, prosthetics of artificial bones) [6]; chemical and nuclear industry (creation of crack-resistant materials) [7]; as well as the manufacture of meso- and nanostructures (MEMS / NEMS) [8]; and so on.

There are many methods for manufacturing volumetric products from functional gradient materials, for example, selective laser sintering and electron beam sintering, microwave heating and so on.
[9-13]. There is also a method of layer-by-layer sintering, which allows to create three-dimensional products on a given computer 3D model. In this method, laser radiation is often used for local heating of the material. Layer-by-layer sintering technologies using an electron beam are applied rarely, which is possibly connected with the need to eliminate a charge on the irradiated surface. The low electrical conductivity of the ceramic powder does not allow electrons to flow to the grounded parts of the holders and the vacuum chamber. Charging the surface can ultimately lead to a deflection of the electron beam from the processing place. The solution of this problem consists in using a forevacuum plasma source of electrons. The working pressure range of this type of source is the range of 1-100 pascals. As it is shown in [14, 15], the secondary plasma produced by the propagation of an electron beam in such pressure range makes leads to effective remove a charge from the irradiated dielectric surface. The purpose of this work was to investigate the ability of using a forevacuum plasma source to produce FGM based on alumina ceramics and titanium.

2. Experimental setup

For the synthesis of gradient metal-ceramics by an electron beam, an electron-beam setup equipped with two plasma electron sources was used. The scheme of the experimental setup is shown in figure 1. For electron-beam irradiation, two identical plasma electron sources located on different flanges of the vacuum chamber were used. The plasma electron source is a three-electrode system consisting of a cylindrical hollow cathode from stainless steel, a flat anode and an extractor [16]. The glow discharge was ignited between the hollow cathode and the anode. From the discharge plasma, electrons are extracted by an accelerating system consisting from an anode with a perforated electrode and an extractor. The perforated electrode in the anode is made in the form of a replaceable grating made from a 1 mm thick tantalum plate. To obtain a large emission current in an electronic source located on the side flange of the vacuum chamber, a 120-hole grid was used. To obtain the minimum diameter of the electron beam (of the order of 1 mm) in an electron source located on the upper flange, a single-hole emission grid was used [17].

Figure 1. The scheme of the experimental setup. 1 – plasma source of focused electron beam, 2 – sintered powder mixture, 3 – plasma source of wide electron beam, 4 – graphite crucible, 5 – infrared pyrometer, 6 – power supplies for electron guns.

The electron source No. 1 located on the side flange formed a powerful electron beam directed horizontally. This source of electrons was used to heat and maintain a given temperature of the
crucible during sintering. The electron source No. 2 was located on the upper flange of the vacuum chamber and formed a narrow-focused electron beam directed vertically downward. This source of electrons was used for accurately setting the temperature of the sintered sample and more uniformly warming it. The electron beam formed by the source No. 2 carried out a scanning along the surface of the sample.

The frequency of the scan determined the speed of the electron beam moving on the entire irradiated target area, and the scan scale determined the size of the irradiated area. It is worth noting that the use of a scanning electron beam is much more efficient than using a wide beam with a cross section commensurate with the sample area. The point is that the power density of the beam has a Gaussian distribution, which does not allow to evenly heat the sample for sintering.

In the process of work, it is necessary to take into account the thermal features of the sample material and the fact that high temperatures do not allow the use of a crucible from any material. So, the crucible made from graphite was used for experiments. To reduce the heat outflow, the crucible was placed on thin holders from tungsten wire with a diameter of 1 mm. This construction was covered with a heat shield to reduce heat flow due to thermal radiation.

3. Materials and methods of analysis

Alumina ceramic (Al$_2$O$_3$) and titanium (Ti) powders were used as the basis for the production of gradient metal-ceramics as the most common materials for the additive production of ceramic products. Two types of alumina powder differing in the size of the primary particles were used - the first type contained particles ranging in size from 1 to 10 $\mu$m; the particles of the other powder had dimensions of up to 30 $\mu$m and were in dense granules with a size of about 100 $\mu$m (figure 2).

![Particles of alumina used for layer-by-layer sintering (SEM image on Hitachi S3400n): a – fine powder, b – granular powder.](image)

**Figure 2.** Particles of alumina used for layer-by-layer sintering (SEM image on Hitachi S3400n): a – fine powder, b – granular powder.

For sintering, powder mixtures of aluminum oxide and titanium in the ratios (by weight) shown in table 1 were chosen. Powder mixture was located by a special dispenser in a cavity of the graphite crucible and then leveled. The powder was not pressed. Samples 1-6 contained one layer from powder mixtures of granular alumina and titanium. The thickness of the powder mixture layer was of the order of 1 mm. Sintering of sample 7 was carried out on a substrate from polished titanium. Sintering of the remaining samples was carried out in a crucible, without any substrate. Samples 7 and 8 contained 2 and 3 layers of different composition, respectively. The thickness of each layer was about 0.2 mm. To prepare the powder mixture for sample 8, fine alumina was used.
Table 1. Composition of a mixture of powders for sintering.

| Component content (% mass) |  |  |
|---------------------------|--|--|
|  | Al₂O₃ | Ti  |
| 1 | 100  | 0   |
| 2 | 80   | 20  |
| 3 | 60   | 40  |
| 4 | 40   | 60  |
| 5 | 20   | 80  |
| 6 | 0    | 100 |
| 7 | 0    | 100 |
| 8 | 100  | 0   |
|    | 50   | 50  |
|    | 0    | 100 |

The preliminary heating by an electron beam of a crucible with a powder took 30-40 minutes. The heating rate was 30°C per minute. When the crucible was heated to a temperature of 600°C, a raster electron beam was switched on and then the heating was carried out by two beams to a temperature of 1400°C for samples 1-6 and 1500°C for samples 7-8. The sample temperature was raised by increasing the power of electron beams from 100 W to 600 W. The exposure at a constant temperature took 20 minutes, after which the sample was cooled by a smooth decrease in the power of the beams. The cooling rate was 40°C per minute. The sintering time was selected based on our experience of sintering compressed alumina and zirconium oxide tablets [18].

The microstructure of the surface, the transverse section and the elemental composition of the sintered samples were studied in a scanning electron microscope Hitachi S3400N equipped with an attachment of the Bruker X'Flash 5010 energy dispersive microanalysis. The temperature of the irradiated surface was measured by an infrared pyrometer 6 (RAYTEK 1MH), with a temperature range of 550-3000°C.

4. Experimental results and discussion

As a result of sintering, a series of samples 1-6, plates of cermet with a thickness of the order of 1 mm were obtained. Figure 3 shows a photo of the surface of the sintered samples 1, 3, 6. In each of the presented photos, crystals of aluminum oxide ceramics of white color and titanium of black hue are clearly visible.

And with a decrease in the percentage composition of aluminum, the size of its inclusions on the surface decreases. The strength of the samples depended on their elemental composition, and was not high enough - all samples were crumbled by manual manipulation. However, samples with a titanium content of more than 60% were more strong.

The investigation result of the transverse section of sample No. 2 on an electron microscope with a microanalyzer is shown in figure 4. Since no compression of the samples was carried out, quite large areas are visible, which are not filled by material. Due to the high porosity, the value of the strength of the samples is low. The analysis of the remaining samples No. 3-5 showed similar results.

Since the main feature of FGM is a gradual change in their thickness properties, it was decided to use a titanium substrate in the form of a plate with the 3 mm thickness as the first layer. The heating and cooling modes of the sample were identical to the sintering regimes of samples 1-6. As a result of sintering, it was possible to obtain a sample of cermet, which held fairly well on the metal substrate.
(figure 5). Figure 5 shows a clear separation of the layers of alumina ceramic, titanium powder and titanium plate serving as a base.

![Figure 3. Surface of sintered samples No. 1, 3, 5.]

The next stage of work was the sintering of a three-layer sample without a substrate. A titanium powder was placed into the cavity in the graphite crucible, then it was leveled. The second layer consisted of a mixture of alumina and titanium in equal proportions by weight. And a fine powder of aluminum oxide was chosen, because experiments showed that using a coarse-grained powder, sintered samples contain a sufficiently large number of large pores. The third layer consisted entirely of a fine powder of aluminum oxide. In this way, a three-layer composite consisting of three layers (Al2O3; Al2O3 + Ti in the ratio 1: 1; Ti) was sintered. The sintering temperature was increased to 1600°C. The graph of the change in the power of the beams during sintering, as well as the surface temperature of the sintered material, is shown in figure 6.

![Figure 4. The result of the study of the composition of sample No. 2 on a microanalyzer.]

The composite after sintering was quite strong. Figure 7 shows the structure of the transverse section of the sample. On the section, the boundaries between the layers are clearly visible: the lower light layer corresponds to titanium, the middle dark layer means mixtures of aluminum oxide and titanium, and the upper light layer corresponds to aluminum oxide.

![Composite structure](image)

**Figure 5.** Photo of the cut of sample No. 7 obtained by electron-beam synthesis.

![Graph](image)

**Figure 6.** Graph of the change in the power of the electron beams (1, 2) and the temperature (3) of the specimen irradiated during the sintering process.

The thickness of each layer averages 0.2 mm. When the surface of the composite was irradiated by the electron beam, the moving of the sintering material on the irradiated surface was not observed. This allows us to speak about the possibility of using an electron beam generated by a plasma electron source for synthesis cermet powders. The technology of obtaining multilayer metal-ceramic products requires further improvement. However, even at this stage, we can talk about the applicability of the electron-beam method for manufacturing gradient materials in the forevacuum region of pressures.
5. Conclusion
As a result of the work, sintering of cermet powders by the electron beam method was carried out. A special feature of the method is the generation and transport of an electron beam in the forevacuum region of pressures. The presented results testify about the principle possibility of using a forevacuum plasma electron source to create materials with volume-varying properties. Using the electron-beam method, strong three-layer metal-ceramic samples with clear boundaries between layers were obtained. The time of isothermal exposure with this sintering method does not exceed 20 min at a power density of the scanning beam of 2 kW/cm$^2$.

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