Modification of Alumina-Zirconia Ceramics Properties by High Current Beam of Low-Energy Electrons

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Abstract – The paper describes experimental data on influence of a high-current pulsed beam of low-energy electrons (HPBLE) on the composition and microhardness of near-surface layers of corundum-zirconium ceramics (CZC) of the composition (in mass%): $20Al_2O_3–80ZrO_2(Y)$. It is found out that electronic processing results in forming of a near-surface layer in ceramics with a chemical composition changed with respect to a specimen volume as a result of essential reduction of corundum phase content.

The existence of strong dependence of measurable value H_v of ceramics from loading on indentor P, caused by the indentation elastic restoration, is established. The influence of electronic processing on process of the indentation elastic restoration is revealed. With *taking into consideration this factor* it has been shown that the modified ceramics layer is characterized by a lower microhardness value than unirradiated layer.

1. Introduction

A wide variety of state-of-the art methods used for active influence on a structural state and properties of materials' near-surface layers is based on application of diverse types of radiation effects. In this respect a comparatively new method for materials processing based on application of high-current pulsed beams of low-energy electrons (HPBLE) [1, 2] is of great interest.

HPBLE effect on a solid is mainly of a thermal nature. They are defined by the processes that depend on a beam power density and are specified by high-speed regimes of heating (up to the fusion temperature during the pulse electrons beam of microsecond duration) and cooling of the processed surface layers.

This kind of processing, approved for metals and alloys [1–3], illustrates a possibility to control a microstructure, phase composition, mechanical properties of near-layers of these materials in quite a wide range.

This paper describes results of the experiments on studying the nature of HPBLE influence on ceramic structures.

2. Experimental technique

Corundum-zirconium ceramics (CZC) of the composition (in mass %): $20Al_2O_3–80ZrO_2(Y)$ was the subject of the study. CZC was an alloy of partially stabilized zirconium oxide and corundum. Structures obtained on the basis of the system Al_2O_3-stabilized ZrO_2, are the most perspective for production of high-strength tool and structural ceramics. A stabilized state of ZrO_2 was achieved by introduction of 3 mol. % of Y_2O_3 [4] into its crystal lattice.

The sintered ceramics from the soot, produced by plasma-chemical method, was in the form of pellets with the diameter of 10 mm and thickness of 3 mm. Radiation processing was carried out in vacuum ($P=10^{-2}$ Pa) in the accelerator SOLO, designed in the Institute of High-Current Electronics (IHE SBRAS). It was done by single beam pulses of low-energy electrons with the following parameters: $E=15$ keV, current density in the pulse – 16 A/cm^2, pulse duration – 50 µs. The mentioned parameters required energy density in the pulse $W_i=12$ J/cm^2. A number of electron beam pulses was $N=10$. Interpulse time was 10 sec. Specimen surface was mirror polished before being radiated. A radiation zone was smaller than the pellet diameter and made up 8 mm.

Composition of specimen near-surface layers was studied by various methods: electron probe X-ray microanalysis (EPXM), X-ray diffractometry and secondary ion mass-spectrometry (SIMS). X-ray-phase analysis was carried out with the help of the X-ray difractometer DRON- 4-07 on a monochromatic FeK_α radiation. EPXM was done with the help of electron probe X-ray microanalyzer EDAX ECON IV. In experiments by means of SIMS a mass-spectrometer MC7201M was used. Microhardness was measured by micro-hardometer PMT-3.

Experimental results

The conducted research enabled to discover the following effects of HPBLE on ceramics. After radiation processing the specimen surface turns black which indicates change in the material stehiometry towards oxygen deficit [5]. Furthermore the formation of a crack network is observed, owing to what the ceramic surface appears divided on separate fragments of average size of about 30 μm. Formation of crack system is caused by a high value of mechanical stresses and a thermal hit the specimens affected due to their fast heating and cooling within the processing condition.

The results, indicating significant phase transformations of the near-surface layers in ceramics caused by the electron beam action, are of the greatest interest. According to the data obtained through X-ray research a set of basic reflexes appropriate to superposition of the reflections stipulated by three phases: tetragonal (t), monoclinic (m) of zirconium dioxide phases, as well as α-Al_2O_3 was observed on ceramics difractograms in initial state. A phase composition of the tested ceramics is given in Table 1.

Table 1. Phase composition of corundum-zirconium ceramics

Phase	*t*-ZrO_2	*m*-ZrO_2	α-Al_2O_3
Phase content before processing, %	60.0	8.6	31.0
Phase content after processing, %	95.0	0	5.0

After HPBLE action on ceramics the diffraction reflections stipulated by m-phase vanished and intensity of the reflections intrinsic to tetragonal phase increased. That indicated a structural change of the zirconium dioxide monoclinic phase into the tetragonal phase ($m \rightarrow t$). One of the probable causes m t change is formation in ZrO_2 crystal lattice of additional number of non-stehiometric oxygen vacancies, that are known to facilitate zirconium dioxide tetragonal phase stabilization [6, 7],. Black color of ceramics proves presence of considerable number of oxygen vacancies. Furthermore, considerable mechanical stresses the specimens affected within pulsed electron beam processing are of certain importance for stimulation of $m \rightarrow t$ change. Probability of polymorphic transformations of the zirconium dioxide crystal lattice under the influence of dynamic load is considered in a number of publications [8–10]. In particular, $m \rightarrow t$ effect of the phase transformation was observed when zirconium dioxide powders were affected by impact mechanical loads [9] and explosion loading took place [10].

It should be mentioned that electronic processing results in reduction of half-width of reflexes, intrinsic to *t*-phase of the zirconium dioxide. This indicates a possibility to change a fine intra-grained structure of the zirconium phase and magnitude of the lattice micro-distortions ($\Delta d/d$). On the basis of X-ray analysis average size (L) of coherent scattering region (CSR) of the zirconium dioxide *t*-phase and magnitude ($\Delta d/d$) have been evaluated by means of complete profile analysis of X-ray-grams with the use of software *Powder Cell 2.4.*

An average size (L) of coherent scattering region (CSR) of the zirconium dioxide *t*-phase (L=28 nm) was twice as large in a ceramic layer modified by HPBLE than in an initial state where L=14 nm. At the same time radiation involved reducing of the amount of crystal lattice micro-distortions ($\Delta d/d$). Before and after the processing magnitudes $\Delta d/d = 3.3 \cdot 10^{-3}$ and $1.8 \cdot 10^{-3}$, respectively.

Analysis of difractograms has shown that processing of CZC with electron beam involved significant intensity reduction of diffraction lines stipulated by corundum phase. Two most probable causes for the mentioned changes should be pointed out. First of all, decrease of corundum phase content in a sensed ceramic layer. Secondly, possible corundum structure disordering to a degree of metastable amorphism under the processing should also be taken into consideration. In this case concentration of aluminum ions in the modified layer should not be essentially changed. Investigations conducted with the application of SIMS and EPXM methods of the elemental composition of the ceramic near-surface layers before and after HPBLE helped make a choice between the mentioned causes.

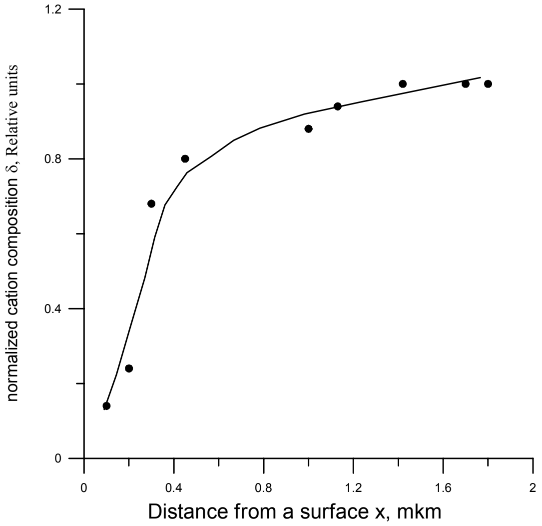

Fig. 1. Change of normalized cation composition (δ) in depth after electronic processing of CZC

SIMS method was applied to measure profiles of distribution of aluminum and zirconium elements in depth after electron processing of specimens. Fig. 1 illustrates dependence of normalized cation composition CZC (δ) in depth, where $\delta = (I_{Al}/I_{Zr})/(I_{Al}/I_{Zr})_{max}$, where I – intensity of mass-spectrum lines corresponding to the measured elements, $(I_{Al}/I_{Zr})_{max}$ – ration of line intensities to the specimen depth. The etch depth was 2 μm. It is obvious that within the limits of the measured depths radiation involves reducing of a magnitude of intensity ratio of the mass-spectrum lines caused by aluminum and zirconium ions. On the basis of the intensity ration of Al and Zr mass-spectrum lines one can conclude that a weight ratio of Al and Zr being part of ceramics increases due to reducing of aluminum content in the sub-surface layers.

While running experiments with the application of EPXM methods, the specimen surface was beforehand covered with a translucent carbon film to avoid specimens charging when a probe electron beam hits the ceramics. Qualitative X-ray spectrum microanalysis of the surface has shown that in contrast to CZC check specimen spectra obtained from the processed surface completely lacked lines caused by aluminum. Besides, an atomic concentration of yttrium ions, stabilizing the zirconium dioxide tetragonal phase, remains fixed. Scanning of the probe beam within the limits of single fragments did not influence measurement results.

The presented experimental data unambiguously indicate reducing of the corundum phase content in the ceramic surface layers. According to the X-ray-phase analysis its content in the sensed surface layer has been reduced to 5 % (Table1).

According to various evaluations an electron beam with the specified parameters can heat a ceramic near-surface layer to T=(2600–3000) K. This temperature is enough to provide melting of a fine surface layer and substance evaporation. Since the temperature of the corundum melting (T=2319 K) is substantially smaller than of the zirconium dioxide (T=2963 K), a more fusible component should be mainly evaporated. As a result a near-surface layer with the chemical composition changed with respect to a specimen volume is formed.

To evaluate electron processing influence on mechanical properties of modified ceramic sub-surface layers micro-hardness has been measured (H_v).

Its testing in fine modified layers by means of micro-indenting requires small loading on the indentor P. Under these conditions a measured resulting size of the indentation can be affected by a well-known effect of its elastic restoration (ER) [11] after the indentor is uplifted. Use of size of the restored indentation at calculation H_v results in overestimated magnitudes of the material microhardness.

It should be borne in mind that the indentation ER process efficiency in the modified specimen layers might vary. It was not possible to determine character of electronic processing influence on the ceramic microhardness without taking into consideration this factor.

This problem can be solved by means of analysis of research results of value P influence on the material microhardness. These research data give an opportunity to apply the following approach giving an opportunity to determine electronic processing influence on the indentation ER and, consequently, to establish true character of electronic processing influence on the ceramic microhardness.

Papers [11, 12] claim that there is the following relation between the indentor load and indentation size:

$$P=C_1d+C_2d^2, \qquad (1)$$

where C_1 and C_2 – coefficients of proportionality, d – length of the indentation diagonal.

According to [12], constants C_1 and C_2 in the equation (1) characterize the indentation elastic restoration and resistance of the deformable material volume, respectively. These coefficients are defined by means of graphical plotting P/d on d.

Estimated values of coefficients C_1 and C_2 of the unirradiated ceramics are given in table 2.

Table 2. Coefficients C_1 and C_2 for CZC before and after HPBLE processing

W_i, J/cm^2	0	12
Number of pulses N	–	10
C_1, N/mm	20.7–30.7	62.5–64.6
$C_2 \cdot 10^{-3}$, N/mm^2	6.1–6.4	2.3–2.6

From the data in table 2 one can see that electron processing has an opposite influence on coefficients C_1 and C_2, so that coefficient C_1 is essentially rising and coefficient C_2 is reducing. Rise of coefficient C_1, testifies that indentation ER after load-off in a HPBLE modified surface layer is more efficient in comparison with unirradiated ceramics. One can assume that as a result of the ceramic specimen irradiation compression stresses arise in near-surface layers. After load-off they intensify the relaxation processes causing reduction of the indentation size, thereby, decreasing internal stresses in its area. Thus, calculations Hv result in overestimated numerical values of microhardness in comparison with the unirradiated ceramics.

Reducing of coefficient C_2 indicates that electron processing causes decreasing in hardness of ceramic near-surface layers by two times and over, converting them into more elastic state. In our opinion, content reduction of the corundum phase with greater hardness to a certain extent may facilitate hardness decrease.

In conclusion, we would like to draw attention to the following fact. Focusing on the results of microhardness measurement with a fixed loading P=200 g, one can see that its change after electron processing is not so essential (H_v=13.6 and 11.1 GPa before and after radiation, respectively). Thus, if ER of the indentation is not taken into account, one can get a falsified concept of modification efficiency of this ceramics property.

3. Conclusions

1. HPBLE processing of corundum-zirconium ceramics results in changing the phase composition of its surface layers, initiating transfer of the zir-

conium dioxide m-phase into a tetragonal modification. This also involves an essential reduction of corundum phase content due to intensive evaporation of a more fusible component.

2. Processes of the indentation ER, after the indentor is uplifted, are more efficient in the ceramic near-surface layers modified with electron processing than in the initial state. Taking into consideration this factor, a real effect of HPBLE impact on the ceramics micro-hardness has been revealed. The results testify that electron processing causes its reduction by two times and over.

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