

Changing Near-Surface Layers Mechanical Properties of Alumina-Zirconia Ceramics by High-Current Beam of Low-Energy Electrons¹

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Abstract – The effect of high-current pulsed beam of low energy electrons (HPBLE) at $E = 15$ keV on mechanical characteristics of near-surface layers of alumina-zirconium ceramics (AZC) of the $20\text{Al}_2\text{O}_3$ – $(77\text{ZrO}_2$ – $3\text{Y}_2\text{O}_3)$ composition (in wt %) is investigated by the method of dynamic indentation. It is shown that electron beam treatment reduces Young's modulus and nanohardness of this ceramic material. The action of HPBLE on structural-phase state of modified subsurface layers of AZC specimens is analyzed. Their elemental and phase compositions are examined using several techniques: electron-probe X-ray spectral microanalysis (EPMA), secondary-ion mass spectrometry (SIMS), and X-ray diffractometry. It is found out that irradiation of the ceramic material by HPBLE stimulates the transitions of an m-phase of zirconium dioxide into a tetragonal modification, and results in a considerable decrease in the alumina phase. Based on the analysis of the data obtained, a conclusion is drawn that it is the processes resulting from irradiation and giving rise to formation of a near-surface layer with a phase composition different from that of the bulk material, which are responsible for the effects of mechanical properties modification.

1. Introduction

Today, advanced ceramics successfully replace conventional materials in a large number of industrial applications, which is demonstrated by an increased production of articles made thereof. In this connection, the investigations aimed at designing new processes to treat ceramic structures, which provide control over their properties, are increasingly appealing. In this respect, the approaches relying on the use of concentrated streams of charged particles, in particular, low-energy high-current electron beams (LEHCEBs) (electron energy, E , of a few tens keV) appear to be exceptionally promising [1, 2]. The effectiveness of LEHCEBs in providing an extensive control over microstructure, phase composition and strength properties of the near-surface layers of solids have been

clearly demonstrated by a large body of experimental data obtained for metals and alloys [2–4].

The character of the electron beam energy dissipation, which via a variety of pathways is predominantly transformed into heat, predetermines special features of the above-mentioned treatment. The energy concentration per pulse is high and could be varied within a relatively large range. Hence, virtually any type of exposure to heat of the near-surface layers of solids could be achieved: heating to predetermined temperatures, melting and high-rate evaporation. A subsequent fast cooling is followed by high-rate crystallization of the melt and generation of thermo-elastic dynamic and quasi-static mechanical stresses in the region under irradiation, which inevitably give rise to high-rate deformation. A combination of the above-mentioned factors peculiar to this kind of electron-beam treatment can initiate structural phase transformations in the near-surface layers of solids, which would eventually affect their physical-mechanical properties.

This work addresses the study of the effects of LEHCEBs on alumina-zirconium ceramics (AZC). The structures produced on the basis of this system are thought to be most promising as concerns the manufacture of high-strength tool ceramics. During their service life, the tool materials are subjected to high dynamic stresses predominantly in the near-surface layers. Thus, the issue of modification of the structural state and properties of the near-surface layers is of special significance.

2. Experimental procedure

The materials under study were alumina-zirconium ceramics of the following composition (in mass %): $20\text{Al}_2\text{O}_3$ – $(80\text{ZrO}_2$ (Y)). The AZC material represented an alloy of partially stabilized zirconium dioxide and alumina. The stabilized ZrO_2 was achieved by introducing an Y_2O_3 impurity (3 mole %) [5]. The ceramics was sintered in a vacuum furnace at $T = 1920$ K for 1.5 h. Prior to the electron beam treatment it was polished to microfinish smoothness.

The specimens were irradiated in vacuum ($P = 10^{-2}$ Pa) in a SOLO accelerator developed and de-

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signed at the Institute of High Current Electronics (HCEI SB RAS). The specimens were treated by single pulses of low-energy electrons having the following parameters: $E = 15$ keV, current density per pulse $- 18$ A/cm², pulse duration $- 50$ μ s, and pulse repetition rate $- 0.1$ Hz. The number of pulses was $N = 2$. With these parameters, the energy density per pulse was $W_p = 13.5$ J/cm². To define the maximum electron penetration depth into the ceramic material, use was made of the following formula [6]:

$$R = 2.76 \cdot 10^{-2} A E^{5/3} / (\rho \cdot Z^{8/9}), \quad (1)$$

where Z , A , and ρ are the effective atomic number, molecular weight, and material density, respectively. According to the calculations, $R \approx 2.2$ μ m. The size of the irradiated region was smaller than a tablet, and was found to be 8 mm.

The study of mechanical properties of thin modified near-surface layers of specimens was performed by the method of nanoindentation using small loads on the indenter. It consisted in a continuous hardness indentation, with the load on the indenter varying linearly over time. This was also accompanied by the measurement of indentation depth, h , and load, P .

The method makes it possible to measure in one cycle the depth of nonrecovered h_{\max} and recovered (plastic) h_0 indents, Young's modulus E (from the tilt of the linear section of the unloading curve), and material hardness H . By applying this method, we can follow the deformation process dynamics in a material microvolume and obtain more complete information on its mechanical characteristics. To this end, in this work we used a CSEM Nano Hardness Tester of the Equipment Sharing Center at the Institute of Nuclear Physics, TPU. Indentation tests were performed using a Vickers pyramid. About 8–10 indents were applied to the specimen surface. The spacing between the dips of the indenter exceeded 20 μ m. The indenter load P was 50 and 300 mN. The statistical error was within 6–10%.

The elemental and phase analyses of the near-surface layers were investigated by several techniques: electron-probe X-ray spectral microanalysis (EPMA), secondary-ion mass spectrometry (SIMS), and X-ray diffractometry. The latter analysis was performed in a DRON-4-07 machine in the monochromatic/monochromated FeK $_{\alpha}$ radiation. The resulting X-ray diffraction patterns were processed by a full-profile analysis using a *Powder Cell 2.4* software system. The data on elemental composition were obtained with a MC7201M mass-spectrometer and an EDAX ECON IV X-ray microspectral analyzer.

3. Experimental results and discussion

Figure 1 shows a typical P – h dependence curve obtained after indenting a ceramic specimen before irradiation for the maximum indenter load $P = 300$ mN.

From a qualitative perspective, its character does not change when lower values of P are used, nor does

it do so after e-beam treatment. The curve consists of two sections. Section 1 corresponds to the process of indenter dipping into the specimen and characterizes material resistance to plastic deformation. Section 2 provides information on deformation behavior of the deformed region in the unloading mode. It is evident that the residual indentation depth h_0 after removal of the indenter is significantly different from its maximum indentation depth h_{\max} . This fact is indicative of an active character of the processes of material recovery in the deformed region in the unloading mode. Their contribution into the changes in indentation size can be estimated using parameter $\alpha = (h_{\max} - h_0)/h_{\max}$. When maximum loads on the indenter are used, $P = 300$ and 50 mN, parameter α achieves the values 0.41 and 0.52, respectively.

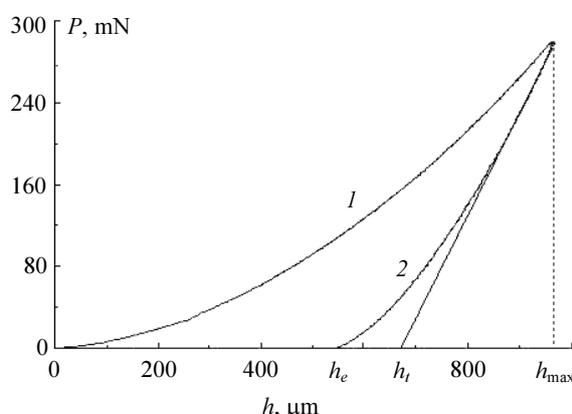


Fig. 1. Dependence $P(h)$ under maximum load on the indenter $P = 300$ mN for AZC specimens before irradiation

The deformation characteristics were determined from interpretation of the resulting P – h curves within the loading and unloading sections by the technique proposed by Oliver and Pharr [7]. According to this technique, Young's modulus E during nanoindentation of a ceramic specimen is estimated from the following relationships:

$$E_r = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A_c}}; \quad (2)$$

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i}, \quad (3)$$

where S is the contact rigidity found from the condition of linearity of the initial section of the unloading curve, $S = dP/dh$; A_c is the projected indentation area corresponding to the contact depth; E_r is the effective modulus determined by Young's modulus and Poisson's ratios of the material under study (E and ν , respectively) and those of the indenter (E_i and ν_i , respectively).

Material nanohardness H was calculated using the following formula:

$$H = P_{\max} / A_c, \quad (4)$$

where P_{\max} is the maximum load on the indenter.

Table 1 lists the deformation characteristics of the ceramic under investigation, which were obtained for two load values, $P_{\max} = 300$ and 50 mN. The loading and unloading time was 1 min for all cases.

Table 1. Mechanical properties of AZC before and after e-beam treatment*

P , mN	H , GPa		E , GPa		H^3/E^2 , GPa	
	I	T	I	T	I	T
300	20.11	15.41	268	201.6	0.13	0.09
50	25.82	16.8	291.3	221.03	0.203	0.097

*In Table 1 the term I means initial state of sample, term T is the surface treated by LEHCEBs.

Based on the data obtained for the indenter load $P = 300$ mN, Young's for untreated specimens was found to be $E = 268$ GPa. According to the literature data [8], for ceramic materials of identical compositions Young's modulus is $E \approx 240$ GPa. It is clear from Table 1 that the listed values are fairly consistent.

Table 1 shows that the resulting values of H and E depend on the load applied. We observe here manifestation of a nanoscale effect. It consists in an increase in strain values with a decrease in P . It should be noted that the scaling effect was established earlier when measuring microhardness of materials by a conventional technique using a PMT-3 commercial hardness meter and small loads [9, 10]. Its occurrence was accounted for by the processes of elastic relaxation on material in the vicinity of the indentation after unloading. Note that the size of the indent decreased. In the calculations, this would yield overestimated microhardness values. As an illustration of a scaling effect, we can quote the following data. With the loads $P = 2$ H and $P = 300$ mN on the indenter, the microhardness of a ceramic material measured by a conventional method was considerably different, and was found to be $H_v = 14.2$ and 23.1 GPa, respectively. Comparison of the cited values sheds light on the extent to which relaxational process in the material in the region of the indentation affect the calculated hardness values in the case of small loads.

Currently, the question of nanoscale effect remains unanswered. The dependence of deformation behavior of material on load could be attributed to a large number of factors. Here belong the processes of elastic recovery of material in the vicinity of the indentation under unloading condition. The method of dynamic indentation allows us to estimate the value of elastic recovery $\alpha_1 = (h_{\max} - h_i) / h_{\max}$, where h_i is a section in the X-axis that is intercepted by a straight line, dP/dh , going across the upper part of the unloading curve. An analysis of the estimates has shown that when a load is reduced from 300 to 50 mN, parameter α_1 is increased, and is found to be 0.28 and 0.35, respectively. This factor could be, therefore, somewhat responsible for nanoscale effect.

Moreover, one has to take into account a reason of a methodological nature. It consists in the fact that in going to small loads and, hence, to smaller indentation depths, the error of determining the contact area increases, and so is that of estimating the deformation characteristics. This is partially due non-ideal nature of the indenter tip. An especially critical role this circumstance plays in the case of Vickers' pyramid. Finally, an increase in hardness with decreasing depth might be of physical origin due to peculiarities of deformation processes in nanovolumes. In the current stage of investigations, we find it impossible to answer the question which of the enumerated actors makes the main contribution into the nanoscale effect.

After treatment by LEHCEBs, we observed a qualitative change in the AZC surface condition. In a light microscope, formation of a net of cracks due to mechanical stresses and thermal shock caused by fast heating and cooling of the specimens was clearly visible. The surface was found to be separated into fragments with an average size of about 22–35 μm . The load–displacement curves upon irradiation of the material by LEHCEBs had qualitatively the same shape as those in Fig. 1. Note that near-surface layers were characterized by lower hardness and Young's modulus (see Table 1). Resistance of material to plastic deformation is assumed [11] to be estimated from the value of $K = H^3/E^2$. After e-beam treatment, this parameter decreases, indicating an increased plasticity of the modified ceramic layers.

In order to identify the causes responsible for modification of mechanical characteristics of ceramics by LEHCEBs, we examined the structural-phase composition of the near-surface layers. The x-ray diffraction patterns from initial ceramics obtained via the x-ray structural analysis exhibited a number of reflexions, which corresponded to the superposition of the reflexions due to three phases: tetragonal (t) and monoclinic (m) zirconium dioxide phases, and an α phase of Al_2O_3 . Listed in Table 2 are the phase compositions of the ceramic under study in volume percent.

Table 2. Phase composition of alumina-zirconium ceramics

Phases	$t\text{-ZrO}_2$	$m\text{-ZrO}_2$	$\alpha\text{-Al}_2\text{O}_3$
Phase content before irradiation, vol. %	62.5	11.6	25.9
Phase content after irradiation, vol. %	93.5	0	6.5

After irradiation of the ceramic material by LEHCEBs, we did not observe any diffraction reflexions due to the m -phase but did observe a higher intensity of the diffractions typical of the tetragonal phase, which indicated a structural re-arrangement of the monoclinic phase of zirconium dioxide into a tetragonal phase ($m \rightarrow t$). One of the probable reasons for the $m \rightarrow t$ transition is formation of an additional number of non-stoichiometric oxygen vacancies in the crystal lattice of ZrO_2 as a result of its partial reduc-

tion, which are known [5] to favor stabilization of the tetragonal phase of zirconium dioxide. The presence of a considerable number of oxygen vacancies is evidenced by the black color of the ceramic material exhibited after irradiation. Also, a certain role in simulating the $m \rightarrow t$ transition might be played by significant mechanical stresses experienced by the specimens under high-current electron beams. A number of studies [12–14] report on a possibility of polymorphous transformations of the crystal lattice of zirconium dioxide under dynamic loads. In particular, the effect of the $m \rightarrow t$ phase transformation was observed in powdered zirconium dioxide subjected to mechanical impact loading [13] and loading by explosion [14].

According to the data presented in Table 1, the LEHCB treatment of AZC gave rise to a considerable decrease in the content of the alumina. Two most probable reasons for this result could be singled out. Primarily, this decrease could have been due to a change in the chemical composition of the probed ceramic layer. Also, we cannot rule out a possibility of alumina structure disordering down to the level of metastable amorphism due to e-beam treatment. In the latter case, aluminum ion concentration in the modified layers would not change considerably. An examination of the elemental composition of the near-surface ceramic layer prior to and after its irradiation by LEHCEBs performed by SIMS and EPMA methods allowed us to choose between the two possible abovementioned causes.

The SIMS technique was used to measure the profiles of aluminum and zirconium distribution with respect to the penetration depth following the e-beam treatment. Figure 2 shows the normalized cation composition of AZC as a function of depth (δ).

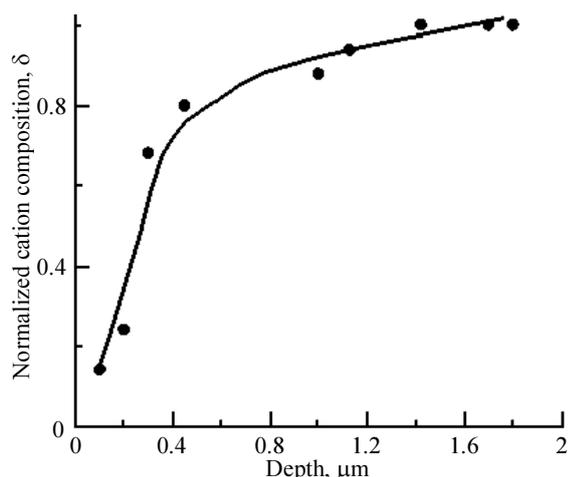


Fig. 2. Variations in the normalized cation composition δ over the depth after irradiation of AZC specimens by e-beams

Here $\delta = (I_{\text{Al}}/I_{\text{Zr}})/(I_{\text{Al}}/I_{\text{Zr}})_{\text{max}}$, where I is the line strength of the mass spectrum of the respective elements under study, $(I_{\text{Al}}/I_{\text{Zr}})_{\text{max}}$ is the line strength ratio in the bulk of the specimen. The etch depth was 2 μm . It is evident that, within the range of the depths in

question, irradiation gives rise to a decrease in the ratio of the line strengths of the aluminum and zirconium mass spectra. Based on the latter, we could draw a conclusion that the weight ratio of Al and Zr contained in the ceramic material decreases due to a decreasing content of aluminum in the near-surface layers.

In the EPMA experiments, the surface of the specimens was preliminarily coated with a semi-transparent carbon film to avoid charging of the specimens by the probing e-beam incident on the ceramic material. A qualitative X-ray spectrum analysis showed that, unlike reference AZC specimens, there were virtually no lines due to aluminum in the spectra from the treated surface, while the concentration of yttrium ions ensuring stabilization of the tetragonal phase of zirconium dioxide remained unchanged. Scanning by a probing beam within individual fragments did not affect the results of measurements. The entire set of the experimental data obtained unambiguously indicated a decrease in the content of aluminum ions in the surface layers of aluminum. According to the data of the X-ray phase analysis, the volume content of the alumina phase in the probed near-surface layer decreased down to 6.5% (see Table 2).

According to a number of preliminary estimates, an electron beam of the parameters in question is capable of heating near-surface layers of the ceramics up to $T = (2600\text{--}3000)$ K. This temperature is quite sufficient to ensure melting of the thin surface layer and evaporation of the material. Since the melting temperature of corundum ($T = 2319$ K) is much lower than that of zirconium dioxide ($T = 2963$ K), it is the material with a lower melting point that would preferably evaporate. As a result, a near-surface layer would form with the chemical and phase compositions differing from those in the bulk.

It is common knowledge that ceramic grains consist of individual sub-grains separated from each other by low-angle boundaries; in other words, they have their own substructure. It is very likely that internal microstresses would be present, which are capable of causing microdistortions of the crystal lattice. According to the results of our investigation, the e-beam treatment gave rise to narrower half-widths of the reflexions typical of the t -phase zirconium dioxide. This fact points to a possible change of the fine intragrain structure of the zirconium phase and the value of lattice microdistortion ($\Delta d/d$).

From the data of the x-ray diffraction analysis we estimated the average size (L) of the coherent scattering region (CSR) of the t -phase zirconium dioxide and the values of lattice microdistortion ($\Delta d/d$). To do so, we applied the method of full-profile analysis of the X-ray diffraction patterns using a *Powder Cell 2.4* software program. In a ceramic layer modified by LEHCEBs, the average CSR size from the t -phase zirconium dioxide ($L = 28\text{--}30$ nm) was found to be twice that in the initial state, for which it was $L = 14$ nm. It should be noted that irradiation gave rise

to lower crystal lattice microdistortion ($\Delta d/d$) values. Prior to treatment, $\Delta d/d = 3.5 \cdot 10^{-3}$, while afterwards this parameter acquired the values $\Delta d/d = 1.4 \cdot 10^{-3}$. These changes in parameters L and $\Delta d/d$ observed in the experiments are consistent with the data on the changes in phase composition of the near-surface ceramic layers. The increase in subgrain size is thought to be associated with two factors.

The first is a decrease in the content of the monoclinic phase, since the presence of additional phases in the crystallite structure generally prevents subgrains from growing. The second factor is a decrease in the fraction of the alumina, which should favor removal of microstresses and in its turn stimulate subgrain growth.

The integral experimental results point to a substantial transformation of phase composition of the near-surface AZC layers under e-beam. We, therefore, believe this factor to be the principal reason for e-beam modification of their properties.

In order to verify this viewpoint, we performed measurement of deformation characteristics of zirconium ceramics (ZC) after a LEHCEB treatment by the method of nanoindentation. The chemical and phase compositions of ZC material were identical to those of the grain composition of the zirconium phase of a two-component AZC system. The values of strain characteristics are listed in Table 3.

Table 3. Strain characteristics of ZC irradiated by LEHCEBs

P , mN	H , GPa	E , GPa	H^3/E^2 , GPa
300	13.2	174.3	0.076
50	17.3	222.1	0.104

A comparison of the data listed in Tables 3 and 1 shows that after irradiation by e-beams the deformation characteristics of the near-surface layers in AZC and ZC materials are fairly similar. The values of Young's modulus obtained for them are fairly consistent with those reported in literature [8, 15] for zirconium dioxide ($E = 170\text{--}198$ GPa). From our perspective, this coincidence is not accidental and agrees well with the experimental data on phase composition measurements in the near-surface layers of this ceramics after e-beam treatment. Since the alumina is characterized by higher values of Young's modulus ($E = 380\text{--}430$ GPa), when its content is reduced we are to expect a lower Young's modulus in the two-component system under study.

A change in the phase composition of the near-surface layers would also affect their hardness. It is well known that microhardness of corundum according to the data reported in a number of works [8, 15] varies in the range 18–20 GPa, and is higher than that of zirconium dioxide. Hence, it is quite reasonable to attribute the reduced microhardness of the ceramics to the alumina contained in it.

4. Summary

1. An irradiation of alumina zirconium ceramics by LEHCEBs results in a lower Young's modulus and nano-hardness on the near-surface layers of the specimens.

2. It is the processes that give rise to formation of a near-surface layer with modified, compared to the bulk, phase composition which are principally responsible for the effects observed in this work. Following an e-beam treatment, the near-surface layers exhibit a lower content of the alumina. Note that the m -phase of zirconium dioxide is nearly completely transformed into a tetragonal phase.

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