Effect of electron beam irradiation on structural phase transformations of zirconia-based composite reinforced by alumina nanofibers and carbon nanotubes

A A Leonov, Yu F Ivanov, M P Kalashnikov, E V Abdulmenova, V D Paygin and A D Teresov

1 Institute of High Current Electronics SB RAS, 2/3 Akademichesky Ave., Tomsk, 634055, Russia
2 National Research Tomsk Polytechnic University, 30 Lenin Ave., 634050, Tomsk, Russia
3 Institute of Strength Physics and Materials Science SB RAS, 2/4 Akademichesky Ave., Tomsk, 634055, Russia

E-mail: laa91@tpu.ru

Abstract. Evolution of microstructure, elemental and phase composition of dense zirconia-based composite under irradiation with electron beam were investigated. Tetragonal zirconia-based composite reinforced by 5 wt% alumina nanofibers and 0.5 wt% single-walled carbon nanotubes was prepared by spark plasma sintering at a temperature of 1500°C. Irradiation of the composite was carried out with a low-energy pulsed electron beam of submillisecond duration in the following mode: beam energy density 15 J cm⁻²; pulse duration 200 μs; pulse repetition rate 0.3 s⁻¹; pulses quantity 10, 20, 30 and 40; residual gas pressure (argon) in the working camera 10⁻² Pa. It has been established that electron beam treatment leads to the formation of modified multilayered surface, the thickness of which varies from 6 to 40 μm. Redistribution of Al atoms in the modified surface layer was detected. The phase evolution dependent on the quantity of irradiation pulses and manifested in the crystalline structure of material.

1. Introduction
3 mol% yttria stabilized zirconia (3Y-ZrO₂) is a technologically important material and has a wide range of structural and multifunctional applications such as solid oxide fuel cells, oxygen sensors, and ceramic membranes because of its superior mechanical properties, good ionic conductivity, and high temperature stability [1–4]. The properties of finished products from 3Y-ZrO₂ strongly depend on the microstructural characteristics of the material, phase composition, state of the surface, etc. [5–8]. Modification of the material surface by intense pulsed low-energy (up to 30 keV) electron beams of micro- and submillisecond duration is a modern method of regulating the microstructure and phase composition of materials [9–11]. Due to high mechanical and chemical resistance of ceramic materials, methods that use electron beams are most effective for their modification [12–15]. In the process of electron beam irradiation, the surface layer of the processed material melts at high-speed, and then cools rapidly, as a resulting in high-speed crystallization of the melt [16–18]. This mode of processing causes a powerful wave of thermal stresses in the materials and accelerates diffusion mass...
transfer [19–21]. Electron beam modification of the materials surfaces has a special perspective and topicality for the formation of gradient ceramic structures, hardened layers or layers with lower strength properties, as compared with the main matrix. However, there is very little information about electron beam irradiation of ceramic multicomponent composites, which is an urgent task. The purpose of this work is to study the structural phase transformations resulting from the electron beam irradiation of a ceramic composite based on 3Y-ZrO$_2$ reinforced with alumina nanofibers (ANF) and single-walled carbon nanotubes (SWCNT).

2. Samples and investigation methods

The initial materials commercially available were nanopowder of 3 mol% yttria stabilized zirconia (TZ-3YS, Tosoh Corporation, Japan), alumina nanofibers (Fibrall, OCSiAl, Russia) and single wall carbon nanotube (Tuball, OCSiAl, Russia). The composite powder based on 3Y-ZrO$_2$ with 5 wt% ANF and 0.5 wt% SWCNT is used in this study. The study results of initial materials and method of preparation of the composite powder are presented in the papers [22, 23]. The composite powder was consolidated via spark plasma sintering (SPS-515S, Syntex Inc., Japan) using 14 mm graphite die and punches at 40 MPa with heating rate of 100°C·min$^{-1}$ and holding 10 min of 1500°C under vacuum. Bulk densities were measured using Archimedes’ method, with distilled water as immersion medium. Theoretical density values for composites were calculated by the rule of mixtures assuming density values of 6.10 g·cm$^{-3}$ for 3Y-ZrO$_2$, 3.99 g·cm$^{-3}$ for ANF and 1.80 g·cm$^{-3}$ for SWNTs [24, 25]. The composite surface was modified with an intense pulsed electron beam at the “SOLO” device (Institute of High Current Electronics SB RAS) under the following mode: beam energy density – 15 J·cm$^{-2}$; pulse duration – 200 μs; pulse repetition rate – 0.3 s$^{-1}$; pulses quantity – 10, 20, 30 and 40; residual gas pressure (argon) in the working camera – 10$^{-2}$ Pa. Investigations of the microstructures of modified surfaces were performed by scanning electron microscopy using the JSM-7500FA (JEOL, Japan). Investigation of the elemental composition and defective substructure was carried out by transmission electron microscopy using JEM-2100F (JEOL, Japan). The phase composition and parameters of the crystal structure of samples were determined by X-ray diffraction (XRD) by using X-ray diffractometer XRD-7000S (Shimadzu, Japan) with Cu-K$_\alpha$ radiation ($\lambda = 1.54056$ Å). The tube voltage and current were 40 kV and 30 mA, respectively. Scan range and sampling pitch were 10° – 120° and 0.03°, respectively.

3. Results and considerations

SPS-sintered composite has a high relative density, about 99.17%; however, some porosity was observed (figure 1a). The initial composite material consists of 3Y-ZrO$_2$ equiaxial grains, alumina grains of complex elongated shape and curved carbon nanotube bundles [26–29].

High temperature sintering (1500°C) led to the consolidation of individual ANFs into large grains. As shown in figure 1a there is no obvious boundary between Al$_2$O$_3$ grains and ZrO$_2$ matrix, indicating that the two phases are well bonded. Carbon nanotube bundles are found within the interior of 3Y-ZrO$_2$ grains or at the interfaces between entangled Al$_2$O$_3$ and ZrO$_2$ as indicated by TEM observations in figure 1b [30–32]. The average grain size of 3Y-ZrO$_2$ was 0.27 μm, which matched the grain size in similar zirconia-based composites with additives Al$_2$O$_3$ nanofibers [22].

Irradiation of the composite with an intense pulsed electron beam leads to the formation of a modified surface layer, whose thickness ranges from 6 to 40 μm and depends on the pulses quantities. The modified layer has several sublayers (figures 2a and 2c). The sublayer adjacent to the irradiation surface has a columnar structure (figures 2b and 2d; sublayer 1). The formation of the columnar structure unambiguously indicates high-speed melting and crystallization of material. The intermediate sublayer (obviously, the thermal effect sublayer) is formed by equiaxial grains with sizes from 0.5 μm to 3 μm (figures 2b and 2d, sublayer 2), which exceeds the grain size (0.27 μm) of the initial material. The longitudinal axis of the columnar grains is perpendicular to the irradiation surface.
Figure 1. STEM image of the cross-section of initial composite.

Figure 2. SEM images of the cross section of samples after electron beam processing at 10 pulses (a), (b) and at 40 pulses (c), (d). The arrow indicates the irradiation surface; numerals indicate sublayers: 1 – surface, 2 – intermediate.

The method of energy-dispersive X-ray spectroscopy (EDS) revealed the redistribution of aluminum in the surface layer of the composite irradiated with an intense pulsed electron beam (figure 3). According to the EDS method results, Al atoms in the initial composite form ANF, which are preferentially, located parallel to the sample surface. In the modified layer, when irradiated by an
electron beam, the Al atoms form thin interlayers along the boundaries of the columnar grains [33, 34].

Figure 3. STEM image of the cross-section of sample irradiated with an electron beam at 10 pulses (a) and elemental distribution maps for Al (b).

To compare the phase compositions, figure 4a shows the X-ray diffraction patterns of the composite before and after treatment with a low-energy pulsed electron beam. In all the samples, it is clear the presence of the tetragonal phase of zirconia t-ZrO$_2$ as the main one [35–37]. In the initial composite, in addition to t-ZrO$_2$, the following phases were identified: cubic phase of zirconia c-ZrO$_2$ (11%), $\alpha$-modification of alumina $\alpha$-Al$_2$O$_3$ (less than 5%) and cubic phase of zirconium carbide c-ZrC (less than 5%) [38, 39]. The electron beam treatment leads to the disappearance of the diffraction peaks of phases c-ZrO$_2$, $\alpha$-Al$_2$O$_3$ and c-ZrC, which is possibly due to the disordering of the structures to the level of metastable amorphization [40, 41].

Figure 4. (a) XRD patterns of pristine (I) and irradiated of electron beam at 10 pulses (II), at 20 pulses (III), at 30 pulses (IV) and at 40 pulses (V); (b) Magnified (111) peak of t-ZrO$_2$ for all samples. All scales are linear.

In addition, electron beam processing may contribute to the formation of new phases. For example, in a sample irradiated with 40 pulses, two peaks are recorded (*) at angles 21.22° and 22.92°, which
presumably correspond to Al$_2$O$_4$C. Figure 4b shows the enlarged part of figure 4a, it reveals that the XRD peak broadening has increased after irradiation (table 1) thus indicating that the long range crystallinity and periodic structure is being compromised, i.e., irradiation has resulted in the deterioration of the crystallinity [42, 43]. The shift of peak positions indicates the enlargement of lattice spacing (as shown in figure 4b). The reduction of peak intensity (figure 4b, V) is an indication of disordering of crystal lattices due to the irradiated defects and/or reduces the amount of phase, which will be further identified in the following experimental results.

Table 1. Structural parameters calculated from the XRD results.

| Pulses | 2θ of (1 1 1) (°) | FWHM (°) |
|--------|------------------|----------|
| 0      | 30.229           | 0.1548   |
| 10     | 30.211           | 0.1546   |
| 20     | 30.271           | 0.1653   |
| 30     | 30.290           | 0.1804   |
| 40     | 30.199           | 0.1694   |

4. Conclusion
In this paper, the dense zirconia-based composite with additives ANF and SWCNT were prepared by spark plasma sintering for investigating the effects of low-energy pulsed electron beam irradiation on the evolution of microstructure, elemental and phase composition. It was found that electron beam processing leads to cardinal microstructural transformations of the surface layer. A multilayer modified volume of material is formed, successively consisting of columnar grains, equiaxed larger grains (compared to grains of the initial material). The redistribution of Al atoms in the surface layer, which form thin interlayers along the boundaries of columnar grains, has been found. The electron beam irradiation significantly affects the phase composition. Changing the volume fraction of phases, the formation of new phases, changing the crystal lattice parameters depend on the quantity of irradiation pulses. These results contribute to a better understanding of the response of ceramic multicomponent composites to electron beam irradiation, and may also be important from the perspective of designing highly nano-crystalline materials for applications in various radiation environments.

Acknowledgments
This work was supported by the program of fundamental scientific research for 2019-2021 (Subject No. 0291-2019-0002).

References
[1] Hannink R H J, Kelly P M and Muddle B C 2000 J. Am. Ceram. Soc. 83 461
[2] Badwal S P S 1992 Solid State Ionics 52 23
[3] Aldebert P and Traverse J P 1985 J. Am. Ceram. Soc. 68 34
[4] Buyakov A S, Buyakova S P, Tkachev D A and Kulkov S N 2018 AIP Conference Proceedings 2051 020046
[5] Tatarko P, Grasso S, Chlup Z et al 2014 J. Eur. Ceram. Soc. 34 1829
[6] Touaiher I, Saâdaoui M, Chevalier J et al’2018 J. Eur. Ceram. Soc. 38 1778
[7] Xu S, Xu Y, Liu Y et al 2017 Ceram. Int. 43 15060
[8] Hu C F, Kim B N, Park Y J et al 2015 J. Ceram. Soc. Jpn. 123 86
[9] Rotshtein V, Ivanov Yu and Markov A 2006 Materials surface processing by directed energy techniques ed Y. Pauleau (Paris: Elsevier) 205
[10] Leonov A A, Kuzickin E E, Shugurov V V et al 2018 J. Phys.: Conf. Ser. 1115 032040
[11] Ivanov Yu, Shugurov V, Kalashnikov M et al 2018 AIP Conference Proceedings 2051 020110
[12] Costantini J M, Beuneu F, Grynszpan R I and Trautmann C 2005 Nucl. Inst. Methods Phys. Res.
[13] Costantini J M, Beuneu F, Morrison-Smith S et al 2011 J. Appl. Phys. 110 123506
[14] Surzhikov A P, Frangulyan T S, Ghyngazov S A et al 2016 Ceram. Int. 42 13888
[15] Tanaka M 2018 Applied Physics A 124 647
[16] Chang Y Q, Guo Q, Zhang J et al 2013 Front. Mater. Sci. 7 143
[17] Liu W, Ji Y, Tan P et al 2016 Materials 9 105
[18] Ghyngazov S A 2018 Nuclear Inst. and Methods Phys. Res Sect. B 435 190
[19] Yasuda K, Kinoshita C, Matsumura S and Ryazanov A I 2003 J. Nucl. Mater. 319 74
[20] Edmondson P D, Weber W J, Namavar F and Zhang Y 2012 J. Nucl. Mater. 422 86
[21] García Ferré F, Mairov A, Vanazzi M et al 2018 Acta Mater. 143 156
[22] Leonov A 2019 Materials Today: Proceedings 11 66
[23] Leonov A A, Abdulmenova E V 2019 IOP Conf. Ser.: Mater. Sci. Eng. 511 012001
[24] Poyato R, Macías-Delgado J, Gallardo-López A et al 2015 Ceram. Int. 41 12861
[25] Abden M J, Afroze J D, Mamun M A and Haque M M 2014 Materials Express 4 317
[26] Wu W, Xie Z, Xue W and Cheng L 2015 Ceram. Int. 41 1303
[27] Yan S, Wu D, Huang Y et al 2019 Materials Letters 235 228–231
[28] Zuoa F, Menga F, Lina D T et al 2018 J. Eur. Ceram. Soc. 38 1796
[29] Liu Y, Ai Y L, He W et al 2018 Ceram. Int. 44 16421–16427
[30] Reyes-Rojas A, Domínguez-Rios C, García-Reyes A et al 2018 Mater. Res. Express 5 105602
[31] Akin I 2015 J. Ceram. Soc. Jpn. 123 405
[32] Leonov A A, Khasanov A O et al 2017 IOP Conf. Ser.: Mater. Sci. Eng. 286 012034
[33] Dey S, Mardinly J, Wang Y et al 2016 Phys. Chem. Chem. Phys. 18 16921
[34] Yang T, Taylor C A, Wang C et al 2015 J. Am. Ceram. Soc. 98 1314
[35] Jiang K, Liu S and Wang X 2017 Ceram. Int. 43 12633
[36] Almeida V O, Balzaretti N M, Costa T M H and Gallas M R 2015 Nano Struct. Nano Objects 4 1
[37] Yi J, Wang T, Xie Z and Xue W 2013 J. Alloy. Comp. 581 452
[38] Couto C A O, Ribeiro S and Passador F R 2018 Cerâmica 64 608
[39] Estili M, Echeberria J, Vleugels J et al 2015 Ceram. Int. 41 4569
[40] Wang L M, Wang S X and Ewing R C 2000 Philosophical Magazine Letters 80 341
[41] Lu F, Wang J, Lang M et al 2012 Phys. Chem. Chem. Phys. 14 12295
[42] Buyakov A S and Kulikov S N 2017 AIP Conference Proceedings 1882 020010
[43] Debelle A, Channagiri J, Thomé L et al 2014 J Appl Phys 115 183504