Modification of Ferrite Ceramics Properties by Intensive Pulsed Beam of Low-Energy Electrons

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Abstract – The influence of intensive pulsed beam of a low-energy electrons (IPBLE) on near-surface layers of ferrite ceramics is investigated. It is shown, that the effect IPBLE on ferrite ceramics results in visualization of its microstructure. At the same time decreasing of grains size in near-surface layers takes place. The effects of significant decreasing of magnitude of microhardness and transition of ferrite near-surface layers from low to high-conductive state under influence IPBLE are detected.

1. Introduction

The experimental researches in the field of structure and properties modification caused by action IPBLE are carried out on metals and alloys, basically [1, 2]. The total experimental data, identically denote an opportunity in enough wide limits to operate by microstructure, phase mixture, strength properties of surface layers of metals and alloys with the help IPBLE. The discovered effects are caused by features of thermal influence of IPBLE on solid states. Under irradiation of materials by IPBLE in the near-surface layer fast processes of heating, melting, evaporation and fast quenching from melt occurs.

In our opinion, effect taking place at interaction n IPBLE with another types of materials and, in particular, on oxide ceramic structures, including ferrite, are of the large interest. As far as we know, in the literature the similar data are absent.

Character of ferrite is the belonging them to compounds of variable mixture. The thermal treatment usually stimulates an oxygen exchange between an oxygen matrix of spinal and environment. Also thermal treatment is capable to result in other deeper scale changes in ceramics structure and composition. Therefore the specific features of thermal influence IPBLE on materials can result in formation of a particular complex of properties in ferrite ceramic.

In the present work we represent results of study of action IPBLE on lithium-titanium ferrite ceramic.

2. Experimental Procedure

Li-Ti ferrite was synthesized by the ceramic technique from a mechanical mixture of the following composition: (in wt %) of Li_2CO_3 – 11.2, MnO – 2.7, TiO_2 – 18.65, ZnO – 7.6, Fe_2O_3 – 59.81 wt. %. Its chemical structure was the following:

$$Li_{0.649}Fe_{1.598}Ti_{0.5}Zn_{0.2}Mn_{0.051}O_4.$$

Samples were formed in tablets of 18 mm diameter and 3 mm thickness by single-axis compaction. Then they were sintered at 1280 K during 2 hours in air. The samples were irradiated in vacuum by single pulsed beam of a low-energy electrons with the following parameters: E = 15 keV, density of a current in a pulse – 28 A/cm^2, pulse duration of 30 μsec. The energy density in a pulse of 12.9 J/cm^2. Quantity of an electron beam pulses was N = 1 and 10.

The effects of an influence IPBLE was revealed by comparison of samples surface layers properties prior to and after irradiation. The following investigation were carried out: microstructures of a surface; microhardness; electrical conductivity. Morphology of a surface was studied by a method optical microscopy. For measurement of microhardness was used device PMT-3. The static electrical conductivity was measured in an interval of temperatures (300–600) K by the method of spreading resistance [3], which allows to determine resistance in thin layers of semiconductor materials.

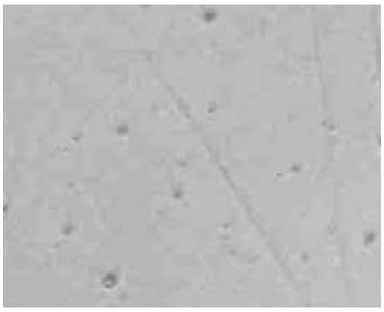
3. Experimental Results

3.1. Metallograph researches

Samples both with polished surface and grinding finish were used in experiments (Fig. 1, *a*). The microstructure of ceramics in that case was not looked through. Metallograph observations have shown that the action even of a single pulse IPBLE results in essential change of a surface samples state (Fig. 1, *b*).

From comparison of Fig. 1, *a* and Fig. 1, *b* one can see that the electron treatment allows to visualize of ceramics microstructure. At the same time the grain boundary were sufficiently well-marked. Simultaneously in separate sites the microcraters were observed. The picture did not change cardinally with increase of number of pulses up to N = 10. Moreover, the grains we observed when the unpolished surface was irradiated.

The energy of pulsed electronic beam injected in a sample causes fast heating of ceramics surface layer. The increased evaporation of substance from area takes place. These processes promote etching of grains boundary. Thus, one of a number the established effects of IPBLE action on ferrite ceramics consists in polishing and etching of its surface, that allows to visualize microstructure of subject.



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a

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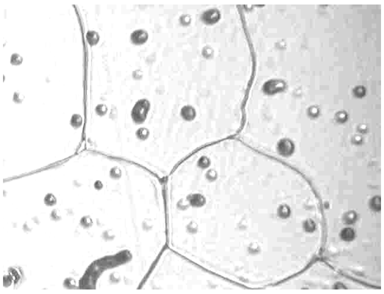
b



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c

Fig. 1 The optical microphotos of the polished surface Li-Ti ferrite ceramics before irradiation (*a*), after irradiation by single pulse of electronic beam (*b*), after chemical etching of unirradiated of ceramics surface (*c*)

Another the most significant effect consist in decreasing of grains size in surface layers under pulsed heating of ceramics by intense energy flows. The optical microphoto of unirradiated ceramics surface after chemical etching is given in Fig. 1, *c*. The analysis has shown, that before electron beam treatment the average size of a grains (l_{av}) amounts 50 μm. According to the data of Fig. 1, *b*, after irradiation the average size of grains in surface layers decreased to a considerable extent up to 20 μm. It is possible to assume that under pulsed heating by IPBLE occurs melting of samples surface and following high-speed recrystallization. It leads to a decreasing of ceramic grains size.

3.2. Research of microhardness

The influence of electronic treatment on microhardness of ferrite ceramics was investigated. Previously, of microhardness (H_V) was determined in unirradiated samples subjected to different loading on indenter P in limits (0.3–2) H. The results are given in the Table 1. It is possible to see, that the magnitude H_V essentially depends on magnitude of loading. In the literature [4] this result is explained by the phenomenon of elastic restoration of an indentation. This phenomenon plays the large role in materials having high hardness in case using of small loadings on indentor. Usually the value of loading should satisfy to the condition of independence H_V from P. In our case this situation takes place at loading $P = 2$H. However, in the irradiated samples under such loading, the measurement of microhardness have appeared impossible. Chips were observed near the region of the indentation. The edges of indentation were badly expressed and are deformed. The same picture took place at decreasing of loading down to $P = 0.5$ H. These phenomena could be caused by the occurrence of significant gradients of mechanical pressure in a region of boundary between the irradiated surface and unirradiated the ceramic bulk.

Table 1

The treatment mode	The loading on indenter P, H	Microhardness H_V, GPa
No treatment	0.3 0.5 1.0 2.0	9,4 8.8 7.0 6.9
Electron treatment, $N = 1$	0.3	5.7
Electron treatment, $N = 10$	0.3	5.9

Therefore, we carried out experiments using loading on indenter $P = 0.3$ H. In such case the indentation shape was not deformed. From the data given in the table follows, that the electron treatment of ceramics results in essential (on the average in 1.6 times) decreasing of magnitude H_V. In our opinion, it can be connected to increase of plasticity of a surface layer that suppresses effect of elastic restoration of an indentation.

According to rough estimations, the extrapolated range of electrons with energy $E = 15$ кeV(R_e) in researched samples amounts 2.3 μm. For the irradiated surface the depth of penetration of Vikkers pyramid amounts about 1 μm at loading $P = 0.3$ H. Thus, the established effect relates to irradiated zone directly.

That fact that deserves attention, that after removal of layers about 15 and 25 μm with irradiated surface, H_V is increased a little and becomes equal 7.2 and

7.8 GPa, respectively. Hence the microhardness retains the lowered magnitude beyond the irradiated zone. Thus, it is possible to speak that the long-range effect takes place [4]. On distance 60 μm from the irradiated surface the radiation changes of microhardness were not noticed.

It is important to note, that thermal annealing of the irradiated samples at $T = 1000$ K during 15 min did not lead to changing of magnitude H_V. It testifies that the radiation changes of hardness are characterized by high stability and are caused by cardinal changes of structural-phase state of ceramics surface layers.

3.3 Research of electrical conductivity

The electrophysical properties of ferrite are closely connected with cation allocation in a crystal lattice, chemical, phase and stoichiometric compositions of ceramics. Taking into account the above results, it was logical also to expect the change of electrical conductivity after irradiation of ceramics by IPBLE.

In paper [6] authors have reported, that Li-Ti ferrite have semiconductor properties and is characterized by conductivity of a n-type. For the temperature range under consideration (300–600) K electrical conductivity of samples rises in according exponential law with one magnitude of activation energy U. In an initial state sintered samples were characterized by low electrical conductivity and rather high ($U = 0.7$ eV) magnitude of conductivity activation energy (Fig. 2). Thus they were high-resistance semiconductors. The results provided evidence on the considerable change of electrical conductivity under the irradiation of Li-Ti ferrite by IPBLE.

As an example the temperature dependence of electrical conductivity of the irradiated samples are given in Fig. 2. One can see that the electron treatment ($N = 10$) of the ferrite ceramics causes an increase of conductivity on several orders. At the same time the activation energy is reduced. Thus the surface layers of high-resistance ferrite ceramics becomes high-conducting.

The similar effects are observed under irradiation of a wide class oxide dielectrics by various types of the accelerated ions [7].

The activation energy is the most important characteristic of electrical conductivity process in substance. Unlike monocrystals polycrystalline ferrite are non-uniform conducting medium. Well-conducting grains are separated by poor conducting grains boundary. Therefore grain boundaries (GB) have a large influence on activation energy of electrical conductivity of ferrite ceramics.

It was pointed out [8], that at measurement of static conductivity the magnitude U in Li-Ti ferrite ceramics is equal to height of grain boundary potential barrier. According [9], the presence of potential barrier results in reducing of electron mobility. As a consequence significant increasing of electrical resistance in polycrystalline semiconductors occurs.

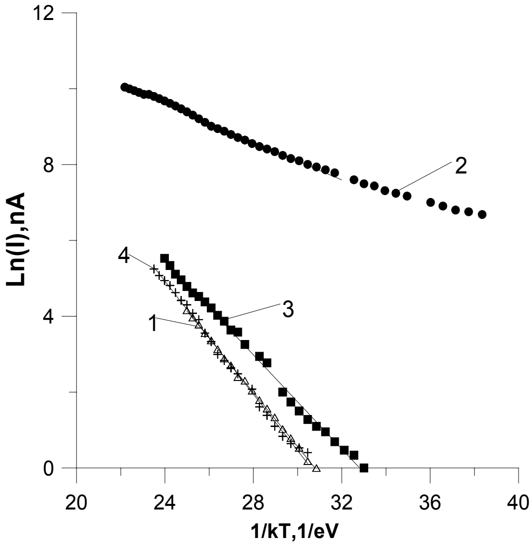

Fig. 2. The temperature dependences of ferrite conductivity current. 1, 2 – before and after electron beam treatment, respectively; 3, 4 – after an air annealing at $T = 670$ K and $T = 720$ K of irradiated sample, respectively

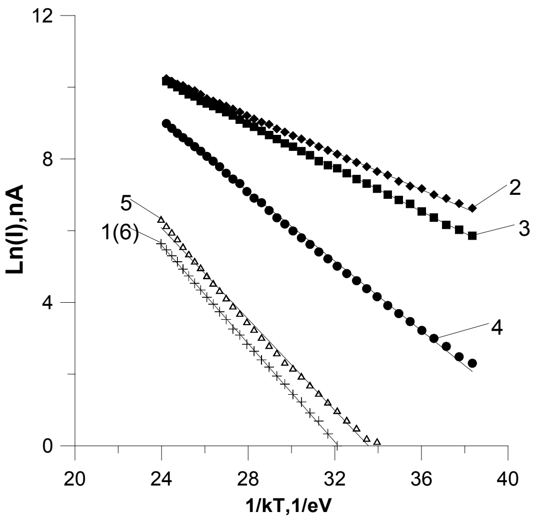

Fig. 3. The temperature dependences of ferrite conductivity current. 1 – in initial state, 2 – after vacuum reduction thermal annealing at $T = 1020$ K; 3, 4, 5, 6 – after following an air annealing at $T = 720$ K, 770, 870, 920 K, respectively

The reason of occurrence of such barrier consists in excess concentration of acceptors in GB area comparison with volume of a grain. The capture of electrons by acceptors creates the negative surface charge which causes increase of electrostatic potential on a grain boundary. The atoms of oxygen is most probable acceptors. During sintering ferrite in an air environment the GB is actively enriched by oxygen due to its more higher diffusion penetrability. In result GB is in more oxidized condition in comparison to volume of a grain. Besides a various impurity cations, which always the GB is enriched, can play a role of acceptors.

Thus, the value of grain boundary potential barrier depends on chemical composition and concentration of charge carriers in GB. Therefore the change U can carry the information about the change of GB state as a result of various treatments.

It is possible to assume that at interaction of the intensity electronic beam with ferrite ceramics there is an active removal of oxygen from area over-oxidized GB in an environment. In result the value of GB potential barrier and hence U is reduced. Accordingly there is a growth of electrical conductivity.

For confirming that this process plays a determining role in formation of high-conductivity state in surface layers of high-resistance ferrite, we have studied the influence of isochronous oxidizing thermal annealing (during 10 mines) in an air environment on electrical conductivity of the irradiated samples.

According to obtained results, the annealing down to $T = 620$ K did not noticeable influence on conductivity of the irradiated samples. However beginning from annealing temperature $T = 670$ K, there is a sharp the increase both of activation energy and electrical resistance of surface ceramics layers modified by IPBLE (Fig. 2). After annealing of ceramics during 10 min. at $T = 720$ K the electrical conductivity completely returns in the initial state. It is possible only in the event that the effect of radiation increase of conductivity is caused by changing of the oxygen contents in ceramics due to of reduction processes, rather than by other an irreversible changes of its composition and structure. During the annealing atmospheric oxygen is adsorbed on a surface and diffuses according to the mechanism grain-boundary diffusion in area of grains boundary of the irradiated ferrite converting their again in oxidized state.

For comparison a similar type experiments were carried out with use ferrite ceramics, which was specially transfered from high-resistance in low- resistance state by a traditional way, namely with the help reduction thermal annealing in vacuum at $T = 1020$ K. The temperature dependence of conductivity of the reduced surface layer is given in Fig. 3. The prepared thus samples were exposed to subsequent oxidizing annealing in an air environment. The experimental results are given in Fig. 3. One can see that the annealing at temperatures $T > 720$ K causes decreasing of ceramics conductivity and increasing of activation energy. At annealing temperature $T = 870$ K the conductivity reaches the initial values.

As testified by the results of this experiments the high-conductivity state formed both by reduction thermal annealing and treatment of ceramics by a pulse electrons beams defined by the same reason, namely, alteration of oxygen stoichiometry.

4. Conclusion

1. It is shown, that the influence of IPBLE on ferrite ceramics is capable to cause the polishing and etching of its surface, that results in visualization of its microstructure. At the same time decreasing of grains size in near-surface layers takes place.

2. The electron beam treatment of ceramics results in significant decrease of microhardness of surface layers.

3. Under action IPBLE the surface layers of high-resistance ferrite ceramics transfers in a high-conductivity state. The given result is caused by alteration of oxygen stoichiometry due to active eliminating of oxygen from area GB.

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