Radiation homogenization of heterogeneous ionic compounds

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Abstract – Experimental data on discovery and study of new phenomenon, involving radiation dissolution of impurity and vacancy in ionic structures are described. This phenomenon is called radiation homogenization of heterogeneous materials with ionic type of chemical link and can be widely used when creating radiation technologies in the field of science of materials.

1. Introduction

In ionic crystals and ceramic, point defects (vacancy and alien admixtures) at high concentrations are in the form of precipitates or precipitate compounds located in the field of interphase boundaries and precipitate compounds, determining heterogeneity of structure. The similar formations cause deterioration of mechanical and electrical properties of materials. The development of dissolution impurity procedure and vacancy phases is necessary for practical science of materials. Thus, it is necessary to view it as a process of homogenization of material structure.

The purpose of the present article is the representation of experimental data on detection of the new phenomenon involving radiation homogenization of heterogeneous ionic structures on a phase composition, which include alkaline-haloid crystals (AHC), ferrite and superconducting ceramics. This phenomenon is observed at a high-temperature irradiation by powerful streams of electrons with energies 1.5 … 3.0 MeV from accelerators ЭЛУ-6, ЭЛУ-7, ИЛУ – 3, which provide power of the absorbed dose 105 … 107 Gy/s. Similar effects are initiated by streams of prompt protons with energy in several MeV.

2. Radiation dissolution of impurity phases in AHC

In doped alkaline-haloid crystals, the divalent admixtures are in three states: precipitates (phase of emission) from impurity – vacancy complexes (IVC), separate IVC and IVC, dissociated on cationic vacancies and divalent impurity ions. By measuring ionic conductivity of alloyed crystals it is possible to judge a degree of precipitation of impurity ions describing phase heterogeneity of a structure.

Studying electrical conductivity of crystals NaBr-$CaBr_2$ before and after electronic irradiation the effect of dissolution of impurity phases is found out.

Fig. 1 shows the temperature dependences of electrical conductivity of crystals NaBr+0.1M%$CaBr_2$ before and after the irradiation by electrons by a dose $6 \cdot 10^8$ Gy. The electronic jet with energy of electrons equal to 2MeV of the accelerator to ИЛУ – 7 was used, the power of a dose in impulse made up $6 \cdot 10^6$ Gy/s. During the irradiation, samples were heated up to 423 K.

For unirradiated samples two-phase type of temperature dependence of an electrical conductivity, typical for alloyed AHC is observed. Temperature of curves break (Tи) determines the transition from associative conductance with activation energy 0.9 V to non-associative with activation energy of 0.7 V. Function ln $\sigma = f(1/T)$ for irradiated samples qualitatively is similar to the same dependence for unirradiated crystals on a higher level of conductance. The processing of the received dependences under the associative theory of ionic conductivity testifies the fact that the irradiation of crystals causes concentration increase of isolated impurity – vacancy complexes with $1 \cdot 10^{14} sm^{-3}$ to $3 \cdot 10^{15} sm^{-3}$.

The growth of break temperature (Tи$_2$) and rate of conductance as a result of irradiation is explained by radiation-stimulated dissolution of impurity phase on single IVC. The effect is thermally stable up to 500K. Thus, at examination of radiation change of NaBr crystals conductance, containing ions of divalent metals, the phenomenon of radiation dissolution of impurity precipitates is observed.

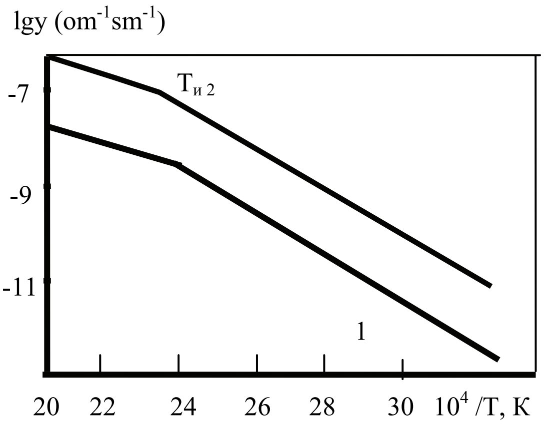

Fig.1. temperature dependence of electrical conductivity for NaBr+0.1M%$CaCl_2$, 1-unirradiated crystal. 2-crystal, irradiated by electrons with the dose 10^7 Gy at T=423K, $W_и = 6.10^6$Gy/s

3. Radiation dissolution of vacancy phases in AHC

It is known that in ionic crystals at low temperatures the superequilibrium vacancies of a biographic origin are in the form of various complexity (of precipitates), forming phase vacancy. Thermal dissociation of these phases in AHC occurs at temperature about 500^{0}C. Similar formations at intensive irradiation dissociate on isolated vacancies with formation of hole and electronic centres of colouring.

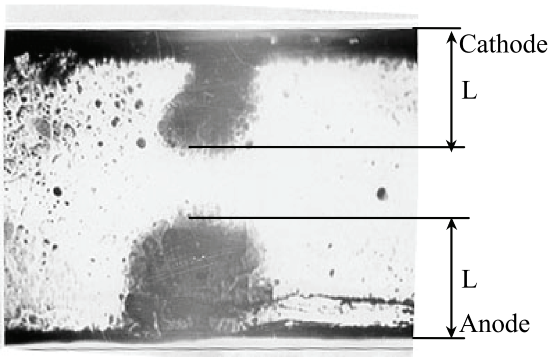

Fig. 2. Formation of electrolytic colouring at 220 ^{o}C in crystals NaCl, preliminarily irradiated by protons from two sides on depth L

At electrocolouring the electrons are injected from the cathode in a crystal and migrate to anode, being partially grasped on anionic vacancies with formation of F-centres, which is visual. If anionic vacancies in a crystal are among vacancy aggregates, then at a motion of electrons from the cathode to the anode, the formation of F-centres and the colouring cloud does not occur.

All the above considered, results of experiments given in [1], should be viewed as convincing confirmation of radiation dissolution of vacancy agglomerates in AHC.

The experiments plan consists in the following. Samples of crystals NaCl with thickness 0.9 mm, previously irradiated by protons with energy 5 MeV from two sides on depth L, were exposed to electrolytic colouring at temperature 220^{0}C. Let's note that the heat processing at 220^{o}C leads to complete fracture of irradiationly created F-centres and is insufficient for dissociation of vacancies aggregates.

Fig. 2 shows microphoto of a front part of a sample, which passed specified processing. It is precisely visible that the cloud of F-centres is shown only in near-electrode parts of a crystal subjected to a proton bombardment. This result testifies the fact that electrons injected in a sample at electrolytic coloring are grasped by anionic vacancies with formation of F-centres only in irradiated areas of a crystal. Through unirradiated part of a sample electrons migrate practically without entrapment on anionic vacancies. Thus, in the irradiated crystal areas anionic vacancies are in a free state. It tells about radiation break of vacancy aggregates. Thus, intensive AHC irradiation causes homogenization of structure consisting in dissolution of vacancy agglomerates.

4. Homogenization of Superconductive and Ferrit Ceramic by Intensive Irradiation

Numerous investigations revealed the high-temperature superconductors of the 1–2–3 types having the structure of orthorhombic perofskite. In this case, the yttrium baric cuprates have the following formula $YBa_2Cu_3O_{7-x}$, where $0 \le x \le 0.5$.

A better high-temperature conductivity is demonstrated by an ideal single crystal state of orthorhombic phase of yttrium baric cuprates. Ceramic structures are far behind, first of all, due to the presence of incidental phases in the form of unreacted initial components (Y_2O_3, CuO, $BaCO_3$) and intermediate metabolites of synthesis in the tetragonal phase not having superconductivity quality. In this connection, the development of methods of incidental phases dissolution, i.e. the phase homogenization of ceramic structure, is a relevant task. The results of high-temperature radiation processing of ceramic (1–2–3), attesting the discovery of a new phenomenon – radiation homogenization of ceramic structures – are stated below.

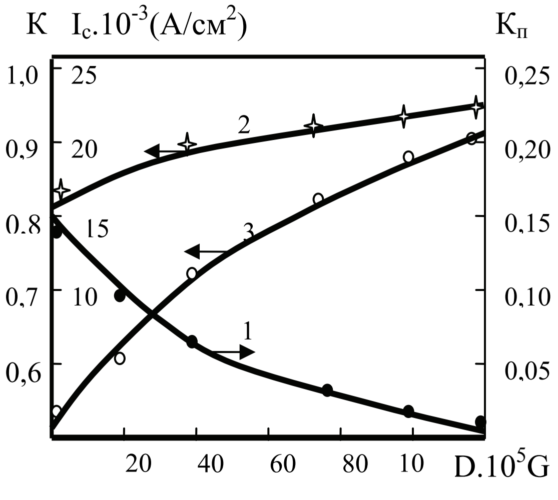

Рис. 3. Dependencies of relative substance of orthorhombic phase К$_0$ (2), impurity phases К$_п$ (1) and critical current density I$_c$ (3) for yttrium baric ceramic on electronic irradiation dose by 400 єC

The ceramic samples $YBa_2Cu_3O_{7-x}$, derived through traditional technologies, were used for radiation modification.

The testing of critical current density was carried out by a four-probe method, the pedestal current being 30mA. Critical current was measured by the sag on the voltage-operated electrodes equal to 2 microvolt. X-ray phase analysis of samples was carried out on the unit ДРОН-3. The substance of a superconductive phase was determined by the method of quantitative analysis of diffractograms against intensity of reflexes within orthorhombic phase $YBa_2Cu_3O_{7-x}$ (К$_0$), to the sum of reflexes within impurity phase as Y_2O_3, CuO, $BaCuO_2$, Y_2BaCuO_5 ($К_{П}$). To modify the yttrium baric cuprates, the pulsed linear accelerator of electrons ИЛУ-6 with the beam parameters: electron energy 2 MeV, beam current in pulse – (0.2–0.8)A, radiation pulse duration equal to 500 microseconds, pulse-repetition frequency (2–60) Hz.

While irradiating the ceramic high-temperature superconductors, the critical current density regularly increases and by the absorbed dose $1.2 \cdot 10^7$ Gy it exceeds initial values more than five times. The cause of the discovered effect becomes clear as a result of X-ray phase analysis of investigated materials. On the diffractograms of non-irradiated ceramic samples, all the reflexes within orthorhombic phase $YBa_2Cu_3O_{7-x}$ are clearly defined. Nevertheless, beside the peaks of a basic superconductive phase, diffractograms also contain responses from CuO and synthesis intermediates in the form of $BaCuO_2$ and Y_2BaCuO_5. The impurity phase substance comes up to 13%. While increasing the irradiation dose the intensity of orthorhombic phase base line also increases, reflexes from impurities fall back and by the dose of $1.2 \cdot 10^7$ Gy present only as remnants. (see Fig. 3).

Thereby, radiation modification by its powerful impact leads to the homogenization of structure of the ceramic high-temperature superconductors, invoking the dissolution of incidental non-superconductive phases.

The research paper [3] contains the results, testifying the homogenizing impact of powerful flows of electrons on the phase composition of sintered ferrites. The object of the research was lithium titanium spinel ferrite of the mark 3СЧ-18, synthesized according to the ceramic technology from the powder mixture in the mass %: Li_2CO_3-11.2; TiO_2-18.65; ZnO-7.6; $MnCO_3$-2.74; Fe_2O_3-59.81. Phase uniformity was controlled using X-ray and magnetic measurements.

In the polycrystalline ferrospinel, the impurities, damping the magnetic properties, are the particles of oxides as MnO, FeO, $LiFeO_2$, etc. These infractions of phase homogeneity of the material induce the elastic stress, which manifest themselves in the amplification of X-ray reflections and in changing on the initial magnetic permeability. Experiment investigations of the phase composition and elastic state of lithium titanium ferrites, carried out according to the methods of X-ray structure analysis and measurement of magnetic behaviour, and showed that sample sintering in an electronic beam with the capacity of an absorbed dose of nearly 10^6 Gy/second leads to the dissolving of intensive impurity phases.

The results stated in this article testify the discovery of a common for many heterogenic ion compounds, including alkaline-haloid crystals and ceramic, of a new phenomenon of impurity and vacancy phases dissolving by the high-temperature irradiation of the materials by the powerful flows of charged particles. This phenomenon is called as homogenization of heterogenic structures and conditioned by the doubled mass transfer in conditions of intensive actuation of electronic subsystem of a substance. The mechanism of radiation homogenization of ion structures is described in the work [4], and this phenomenon can form the basis of radiotechnologies of producing functional ceramic with the improved properties. [5].

Radiation technologies of high-grade ceramic production

The works of the mentioned authors, basing on the phenomenon of the radiation homogenization of the heterogenic ion structures, offer technological schemes of production of high-grade ceramic of different functional purposes using the methods of electron-beam sintering and modification of articles. [5–9]. Ceramics processing is carried out in the electron flow with the energy equal to (2–4) MeV, providing the average power of an absorbed dose (10^5–10^6) Gy/seconds.

Radiation sintering leads to the decrease of the sintering temperature by 150…200^0C, shortening the sintering period tens times, acquiring of the homogeneous finely crystalline structure, improving the performance properties of ceramic several times. This effect is found in the ferrite, superconductive, dielectric, instrumental ceramic.

Such improvements of the ceramic characteristics also occur by the electron-beam modification of ceramic structures. It is evidenced by the results of experiments, obtained for the corund-zirconium (CZ) ceramic and listed in the table below.

Table. Impact of radiation modification on the mechanical characteristics of CZ ceramic

	Durability y_{prod} (MPa)	Durability (hPa)	Crack resistance K_{1c} ($MPa.m^{1/2}$)
Before processing	300–400	8–10	7–11
After processing	1000–1200	15–18	15–21

Therefore, the offered technology of electron-beam modification makes it possible to produce CZ ceramic with the record mechanical characteristics, which are of the level of those of the best types of the hard alloys. And regarding the wear resistance and the operational temperature of radiation modification, CZ ceramic is more preferable in comparison with other types of the high-strength materials.

Conclusion

The findings, stated in the present article, testify the radiation dissolving of impurity and vacancy phases in the compounds with ion type of chemical bond, which can be qualified as discovery of a new phenomenon, connected with the phase homogenization of heterogenic ion structures by the intensive electron irradiation.

This conclusion has an obvious interest for development of prospective radiation technologies. The radiation homogenization of materials revealed in this work is conditioned by the primary absorption of irradiation energy on the heterogeneity of the structure, which leads to their dissolving. This effect is not only a characteristic of electron beams, but also has to occur in the case of using other types of radiation, which primarily include microwave radiation. Further development of the present work items can be connected with the creation of electron-beam microwave technologies of nanoceramic production.

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