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RADIATION STIMULATED VIOLATIONS OF MAGNETIC ORDER IN THE Fe-Be LAYERED SYSTEM IRRADIATED BY KRYPTON IONS¹Ozernoy A.N., ¹Vereshchak M.F., ¹Manakova I.A., ²Shokanov A.K.,
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Studies of structural and phase state of Be-Fe-Be three-layer system were conducted using Mössbauer spectroscopy method at ⁵⁷Fe nuclei after krypton ions irradiation with energy of 280 keV and subsequent isochronous annealing. Under irradiation, a local concentration of beryllium atoms was observed in the subsurface layer of the layered system samples. This concentration causes transition of a substantial part of the Fe atoms in the subsurface layer from a magnetic ordered state to the paramagnetic one. Post-radiation isochronous annealing results in almost complete recovery of pre-implantation local concentration of components and restoration of structure of the irradiated subsurface layer. Presented in the paper experimental results show that the implanted krypton has a great impact on the phase state of the layered system, and they can be useful to better understand and predict the effects of the gas discharge in neutron fields on radiation effects in structural materials of nuclear and thermonuclear facilities.

Keywords: Mössbauer spectroscopy, subsurface layer, layered system, irradiation.

Introduction

The ever increasing demand for new materials having specific properties and the ability to operate in extreme conditions does not diminish the relevance of the work on their search. So, in creation of materials for the first wall of a thermonuclear reactor, the idea of developing gradient composites, i.e. materials, the composition of which varies along the thickness from the surface facing the plasma to the surface contacting the thermal control material, is considered the advanced one.

For directional modification of subsurface layers of materials in order to control their properties, methods of ion-plasma coating are used; they make it possible to create a variety of composites. Initial non-equilibrium arrangement of atomic components in them and subsequent thermal effects lead to three dimensional directivity of phase formation processes and occurrence of layered systems. Earlier conducted systematic studies [1-7] of heat induced diffusion and phase transformations in binary layered systems showed that under heat treatment of Fe-Me (where Be, Ti, Al, Sn are Me) layered systems due to inter-diffusion of components there is a three dimensional directivity of phase formation process and, as a consequence, an inhomogeneous depth-distribution of phases.

We established the sequence and defined the characteristic periods of formation of thermally stable systems, in the surface layer of which there is an intermetallic compound, and in its bulk there is a solid solution of coating in α -Fe.

Studies of phase transformations in layered systems based on transition metals under heating performed within a having previously developed in Institute of Nuclear Physics (INP RK) thermodynamic approach [8], led to the creation of new materials with thermal stability at pre-set temperatures. Therefore, the task of their tests under conditions similar to those realized in nuclear and thermonuclear facilities, due to the absence of any information about it, seems highly topical problem.

This problem can be solved by means of Mössbauer spectroscopy in the backscattering geometry pattern with the registration of conversion electrons (CEMS). As the conversion electrons path in the material is measured alike the size of the affecting zone of a beam of accelerated light or heavy ions of certain energy, modeling high-dose exposure of a material by neutrons, Mössbauer spectra adequately reflect the electronic state of the resonant atoms in the damaged zone.

In order to obtain new experimental data on the properties of the created thermally stable materials and Be-Fe-Be layered system of in particular, we conducted studies of its resistance to accelerated krypton ion beams generated by DC-60 accelerator. The paper presents experimental results showing new features of occurrence of krypton in iron-beryllium layered system subjected to irradiation and subsequent isochronous annealing.

The experimental technique

The samples were made of reinforced iron enriched in ^{57}Fe isotope to 89% using the technique of ion-plasma coating. Iron foil slices with thickness of 10 microns were produced from the plate by rolling it between the rollers of hardened carbon steel. Then, recrystallization annealing was performed at the temperature of 850°C in vacuum of $1 \cdot 10^{-6}$ mm; its duration was 3 hours.

At the ion-plasma unit "Argamak", using magnetron sputtering method, both sides of the foil were coated by a layer of beryllium metal with thickness of 0.9 and 1.0 μm respectively. Substrates to be coated were placed on a massive copper holder, this made it possible to maintain at least 150°C temperature. For better adhesion, the surface was engraved with argon ions before coating. Beryllium layers thickness was selected so that under the annealing process the diffusion pair was within the two-phase area $\alpha\text{-Fe(Be)-FeBe}_2$ in accordance with the equilibrium state diagram.

After the coating the layered system was subjected to isothermal annealing step with the interval of 5 hours at 650°C temperature. The average concentration of beryllium $C_{\text{Be}} \sim 20\text{at.}\%$ exceeded the solubility limit at this temperature. The total annealing time was 20 hours. After each stage, the samples were tested by methods of absorption Mössbauer spectroscopy (MS) and backscattering geometry in the electron channel (CEMS). As it was shown previously [1,2] interdiffusion of components under thermal annealing results in three dimensional directivity of phase formation process and, as a consequence, to non-uniform depth distribution of the phases at samples and the formation of the thermally stable at $T \leq 650^\circ\text{C}$ layered system under 20 hours long annealing. Thus, the samples were made with the surface layer on both sides containing mainly the intermetallic compound $\beta\text{-FeBe}_2$, and in the bulk having an iron-based $\alpha\text{-Fe(Be)}$ solid solution.

Then the samples were exposed to beams of krypton ions with the energy of 280 keV to the doses of $5 \cdot 10^{16}$, $1 \cdot 10^{17}$ ions/ cm^2 at the DC-60 accelerator in Astana branch of the INP RK.

The results of calculations using the well-known computer program STRIM-2008 [9] allowed us to estimate the effect of the ion beam on the crystal lattice of the irradiated material, usually expressed as number of displacements per atom.

After irradiation of the Be-Fe-Be layered system by krypton ions with the energy of 280 keV and a dose of $5 \cdot 10^{16}$ ions/ m^2 it was 17 units of dpa, and the projective range of these ions in the Fe-Be system was of the order of 72 nm. Since the penetration depth of the ions in the material was selected to be measured alike the thickness available for sensing by CEMS method, the registration of internal conversion electrons allowed us to examine the zone subjected to radiation in detail. Mössbauer absorption spectra make it possible to observe the phase composition, averaged over the bulk of the sample. As a matter of fact, the area of the material subjected to irradiation was negligible and was beyond the sensitivity of the MS method. Measuring of MS and CEMS spectra were performed with MS-110Em spectrometer at room temperature. The source of γ -quanta was ^{57}Co in the chromium matrix. Analysis and processing of Mössbauer spectra were performed using methods of simulation decryption and restoring the distribution functions of hyperfine parameters of the partial spectra using MSTools software package [10].

Results and discussion

Measurements of the Mössbauer spectra of samples of the Be-Fe-Be layered system under the backscattering geometry with the registration of internal conversion electrons (CEMS) after isothermal annealing showed that FeBe_5 intermetallic compound was formed in the subsurface layer after 5 hours of annealing. Further annealing results in diffusion of Be in the bulk of the substrate with the disintegration of the FeBe_5 intermetallic composition and forming a solid solution of beryllium in the iron of a limit concentration, and the FeBe_2 intermetallic composition as well. Thus, after the last annealing stage (20 hours), the samples had layered structure represented on both sides of the sample in the subsurface layer by mainly FeBe_2 β -beryllide, and in the bulk it was represented by solid solution of α -Fe(Be).

The data obtained in these experiments give a good fit to the results of samples measurements on geometry of absorption. Examined by this method alloy is presented in two phases – those of β - FeBe_2 and α -Fe(Be).

CEMS spectra from the irradiated side of the samples of the layered system under study, depending on the radiation dose by krypton ions are shown in Fig. 1. It is evident that after the first dose of $5 \cdot 10^{16}$ ions/cm² in the central part of the spectrum on the background of components of the partial spectra of the initial phases, there appeared a number of additional spectral lines, indicating the transition of part of iron atoms in the alloy investigated in another, different from the original, structural and phase state. Iron atoms included in the $\text{FeBe}_{2+\delta}$ intermetallic composition underwent effect of irradiation first. At the dose of $5 \cdot 10^{16}$ ions/cm² there appear iron atoms with lower values of the H_n hyperfine magnetic fields and atoms in the paramagnetic and possibly superparamagnetic state. Reduction in the H_n magnetic fields at iron atoms nuclei can be explained by the violation of the long-range order in the arrangement of atoms due to the occurrence of vacancies and interstitial atoms (up to amorphization) that results in reduction or breaking of the exchange coupling between them. Lines of the paramagnetic type in the spectrum can be caused by complete breakage of the exchange coupling due to the increased local concentration of Be, or by significant reduction in the particle size of the intermetallic compound as a result of radiation effect. Increase in the dose results in a slight growth of the proportion of iron atoms in the (super) paramagnetic state. At the radiation dose of $1 \cdot 10^{17}$ ions/cm² radiation damage resulted in the breakdown of the magnetic order in the FeBe_2 intermetallic compound, ~34% of the iron atoms went into the (super)paramagnetic state, compared to 33% at the dose of $5 \cdot 10^{16}$ ions/cm².

To investigate the (super) paramagnetic component of the Mössbauer spectrum, a refrigerant agent was introduced into the chamber for registration the conversion electrons and spectra of cooled to -70°C samples were taken. The relation between the partial spectra didn't change. Therefore, we can assume that the paramagnetic component in the spectra is not primarily associated with particle sizes of the intermetallic compound (their superparamagnetic behavior), but with an increase in the local concentration of beryllium and breaking of exchange coupling between atoms of Fe in the radiation effect area.

Crystal lattice defects (local stoichiometric impurity, vacancies, interstitial atoms, surface defects – grain boundaries and stacking faults, lattice deformation) under radiation of the surface layer of the material substantially alter CEMS spectra of ^{57}Fe nuclei in the radiation effect area. However, the quantity of nuclei ^{57}Fe , located near such defects, with respect to all of the iron atoms in the sample is small and is beyond the sensitivity of the MS method.

In fact, the MS spectra analysis revealed no significant phase and structural changes in the bulk of the material resulting from the irradiation and a subsequent heat treatment. Therefore, the effect of irradiation extends to the depth of the projected range of the implant, without affecting the basic, bulk part of the sample; its thickness is 12 μm .

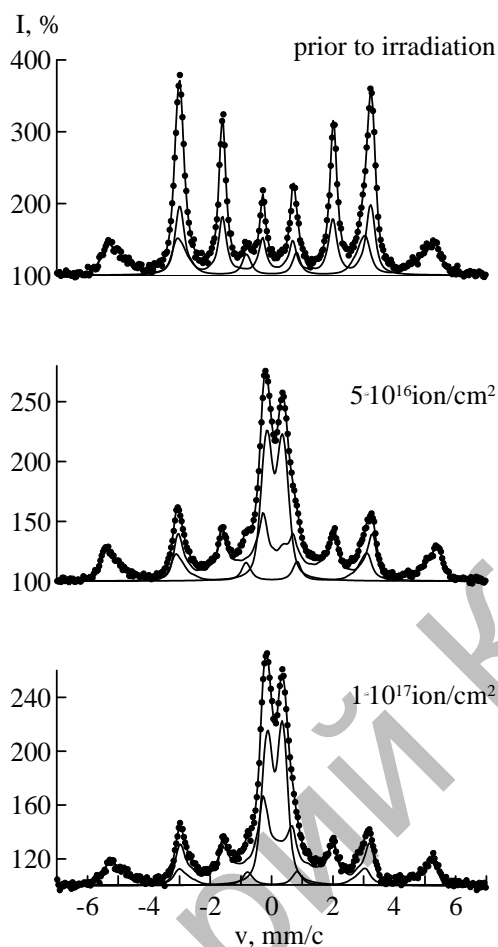


Fig. 1. CEMS spectra of Be(0.9 μm)- ^{57}Fe (10 μm)-Be(1.0 μm) layered system depending on the radiation dose

Under krypton ions irradiation one can expect physical processes common to all implants, including dispersal of the surface layer atoms, phase formation and their dissolution, ion mixing as well as the formation of strongly heated areas (thermal spikes) with their subsequent hardening at a speed of 10^{10} - 10^{15} K/sec resulting in amorphization of the irradiated material.

It is regarded as firmly established that under irradiation of solids, the prevailing causes of formation of structural damage are cascades of atom-atom collisions. Originating from high-energy primary knocked atoms, the cascades cover large areas of the crystal and generate a large number of substitutions, large vacancy clusters, on the periphery of which the interstitial atoms are located. Lifetime of these areas in the damaged zone is about 10^{-13} - 10^{-12} sec, and is immediately followed by evolution – annealing of defects, i.e. healing process of the depleted zone. At the same time, a separation of atoms may occur in the cascades of atom-atom collisions and, therefore, formation of an area enriched in one component of the alloy. In this case, it is beryllium. After irradiation with Kr^+ ions at a dose of $5 \cdot 10^{16}$ ions/ m^2 , the Be-Fe-Be layered system was subjected to isochronous annealing in vacuum for four hours at temperatures from 200°C to the temperature of the synthesis of the initial samples (650°C) at a pitch of of 50°C .

Fig. 2 shows the most characteristic CEMS spectra of ^{57}Fe nuclei samples subjected to isochronous annealing after irradiation. Immediately note that the analysis of the absorption spectra revealed no significant phase and structural changes in the bulk of the samples after irradiation and subsequent heat treatment. Therefore, the effect of irradiation extends to the depth of the projected range of the implant, without affecting the basic matrix.

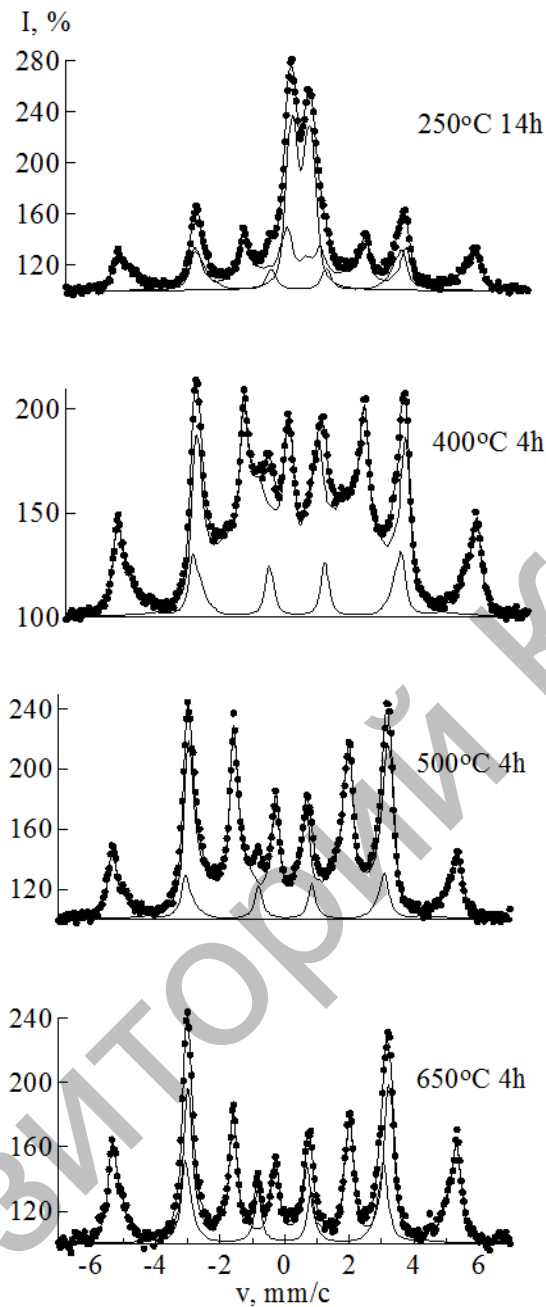


Fig. 2. CEMS spectra of Be (0.9 μm)- ^{57}Fe (10 μm)-Be (1.0 μm) layered system at different stages of isothermal annealing

Significant changes are observed in the spectra of the samples after annealing at 400°C temperature. It is evident that iron having been in the paramagnetic state, get into a magnetically ordered state. In the CEMS spectra the paramagnetic component almost completely disappears and along with a partial spectrum solution of $\alpha\text{-Fe(Be)}$ one can observed only contribution from the Fe atoms with the distribution of hyperfine magnetic fields H_n in a wide range of its values $10 < H_n < 200$. This distribution is due to wide range of homogeneity of the $\text{FeBe}_{2+\delta}$ intermetallic compound, as well as the residual defects that are healed at higher temperatures. At $\delta > 0$ concentration of beryllium, and defects in the structure of the intermetallic compound, in the

immediate environment of the Fe atoms, instead of magnetoactive Fe atoms there appear Be atoms or vacancies, which leads to a considerable reduction of the hyperfine magnetic field at ^{57}Fe nuclei. Subsequent annealing of the samples at 650°C temperature, when migration and annealing processes of induced radiation defects significantly activate, results in almost complete recovery of the initial state of the Fe atoms as before ion irradiation.

Conclusion

Krypton ions impact on the Fe-Be layered system leads to the occurrence of additional spectral lines in the central part of the spectrum on the background components of the initial phases that indicates the transition of a part of the iron atoms in the test layer into another, different from the original structural and phase state of the material. Moreover, the degree of this transition depends on the radiation dose.

In the area of the projective range of ions a violation of magnetism takes place. Part of iron atoms gets into the paramagnetic state due to the formation and quenching of heated areas (thermal spikes). Another part gets into states with lower effective fields due to damage of the material in the areas of cascades of atom-atom collisions with the subsequent separation of atoms while "healing" these areas.

Isochronous annealing results in restoration of magnetic properties of the irradiated material. At 400°C temperature the paramagnetic component of the spectrum disappears almost completely due to crystallization of the amorphous phase. However, the proportion of the restored distribution function of hyperfine magnetic fields in the range of $20 < H_n \leq 150 \text{ kOe}$ still remains substantial. Annealing at 650°C temperature brings Mössbauer parameters of the irradiated material back to the original state.

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