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INVESTIGATION OF STRUCTURE AND PROPERTIES OF BARRIER LAYERS IN METALS (Fe, Cu) AT LOW TEMPERATURES

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Experimental studies of the effect of a barrier layer on the kinetics of thermally induced diffusion processess and phase transformations in a layered Fe–Be *syatem are investigated at the energy ~1.6 MeV. Thermal stability of the barrier layer in the* $Fe:O^+$ *system is validated and a possibility of its use as a subsurface layer for a beryllium coating is demonstrated. For the* $Cu:O^+$ *system it is shown that the implanted layer in the matrix comes apart already at the annealing temperature ~180°C and could not be used in a copper matrix as a subsurface barrier layer. For the first time, a method is proposed for retardation of diffusion and phase formation processes and realized in a layered iron – beryllium system using an implanted layer of oxygen ions. The sequence and characteristic times of thermally-induced phase-transformation processes taking place in the subsurface layers and in the bulk of the* Fe *(10 μm) systems:* O^+ *–* Be *(0.7 μm) –* ^{57}Fe *(0.1 μm) and* Fe *(10 μm) –* Be *(0.7 μm) –* ^{57}Fe *(0.1 μm) are determined.*

Keywords: oxygen ion implantation**,** barrier layer, thermal stability, phase transformations.

INTRODUCTION

The development of new efficient processes for engineering materials operating in aggressive media under conditions of thermal, radiation and other stresses is an urgent task of modern materials science [1].

At present, a good deal of attention is given to the metal – metalloid implantation system, since by forming an interstitial phase in the subsurface layers of an irradiated metal it is possible to improve its strength and corrosion-resistant properties. The data of these investigations could be used in practice via formation of heat-resistant coatings on the specimens, thus new technological methods have to be developed for deposition of high-temperature protective coatings [1, 2].

In this study we propose to form barrier coatings using ion implantation processes. A successive implementation of ion implantation and plasma-assisted ion sputtering results in the formation of a layered system representing a matrix with a subsurface barrier layer and a protective coating. In accordance with the experimental design, we put forward the following tasks: i) to form barrier coatings in metals, Cu and Fe, by implanting oxygen ions and investigate their stabilityc; ii) to study the influence of the resulting barrier layer on the kinetics of thermally-induced diffusion and phase formation in the layered systems in question; iii) to determine the relative phase content and routes of phase transformations in the subsurface layers and in the bulk of layered systems under conditions of successive isothermal annealing; iv) to implement the method of deceleration of diffusion and phase formation

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TABLE1. Characteristics and Irradiation Conditions

No.	Specimens	Specimen thickness	Implanted ion	Accelerator type	Irradiation energy	Ion fluence, ion/cm^2	Ion path length R, nm
1	Cu	1 mm	O^+	DC-60 (Astana)	100 keV	$2\cdot10^{18}$	290
2	Fe (α-iron)	10 μm	O^+	UKP-2-1 (Almaty)	1.6 MeV	$1.1\cdot10^{18}$	950

processes in the layered systems formed using a barrier coating; and v) to develop an approach for reconstruction of the distribution function of the impurity atom concentration in the matrix – impurity solid solution using the X-ray diffraction data, and realized them in this study.

ANALYTICAL PROCEDURES

The analytical techniques included Mössbauer spectroscopy (MS) with registration of γ-quanta in the transmission-mode geometry, conversion electron Mössbauer spectroscopy (CEMS) in the backscattering geometry, and Rutherford backscattering (RBS) of protons. These methods were chosen for the following reasons: MS provides information on the phase state averaged over the specimen thickness, CEMS provides data from the specimen subsurface layer ~0.1 μm and in the bulk (down to ~3 μm), and RBS allows determining the oxygen penetration depth into Fe with respect to the specimen thickness [3–5].

Preparation of the specimens for analysis was carried out in a standard vacuum furnace (at $P = 5\cdot10^{-6}$ mm Hg), the time to achieve the specified temperature was ~30 min, the specimens cooled together with the furnace, and the temperature measurement error was within ±5°C. The substrate thickness was determined by a conventional micrometer, its measurement error being ±1 μm. The specimens after their preparation (rolling) for investigations were subjected to thermal annealing at the temperature 850°C for 3 hours. The experiments on irradiation of thus prepared specimens were performed using the UKP-2-1 (NPI at the NNC, Almaty) and DC-60 (Gumilyov ENU, Astana) facilities. At every stage of the experiments, after annealing the specimens were examined by CEMS of ^{57}Fe nuclei, X-ray phase analysis and RBS of protons.

After thermal annealing of the α-Fe (10 μm) specimens without oxygen and with implanted oxygen layer, a 0.7 μm layer of beryllium was deposited on them using the plasma-ion process. In order to improve sensitivity of the Mössbauer spectroscopy procedures, a Fe^{57}-enriched layer ~0.1 μm thick was formed using a PVD method. Thermal annealing of these systems was performed in a standard-design vacuum furnace at the temperature $T = 700$°C, the annealing time was counted from the point $\tau = 0.5$ hour with the time step being $\Delta\tau = 2.5$ hours. The annealing modes were selected taking into account the phase diagram features of the Fe:O^+ and Fe–Be systems [5–9].

RESULTS AND DISCUSSION

Figure 1 presents an RBS spectrum from the specimen prior to and after implantation and a profile of the barrier layer distribution in the iron matrix obtained in the UKP-2-1 accelerating charge-exchange complex.

During the experiments we determined the depth of oxygen penetration into the α-Fe matrix and the oxygen concentration over the specimen depth after implantation.

Let the number of ion (proton) energy loss per unit length be equal to dE/dx. Then the total energy loss ΔE, for the ion reaching depth t, would be proportional to t

$$\Delta E = \int_0^t (dE/dx)dx \approx dE/dx\,|_{\text{in}}\; t\,,$$

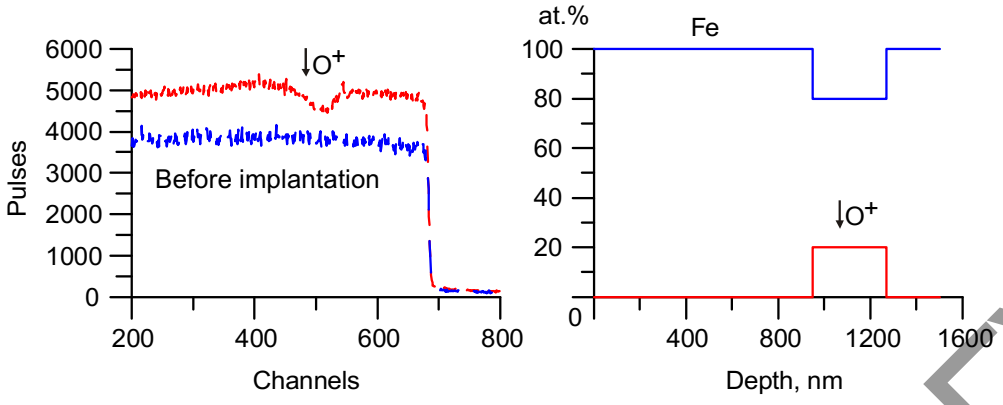

Fig. 1. RBS spectrum from the specimen prior to and after implantation and a profile of the barrier layer distribution in the iron matrix.

where $dE/dx\,|_{in}$ is the energy loss of a particle before dissipation calculated for the average energy between the initial E_0 and $E_0 - t\,(dE/dx)$. At depth t, the particle has the energy given by

$$E(t) = E_0 - tdE / dx\,|_{in}.$$

After dissipation within a large angle, the particle's energy becomes equal to $kE(t)$, where the kinematic multiplier k is found from the following formula:

$$k = [(M_1 \cos\theta + (M_2^2 - M_1^2 \sin^2\theta)^{1/2}) / (M_1 + M_2)].$$

Here M_1, M_2 are the ion (proton) and target nucleus masses, respectively, and θ is the scattering angle. The measured scattered ion energies at a known scattering angle θ allow us to determine M_2. Having changed the direction of its motion, the particle keeps on decelerating in its return path towards the detector; it reaches the latter having the energy

$$E_l(t) = kE(t) - (t/\cos\theta)dE/dx\,|_{out} = -t(kdE/dx_{in} + (1/\cos\theta)\,dE/dx\,|_{out}) + kE_0.$$

Then the spectral width of the energy ΔE of particles, backscattered by the film of width Δt, would be equal to

$$\Delta E = \Delta t\,(kdE/dx\,|_{in} + (1/\cos\theta)\,dE/dx\,|_{out}).$$

Backscattering spectrometry allows determining compositional changes with the depth. The relationship between the energy resolution δE_1 and the depth resolution δt is given by

$$\delta t = \delta E_l/(kdE/dx\,|_{in} + (1/\cos\theta)\,dE/dx\,|_{out}).$$

The best depth sensitivity is found in the case of maximum energy losses accompanying scattering in the bulk of the specimen. This is achieved by the use of grazing-incidence small-angle scattering, which ensures a depth resolution of 2 nm with conventional semiconductor detectors. In the latter case, such factors affecting the resolving power as the end capture angle of the detector, surface roughness, and energy struggling have to be taken into account. The resolving power variations are minimal at the angle θ = 180°C. The difference between the particles backscattered from the elements with different values of Z is also maximal at the scattering angle 180°C. It is for this reason that backscattering spectrometry is commonly implemented at the values of θ close to 180°. In this case, the energy variance introduced by the limited solid angle of the detector is minimal, while the capacity of discriminating the specimen atoms with different masses is maximal. Recently, specialized surface-barrier detectors have been developed, which

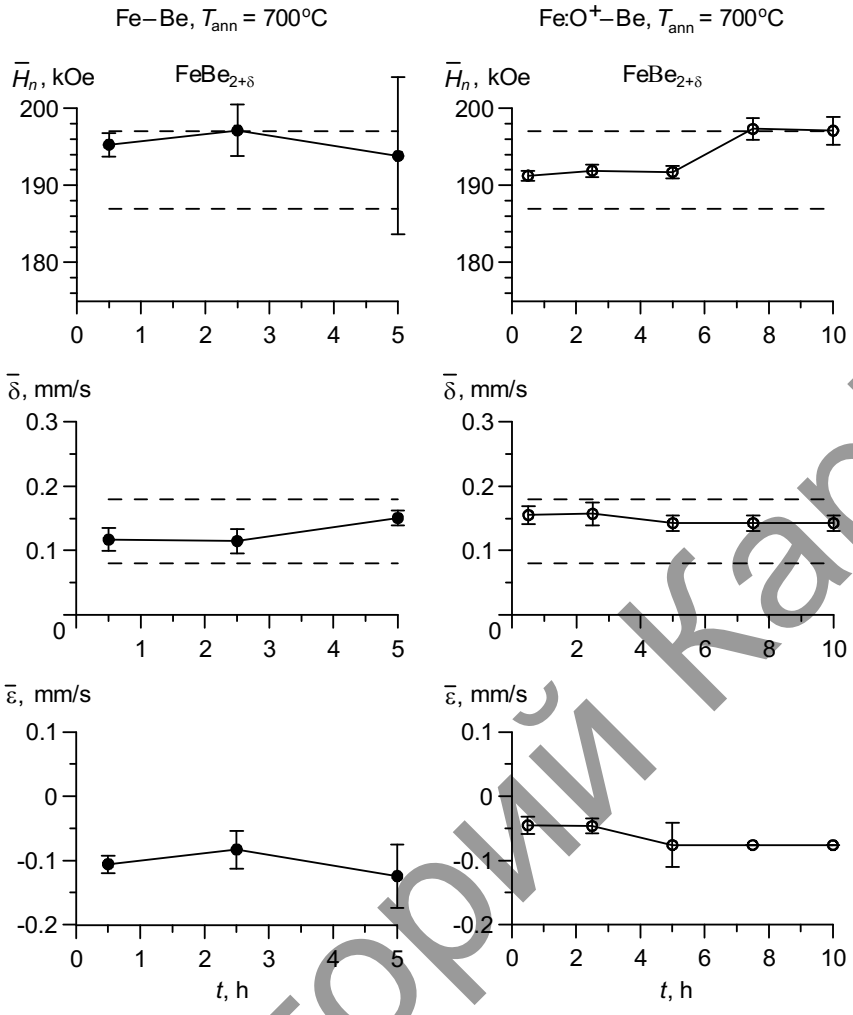

Fig. 2. Average values of the effective magnetic fields H_n, shears δ and quadrupole displacements ε of the Mössbauer spectra for the $FeBe_{2+\delta}$-phase in Fe–Be–^{57}Fe and Fe:O^+–Be–^{57}Fe as a function of the isothermal annealing time t_{ann} at T_{ann} = 700°C.

have an opening in the center for the beam. The spectra of backscattered ions and the element distribution over the specimen depth were processed and analyzed by the RBS-technique using the RUMP simulator. The RUMP concentration profile of elements is represented as an interchange of layers of varied thicknesses and compositions, wherein the concentration of elements is prescribed as a stoichiometric formula. The number of layers of similar compositions is limited to 100, while the number of elements per layer is unlimited. In addition to simulations of the theoretical spectrum and the online fitting procedure, this software makes it possible to autofit the theoretical spectrum to the experimental one having no more than eight variable parameters. The error in the case of film thickness determination using autofit is as low as $\Delta t/t \approx 6\%$.

Using the MS analytical data, we calculated the average values of the effective magnetic fields H_n, shears δ, and quadrupole displacements ε of the MS spectra for the $FeBe_{2+\delta}$-phase in the layered Fe–Be–^{57}Fe and Fe:O^+–Be–^{57}Fe systems as a function of isothermal annealing time t_{ann} at the temperature T_{ann} = 700°C (Fig. 2). The Mössbauer values of superfine parameters are consistent with the data obtained in [7]. The dash-line boundaries in Fig. 2 indicate the values reported in the literature.

In order to determine the characteristic time of the $FeBe_{2+\delta} \rightarrow$ Fe(Be) phase transformation, the following kinematic equation was proposed:

TABLE 2. Parameters of Mössbauer Spectra for $FeBe_{2+\delta}$ after Isothermal Anneals at T_{ann} = 700°C

	Fe–Be–^{57}Fe				Fe:O^+–Be–^{57}Fe			
t_{ann}, h	δ, mm/s	ε, mm/s	H_n, kOe	I, %	δ, mm/s	ε, mm/s	H_n, kOe	I, %
0.5	0.112 ± 0.01	–0.102 ± 0.03	195.3 ± 1.5	3.8 ± 0.7	0.154 ± 0.01	–0.058 ± 0.02	191.2 ± 0.6	13.8 ± 0.9
2.5	0.115 ± 0.01	–0.083 ± 0.03	197.1 ± 0.7	1.1 ± 0.7	0.155 ± 0.04	–0.074 ± 0.06	191.1 ± 0.8	11.4 ± 0.7
5.0	0.145 ± 0.01	–0.164 ± 0.03	195.4 ± 1.1	0.5 ± 0.5	0.145 ± 0.01	–0.050 ± 0.03	191.7 ± 0.8	3.9 ± 0.7
7.5	–	–	–	–	0.143*	–0.076*	197.3 ± 1.4	0.7 ± 0.2
10.0	–	–	–	–	0.143*	–0.076*	197.1 ± 1.8	0.9 ± 0.5
15.0	–	–	–	–	–	–	–	–

Note. δ_{max}, ε_{max} are the Mössbauer line shear and quadrupole displacement, corresponding to the maximum value of the distribution function, H_n is the superfine magnetic field, I is the intensity, and an asterisk * marks the values fixed during spectrum processing.

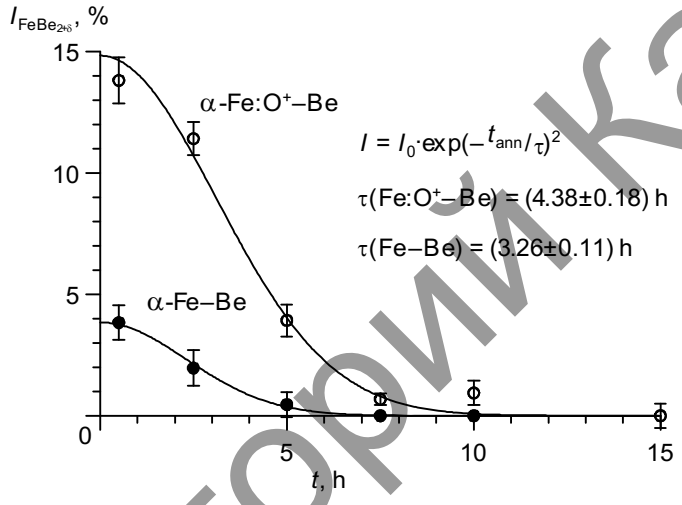

Fig. 3. Partial spectral intensities of the $FeBe_{2+\delta}$-phase in the Fe–Be–^{57}Fe and Fe:O^+–Be–^{57}Fe layered systems versus the time of isothermal annealing at t_{ann} at T_{ann} = 700°C.

$$I(t_{ann}) = I_0 \exp\left(-\frac{t_{ann}}{\tau}\right)^2,$$

where I_0, the partial spectral intensity, is a constant value, τ is the characteristic time of variation of the relative partial spectral intensity of the $FeBe_{2+\delta}$-phase , and t_{ann} is the time of isothermal annealing.

Having processed the $I(t_{ann})$ curves using the MSTools KINETIC software program [8, 9], we obtained the following values of the kinetic equation parameters for the systems with and without barrier layers: τ(Fe:O^+–Be) = (4.38 ± 0.18) h and τ(Fe–Be) = (3.26 ± 0.11) h, respectively.

Figure 3 depicts for the Fe–Be–^{57}Fe and Fe:O^+–Be–^{57}Fe layered systems the plots of relative partial spectral intensities of the $FeBe_{2+\delta}$-phase for the ^{57}Fe nuclei versus the anneal time t_{ann} at the temperature T_{ann} = 700°C. These plots validate a complete solution of the $FeBe_{2+\delta}$-phase followed by the formation of a solid solution of beryllium in the iron matrix.

Table 2 presents the Mössbauer parameters of the respective spectra for the $FeBe_{2+\delta}$-phase after isothermal anneals at T_{ann} = 700°C.

SUMMARY

As a result of investigations by the methods of Mössbauer spectroscopy on the ^{57}Fe nuclei and Rutherford backscattering of protons it has been established that a barrier layer affects the kinetics of thermally induced diffusion and phase transformation processes in a layered Fe–Be system. The $Fe:O^{+}$system, using which the method of deceleration of diffusion and phase transformation processes in a layered iron – beryllium system was realized, has been found to be stable. It has been shown that the barrier layer restricts the zone of beryllium solution in the subsurface layer. For the first time, we have proposed and implemented the method of deceleration of diffusion and phase transformations in a layered iron – beryllium system using an implanted layer of oxygen ions. The sequence and characteristic times of thermally-induced $FeBe_{2+\delta} \rightarrow \alpha$-Fe(Be) phase transformations in the subsurface layers and in the bulk of the Fe (10 μm): O^{+} – Be (0.7 μm) – ^{57}Fe (0.1 μm) and Fe (10 μm) – Be (0.7 μm) – ^{57}Fe (0.1 μm) systems have been determined.

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