

Irradiation of Fe-Mn Supersaturated Solid Solution with Ions of Various Atomic Masses (Ar^+ , Xe^+) and Analysis of the Role of Nanosized Dynamic Effects in the Activation Processes of Long-Range Type

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Abstract. A multiple increase in the atom mobility in metastable supersaturated (quenched from 850 °C) Fe-8.16 at % Mn solid solution is detected at temperatures less than 250°C under irradiation with 5-keV Ar^+ and Xe^+ ions of different masses. The irradiation-induced atom redistribution in the entire volume of foils 30 μm thick at a projected Ar^+ and Xe^+ ion ranges as much as 20-30 nm only is found and studied by the transmission Mössbauer spectroscopy. Long-range effects at low irradiation doses and anomalously low temperatures are attributed to "radiation shaking" of metastable media with post-cascade solitary waves in contrast to thermally stimulated radiation-enhanced processes in the narrow nanoscale near-surface layers of the alloy. It has been shown that heavier Xe^+ ions at higher irradiation doses have a stronger impact on the solid solution than Ar^+ ions.

1. Introduction

In work [1] it has been shown that upon irradiation of materials with heavy ions of low and medium energy (from a few tens to several hundreds of keV), the source of defects is only a surface layer less than 1 μm thick rather than entire volume of material in contrast to severe plastic deformation.

In the case of neutron irradiation, defects in material are accumulated slowly due to the high penetrating ability of neutrons (neutron interaction cross section is by 6-7 orders of magnitude smaller than that of ions). This is the reason of why primary recoil atoms and cascades of atomic displacements formed by these atoms under neutron irradiation are separated by distances much greater than those under ion irradiation when accumulated fluences (cm^{-2}) are the same.

Nevertheless, low-dose and long-range effects under neutron and ion irradiation are well-known. These effects manifest themselves by dramatic changes in the structure and properties of materials at a small number (< 0.001) of displacements per atom and by the fact that the distance at which the changes occur is several orders of magnitude greater than the projected range of implanted ions (or primary recoil atoms under low-dose neutron irradiation).

These effects seem to represent two sides of the same coin, and cannot only be explained by relatively slow processes, for example, by radiation-enhanced or radiation-induced diffusion, which



well represent radiation swelling and radiation-induced creep in the framework of the classical radiation physics.

It is easy to estimate, as it has been done in [1], that the diffusion length of vacancies is certainly not more than 1 μm for a few seconds of irradiation at room temperature in metals with a melting temperature of $T_{\text{melt}} > 1000$ K. There is a large number of studies, which indicate dramatic changes in the structure and properties in the entire volume of materials irradiated with accelerated ions for several seconds. These changes occur without heating and other obvious factors causing such effects at a depth from several tens of **micrometers** to several **millimeters** [2-4]. Low-dose and long-range effects in highly-defected quenched and highly-deformed materials with numerous traps and sinks for the radiation-induced defects also cannot be explained by the role of more mobile interstitial atoms.

It is suggested in [2-4] that the role of nanosized radiation-dynamic effects under cascade-forming corpuscular radiation is significant and crucial in some cases. Nanoregions of cascades of atomic displacements are zones of explosive energy release. The temperature of the cascade regions thermalized for 10^{-12} s is 5000-6000 K and above (the rate of energy release is comparable to that during nuclear explosion). A sharp increase in the temperature and pressure [5] in these regions causes the emission of powerful elastic and shock **postcascade** solitary waves.

It is known that a nonideal state of solid solutions, which often manifests itself near the temperature and concentration phase transitions, can have a significant effect on the properties of materials.

The thermodynamics equations imply that the tendency of solid solutions to the atomic ordering and concentration segregation, at a certain ratio of the energy of interatomic interactions between components can be characterized by an extremely low critical temperature, when the diffusion mobility of the atoms is extremely small. Nevertheless, there are instances where some alloys after long-term service (over hundreds and thousands of hours) at relatively low temperatures exhibit changes in the properties. As a result of special investigations it was found that this is due to intraphase processes, for example, the concentration separation of solid solutions into substitutional impurities [6]. The reason for the changes in the properties of alloys can also be a short or long-range atomic ordering formed in them.

New potential for the control of the atomic structure of materials at low temperatures (due to a sharp increase in the atom mobility throughout the volume of the material [3] far beyond the above calculated diffusion length) is offered owing to the discovery of the mentioned radiation-dynamic effects caused by radiation shaking of condensed matter with post-cascade shock waves under ionizing radiation.

As shown in [5, 7], the temperature and pressure in the regions of nanosized thermal peaks strongly depend on the mass and energy of bombarding ions. The density of the released energy in the dense cascades of atomic displacement increases with ion energy reduction and an increase in the ion mass. So-called metastable media with increased stored energy in a state corresponding to intermediate free energy minimum rather than the absolute one are in a greater extent exposed to external exposure. In particular, this refers to quenched alloys.

In the present study, we investigated the effect of low-energy Ar^+ (39.95 amu) and Xe^+ (131.29 amu) ions (~ 5 keV), which differ from each other in their atomic mass, on the quenched iron alloy with 8.16 at % Mn (having a tendency to atomic separation) at low temperature (250° C), when the diffusion of substitutional impurities is almost frozen. At the same time, it is shown [2-4] that the atomic mobility in these alloys at lower temperatures can be repeatedly increased by ion irradiation. This refers to the near-surface layers of irradiated materials, the length of which is several orders of magnitude greater than the projected range R_p of the implanted ions (and reaches $10^5 R_p$ or more [4]). Concentration profiles of the Ar^+ and Xe^+ ions are shown in Figure 1. As can be seen, the ranges of the ions under consideration are extremely small and less than 0.02-0.03 μm , which is about 10^3 times smaller than the thickness of the studied iron-manganese alloy foils under ion irradiation.

X-ray diffraction is ineffective for the analysis of the processes taking place due to similarity of electronic scattering factor of Mn and Fe, which are neighbors in the periodic table, low manganese

concentration, nanosized intraphase separation, and the precipitation of the second phase (austenite). Therefore, we used the Mössbauer effect, as in [8], for the analysis of these processes.

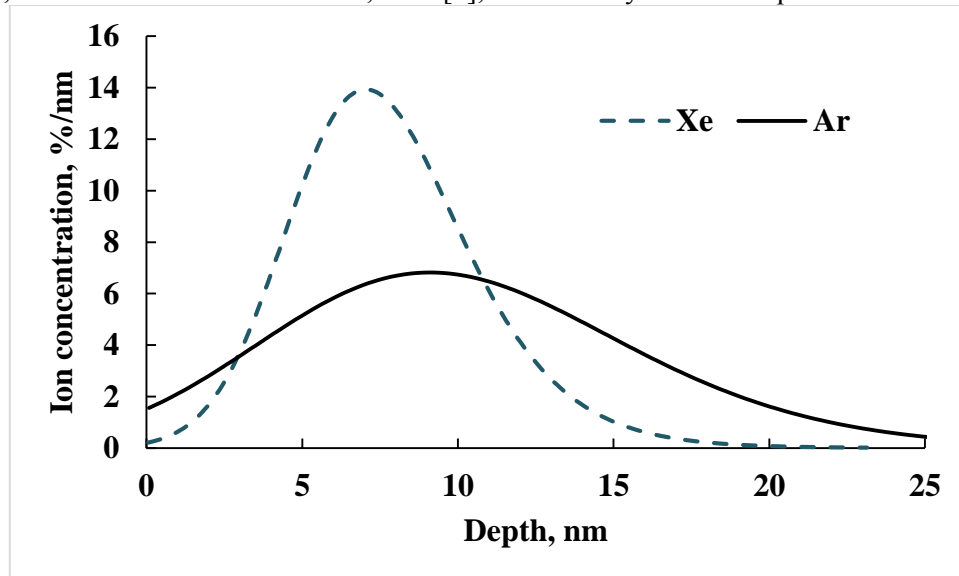


Figure 1. Concentration profiles of the Ar^+ and Xe^+ ions in the Fe-Mn alloy (calculated using kinetic Boltzmann equations [5] method).

2. Experimental

The Fe – 8.16 at % Mn alloy under study according to the chemical analysis had the following content of impurities: 0.070 C, 0.020 N, 0.008 S, and 0.010 wt % P. The alloy was melted in an induction furnace in the argon atmosphere. The ingots were forged to obtain rods 6×12 mm in cross section and rolled at 1000°C to form sheets 0.5 mm thick. Pretreatment consisted of normalizing (900°C), annealing (600°C), and sample quenching from 850°C and from γ region (corresponding to the equilibrium fcc γ phase) in a 15% solution of NaCl. After quenching the alloy has a bcc α' -martensite structure with 3-5% of the retained γ phase (austenite). Thin foils for Mössbauer studies were mechanically and electrolytically polished in electrolyte (12 g Cr_2O_3 and 100 mL H_3PO_4). The thickness of the samples was 25 μm .

The samples were irradiated in a continuous mode using an ILM-1 ion beam implanter equipped with a PULSAR-1M ion source based on a low-pressure glow discharge with a hollow cold cathode [9], which also can operate in a pulsed-periodic mode. The samples were irradiated with Ar^+ and Xe^+ ion beams at an energy of 5 keV and current densities from 150 to 170 $\mu\text{A}/\text{cm}^2$ (the current density was continuously varied to achieve the desired temperature). The samples were hanged with thin threads with a low heat conductivity, so that heat removing from a sample was carried out exclusively by radiation. This made it possible to predict the temperature of the sample theoretically [10] (using the emissivity factor chosen in advance from the experiment). In the course of irradiation, the sample temperature was controlled with the help of a thin chromel-alumel thermocouple connected with an Advantech Adam 4000 automated system designed for digital signal registration.

Mössbauer studies were performed using an SM-2201 automated Mössbauer spectrometer under constant acceleration conditions. Isotope ^{57}Co served as the source of γ quanta in Rh. The speed scale of the Mössbauer spectra was calibrated with respect to pure iron.

3. Results and discussions

Mössbauer spectra of the Fe – 8.16 at % Mn alloy after irradiation with low argon and xenon ion fluences ($E = 5$ keV, $j = 150$ -170 $\mu\text{A}/\text{cm}^2$) significantly change (Figure 2). In particular, the intensity of the components of the external peaks vary, which correspond to the presence of $l_I=0$ and $l_I=1$ of atoms

Mn near atom Fe. Component $l_I=0$ decreases, whereas $l_I=1$ increases (indicated by arrows in Figures. 2b, 2c), which clearly indicates the redistribution of atoms in the solid solution [11].

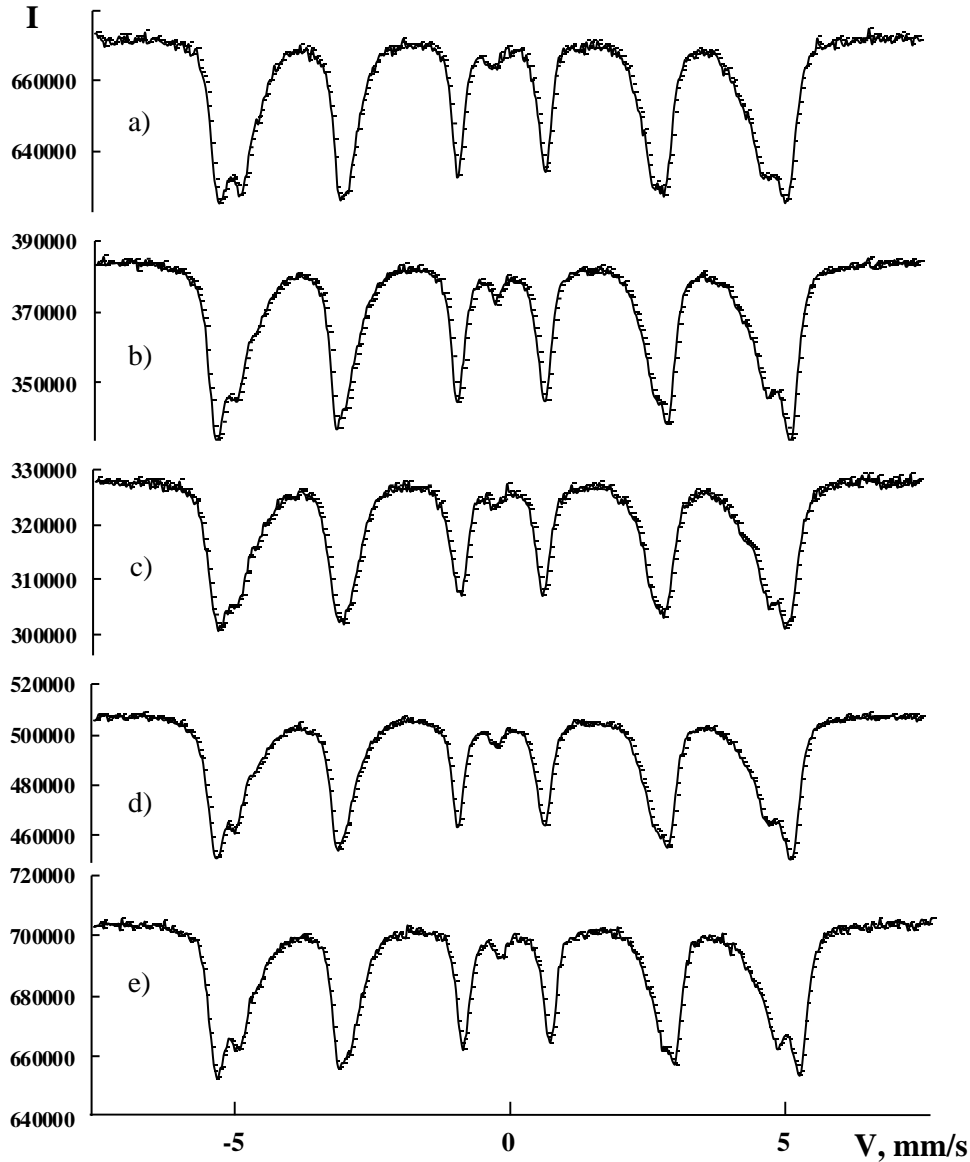


Figure 2. Mössbauer spectra of the samples of the Fe – 8.16 at % Mn alloy after (a) quenching and irradiation at the following various fluences of (b, c) Ar^+ and (d, e) Xe^+ ions: (b, d) heating to 250 °C (without holding); (c, e) heating to 250 °C (for 20 s); dotted lines correspond to experimental data.

The short-range order parameter according to Cowley [12] in the first coordination sphere α ($\alpha = -\frac{\epsilon_{ab}}{c_a c_b}$, here a - Fe, b - Mn, ϵ_{ab} – pair correlation parameter [13]) was determined by

analyzing the external shape of the peaks, which corresponded to such nuclear transitions as $+1/2 \rightarrow +3/2$ and $-1/2 \rightarrow -3/2$, and the Mössbauer spectra (since they have the highest intensity and resolution), taking into account electric and magnetic interactions in the radius of the first coordination sphere using the method described in [11, 13], where a method for calculating a statistical error of the parameter α by referring the structural matrix is described. This approach is justified because,

according to [14], the effect of the second, the third, and other remote coordination spheres on the parameters of hyperfine interactions is relatively weak for the above-mentioned concentration of Mn.

The values of parameter α , obtained from the processing of the left and right Mössbauer spectra peaks within the error were zero for all quenched samples.

The intensities of Mössbauer lines after irradiation with Ar^+ ions significantly change already at a fluence of $\sim 1 \cdot 10^{16} \text{ cm}^{-2}$ (exposure time was only $\sim 10 \text{ s}$). During this time the temperature of the samples reaches a stationary temperature of 250°C , the samples were treated without holding at this temperature. This means that the alloy under Ar^+ and Xe^+ ion irradiation acquires short-range atomic separation for a very short period of time. The value of short-range atomic order α_1 thus becomes positive ($\alpha = 0.17\text{--}0.18$) both for Ar^+ and for Xe^+ (see Figure 3). A further increase in the irradiation time to 30 s (fluence of $\sim 3 \cdot 10^{16} \text{ cm}^{-2}$) causes a decrease in the short-range order parameter to $\alpha = 0.16$ in the case of Ar^+ ion irradiation and to $\alpha = 0.12$ in the case of Xe^+ ion irradiation.

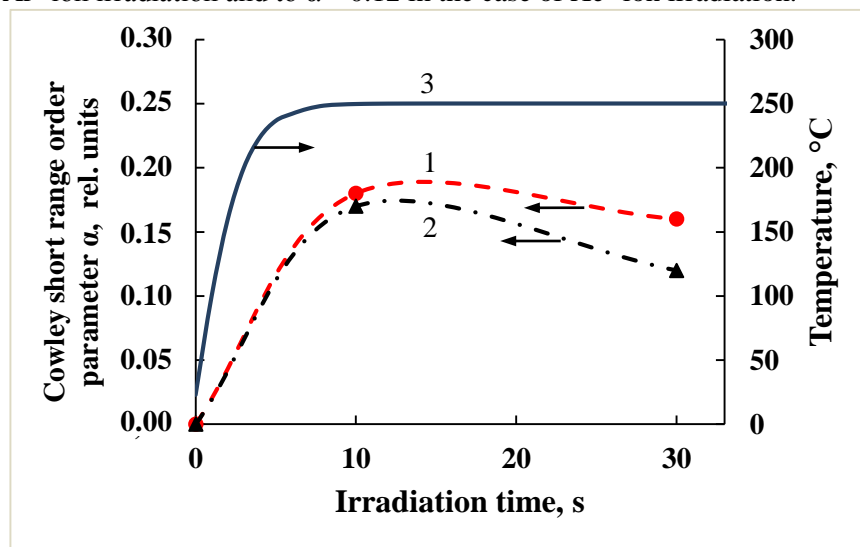


Figure 3. Cowley parameter of short-range atomic order as a function of the irradiation time: (1) irradiation with Ar^+ and (2) Xe^+ ions. Curve 3 indicates the temperature of the samples as a function of the irradiation time under given irradiation conditions.

This can be explained by the fact that solid solution depleted with manganese at low temperatures may tend to not only short-range separation, but also to short-range atomic ordering found in [8]. In contrast to the separation, this leads to the change in the intensities of spectra components corresponding to $l_1 = 0$ and $l_1 = 1$ impurity atoms in the immediate vicinity of iron atoms.

That is, during the first seconds of irradiation, the solid solution is separated into zones depleted and enriched with manganese atoms. Thereafter, the atomic ordering can occur in the formed zones, leading to an increase in the effective concentration of manganese in the first coordination sphere of iron atoms. The latter indicates the complex ratio of the energy of the pair interaction aa , bb and ab in the iron-manganese system. It may be necessary to refine the model of the atomic redistribution in the iron-manganese alloy, and, consequently, the model approximating the Mössbauer spectra to describe this process in detail. In particular, this concerns not only the effect of the first coordination sphere, as was done in [8] and in this work, but also more distant coordination spheres (at least the 2nd coordination sphere).

Data of [8] somewhat differ from those of the present study, which may be explained by the different composition of alloys used (in particular, the difference in the concentration of interstitial impurities). The alloy used in the present work contains more interstitial impurities than in [8], which is manifested in the presence of a small amount of retained austenite in the quenched alloy (central peak in the center of the Mössbauer spectra, Figure 2).

It should be noted that parameter α in the case of heavier Xe^+ ions more significantly decreases (i.e., an increase in the effective concentration of Mn in the nearest neighborhood of Fe), which is in agreement with a large energy release in dense cascades of atomic displacements generated by Xe^+ ions, compared to those generated by Ar^+ ions.

4. Conclusion

Our investigation is an indirect proof of the fact that nanosized dynamic effects (appeared due to the formation of thermal peaks) play the significant role in the effect of accelerated Ar^+ и Xe^+ ions on the structural state of the metastable quenched Fe – 8.16 at % Mn alloy. The temperature of the thermal spikes was measured in [5, 7]. Indeed, the short-range atomic ordering of the short-range separation type is formed at the projected range of the used ions less than 0.02-0.03 nm and temperatures less than 250°C, which are insufficient for the redistribution processes of substitutional atoms in the target volume (25 μm thick) due to thermally and radiation-stimulated diffusion, for the first 10 s of irradiation. The ordering degree somewhat decreases (substantially more for heavier Xe^+ ions) at a further increase in the fluence; which seems to be caused by the complicated structure of atomic ordering, to reliably identify the type of which additional data are required.

In this connection, it seems interesting to study in detail the regularities of the processes using various types of ions and irradiation modes and theoretical models for describing the experiments.

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