Structural-and-Phase Transformations in Fe-4.10 and 7.25 at.% Mn Alloys under Intensity External Actions

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Abstract: The effect of high-pressure torsion (HPT) \((P = 8 \text{ GPa}, \varepsilon = 5.9)\) and irradiation with continuous beams of \(\text{Ar}^+\) ions with energy \(E = 15 \text{ keV}\) on the atomic structure and phase composition of initially quenched iron alloys with 4.10 and 7.25 at.% Mn was studied by the method of Mössbauer spectroscopy. The supersaturated \(\alpha\)-solid solution of Fe-7.25 at.% Mn, in contrast to the stable Fe-4.10 at.% Mn, which passes into a highly nonequilibrium metastable state as a result of HPT deformation, is transformed under the influence of ion irradiation at an abnormally low temperature of \(280^\circ\text{C}\) into a two-phase \(\alpha + \gamma\)-state with a highly enriched \(\gamma\)-phase (austenite) (38.4 at.% Mn) and a depleted \(\alpha\)-solid solution with 5.76 at.% Mn. The rapid processes with the formation of the \(\gamma\)-phase with a concentration of Mn close to the extrapolation estimate using the equilibrium phase diagram are explained by the cascade radiation shaking of the material by post-cascade powerful elastic and shock waves. Cascade radiation shaking plays the role of temperature and opens up the possibility of achieving states close to equilibrium in the absence of thermally activated processes at record low temperatures.

Keywords: Fe-Mn alloy; ion irradiation; austenite formation; severe plastic deformation; high-pressure torsion; long-range effects; Mössbauer spectroscopy

1. Introduction

The study of phase and intraphase transformations under conditions of intense external influences on condensed media, including metals and their alloys, is becoming increasingly important in connection with the extreme loads that functional materials must withstand in modern technical devices. This applies to electrical, magnetic, mechanical, including shock, as well as radiation and other types of exposure.

It is well known that the result of the transformation (restructuring) of a particular environment is determined both by the nature and intensity of the external influence, and by the response of the environment. It is clear that if the medium is in a state of thermodynamic equilibrium, then external disturbances will reversibly or irreversibly deflect it from this state. Media that are in a certain intermediate, metastable state with increased energy, under intense external influences, can, on the contrary, undergo transformations with a transition to states closer to equilibrium [1–3].

As noted in [4] in relation to metal alloys, depending on the relative role of dislocation, migratory, and other processes occurring during external influences and at the stage of relaxation of the medium, diametrically opposite effects can be observed.

Recently, there has been an increasing interest in structural and phase transformations in alloys under such types of action as mechanical alloying (mechanical synthesis) and severe plastic deformation. In [2,4–8], impressive processes of structural-phase transformations with the formation of strongly nonequilibrium states were recorded. There are a large number of examples of the formation of nonequilibrium highly defect states under the action of continuous and powerful pulsed ion beams [9–26]. In works [1,3,27–32], reverse processes of instantaneous rearrangement of nonequilibrium (metastable) media during ion bombardment at anomalously low temperatures with the transition of these media to...
states approaching equilibrium as much as possible were found. In papers [1,30,31], on the basis of experimental [27–29,32] and theoretical studies the idea has been put forward of using cascade radiation shaking under cascade-forming types of irradiation instead of temperature for a gigantic increase in the low-temperature atom mobility.

To study the basic laws of such phenomena, it is reasonable to use relatively simple in composition model materials, which are well studied in states close to equilibrium. An important point is the possibility of constructing equilibrium phase diagrams at low temperatures and presumely detecting unknown phases.

The aim of this study was to study the effect of severe plastic deformation and ion bombardment (applied separately and sequentially) on the structural-phase state of binary Fe-4.10 alloys, 7.25 at.\% Mn at room temperature after quenching from the γ-region in the state corresponding to equilibrium or supersaturated (in the case of \(c > 5\) at.\% [33]) α (bcc)-solid solution.

2. Materials and Methods

Iron alloys with 4.10 and 7.25 at.\% Mn were melted in an induction furnace in an argon atmosphere in the form of ingots weighing 40 g. After homogenization, they were quenched from 800 °C in order to ensure an atomic disordered state. As a result, at room temperature, they had the structure of a disordered α (bcc) solid solution. Then the ingots were cut into plates, which were polished mechanically and electrochemically to a thickness of about 300 \(\mu\)m. This was the initial state of the material before the treatments described below were applied.

Some of the samples were subjected to severe plastic deformation by high-pressure torsion (HPT) (at \(P = 8\) GPa) in rotating Bridgman anvils to the degree of deformation \(e = 5.9\) (3 turns in the anvils) at a rate of \(e = 2.4 \times 10^{-2}\) s\(^{-1}\) (0.3 rpm) at 25 °C. After this treatment, the samples were in the form of a disk with a thickness of 150 \(\mu\)m and a diameter of 7 mm. To carry out Mössbauer and X-ray studies, the plates and disks were mechanically thinned on abrasives, as well as using cast iron laps and diamond pastes of different grain sizes to a thickness of about 50 \(\mu\)m, followed by chemical etching and electropolishing to a thickness of 20 \(\mu\)m.

Some of the samples 20 \(\mu\)m thick in the initial (1) and deformed (2) states were irradiated with continuous beams of Ar\(^+\) ions with an energy of 15 keV at an ion current density of 200 \(\mu\)A/cm\(^2\). Irradiation was carried out on an ILM-1 ion implanter with a PULSAR-1M ion source based on a low-pressure glow discharge with a cold hollow cathode [34] (allowing operation in both continuous and pulsed modes). During irradiation, the samples were moved under a ribbon beam of ions with a width of 3 cm, uniform over the cross section, at a speed of 1 cm/s with the accumulation of fluence at each point \(F = 3.75 \times 10^{15}\) cm\(^{-2}\) (for 3 s of irradiation).

The temperature of the samples during irradiation was controlled by a thin chromel-alumel thermocouple and did not exceed 280 °C. Figure 1 shows the temperature regime of heating cooling samples Fe-4.10 and 7.25 at.\% Mn (20 \(\mu\)m thick) by an Ar\(^+\) ion beam with the above parameters: \(E = 15\) keV, \(j = 200\) \(\mu\)A/cm\(^2\), \(F = 3.75 \times 10^{15}\) cm\(^{-2}\), in the course of irradiation. To obtain this curve, a thermocouple was welded to a witness sample made of an alloy 7.25 at.\% Mn of the same dimensions and thickness as the samples under study. The witness moved under the ion beam together with the irradiated Fe samples with 4.10 and 7.25 at.\% Mn. As can be seen from Figure 1, the duration of heating (exposure to the ion beam) was only about 3 s. The temperature measurement error according to the metrological certification of its monitoring system is ±5 °C.
The precise setting and reproducibility of the heating-cooling curves (see Figure 1) was ensured on the basis of a series of preliminary experiments with variations in the parameters $E$, $j$, the width of the ribbon ion beam and the speed of the target movement. Mössbauer studies were carried out on a combined Mössbauer spectrometer [35] containing a Doppler modulator MVT-1000 (Wissel GmbH, Mömbris, Germany), a Doppler modulation system SDM-007/SM2201 (Pilot Plant of Scientific Instrumentation RAS, Chernogolovka, Russia), a K-16 controller for communication with a computer, a spectra storage device (MS1101), built into a personal computer with a spectrometric amplifier and a differential discriminator at the input, and a gamma radiation detector with a proportional counter SI11R-3.

Mössbauer spectra were measured at room temperature in a constant acceleration mode. The source of $\gamma$-quanta was $^{57}$Co in Rh. The calculation of the Mössbauer spectra was carried out using the algorithms described in [36–39] (see Section 2 for more details), as well as the software package [40] for reconstructing the $P(H)$ distribution functions of hyperfine magnetic fields.

X-ray structural studies were performed at the Shared Use Center of the Institute of Electrophysics of the Ural Branch of the Russian Academy of Sciences on a D8 Discover X-ray diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) in copper radiation (Cu $K\alpha_{1,2}$, $\lambda = 1.542$ Å) with a graphite monochromator on a diffracted beam. Data processing was carried out using the TOPAS 3 program.

3. Results and Discussion

The study of the processes of atomic rearrangements using diffraction methods in alloys with close electronic scattering factors of components (such as Fe and Mn), closely located in the periodic table, is significantly difficult. This is aggravated by the low manganese content in the studied alloys. In addition, reciprocal lattice sites and diffraction maxima are not formed when phases with sizes less than 8–10 nm are precipitated.

In this regard, to analyze the structural and phase rearrangements in Fe-4.10 and 7.25 at.% Mn alloys, initiated by severe plastic deformation and ion irradiation, we used the Mössbauer effect as the main research method.

For concentrations $c < 10–15$ at.% of the second component, the Mössbauer spectra of single-phase ferromagnetic alloys based on iron in a fairly good approximation can be represented by a superposition of several Zeeman sextets of lines (Figure 2) [39,41], the areas under which are proportional to the probabilities $W(l)$ of the presence in the
first coordination sphere of a $^{57}$Fe atom $l_1 = 0, 1, 2, \ldots$ of atoms of the second component ($S_0 \sim W(0), S_1 \sim W(1), S_2 \sim W(2), \ldots$), in this case of Mn atoms. As shown in [36,39,42], at a manganese content of 7–8% at.%, it is justified to take into account the influence of atoms of only the first coordination sphere, since the influence of the second coordination sphere is an order of magnitude weaker than the first and leads only to broadening and additional displacement of spectral lines. In the presence of short-range atomic order (short-range ordering or separation) in the alloy, the observed probabilities are determined not only by the average concentration of manganese, but also by the degree of short-range atomic order $\alpha$: $W(l_1) \equiv W(l_1, \alpha_1)$, and are described by the binomial distribution [36,41]

$$W(l_1, \alpha_1) = C_{\alpha_1}^{l_1}[c(1 - \alpha_1)]^{l_1}[1 - c(1 - \alpha_1)]^{z_1-l_1},$$

where $c = 0.0725$ is the concentration of manganese in the alloy, $\alpha_1$ is the Cowley-Warren short-range order parameter ($\alpha_1 = -\varepsilon_{ab}(\rho_1)/c(1-c)$), where $\varepsilon_{ab}(\rho_1)$ is the pair correlation parameter for the nearest atoms Fe (a) and Mn (b)), and $z_1$ is the coordination number of the 1st coordination sphere in the bcc lattice. As noted in [24], $c^* = c(1 - \alpha_1)$ is the effective concentration of the second component in the alloy. In alloys prone to delamination and precipitation of the second phase, the value of the parameter $\alpha_1$ takes on a maximum value by the time of this phase precipitation. Then $c_1 = c^*_{\text{min}}(1 - \alpha_{1\text{max}})$ and $c_2$ are the concentrations of the second component in the initial and formed phases.

$$I(v_j) = I(\infty) \left\{ 1 - \sum_{i=1}^{6} \sum_{l_i=0}^{z_1} a_i \frac{W(l_1, \alpha_1)}{1 + 4/\Gamma_i^2 [v_j - \delta_0 - l_1 \Delta \delta_1 - A_i(H_0 + l_1 \Delta H_1)]} \right\}$$

Figure 2. An example of the decomposition of the Mössbauer spectrum of the Fe-6.29 at.% Mn alloy in a single-phase state into constituent sextets [41].

The approximation of single-phase Mössbauer spectra (100% of $\alpha$-phase) was carried out using a physical model [37,39], within which the intensities of all sextets of lines $W(l_1, \alpha_1)$ are completely determined by only one parameter $\alpha_1$ (due to the weak influence of the second coordination sphere, and the model [37,39] is easily simplified to take into account only the 1st sphere):
The Mössbauer spectrum and the distribution densities of effective magnetic fields $P(H)$ reconstructed from it for the Fe-4.10 at.% Mn alloy subjected after quenching to two successive operations, (1) HPT and (2) ion irradiation, are shown in Figure 3a. This spectrum and functions $P(H)$ are completely identical to those for the initial hardened state (the calculated value of the parameter $\alpha_3$ is equal to zero within the error). The calculated functions $P(H)$ (Figure 3a) are of interest only for observing their evolution with an increase in the manganese content in the alloy. The result obtained indicates the absence of any obvious changes in the phase composition and the formation of a composite short-range atomic order in this alloy.

**Figure 3.** Mössbauer spectra of alloys Fe-4.10 and 7.25 at.% Mn and calculated distributions of effective magnetic fields $P(H)$ in the $\alpha$-phase: (a)—Fe-4.10 at.% Mn (quenching + HPT+ irradiation); (b–d)—Fe-7.25 at.% Mn: (b)—quenching + irradiation, (c)—quenching + HPT + irradiation (sextet—depleted $\alpha$-phase, singlet—$\gamma$-phase), (d)—quenching + HPT.

The results of the analysis of the experimental curves of the resonance absorption of the Fe-7.25 at.% Mn alloy for all types of treatment applied to it are given in Table 1.
Table 1. Results of the analysis of the Mössbauer spectra of the Fe-7.25 at.% Mn alloy after various types of processing.

| Processing               | W(0)  | W(1)  | W(2)  | $S_α - n_{Fe}^1$ | $S_α - n_{Fe}^2$ | \(c^i\) \((c_1)\) | \(c_2\) | \(c_α\) \((c_α_{max})\) | \(<H>\) |
|--------------------------|-------|-------|-------|------------------|------------------|-------------------|-------|------------------|--------|
| Quenching                | 0.555 | 0.339 | 0.091 | 1.00             | 0.00             | 0.0711            | —     | 0.02             | 317    |
| Quenching + HRT + irradiation | 0.558 | 0.338 | 0.089 | 1.00             | 0.00             | 0.0703            | —     | 0.03             | 317    |
| Quenching + HRT + irradiation | 0.624 | 0.303 | 0.064 | 0.969            | 0.031            | (0.0573)          | 38.4  | (0.21) ^2        | 320    |
| Quenching + HRT          | 0.562 | 0.336 | 0.088 | 1.00             | 0.00             | 0.0696            | —     | 0.04             | 318    |

\(^1\) In this table lacks the value of the contributions (in the first approximation, additive) to the affective magnetic field at the Fe atom nucleus \(l_1\) and the isomeric shift \(l_1\) (relative to pure iron) from the nearest Mn atoms. It was found \([39,42]\) that these contributions are concentration-dependent and structurally sensitive. However, in the present work, we did not set the task of studying the regularities of changes in these contributions. The calculated value of \(l_1\) for Fe-4.10 and 7.25 at.% Mn alloys for all types of their processing is negative and ranges from \(-6.9\) to \(-7.3\%\) with an error of 0.1%. The value of the contribution to the isomeric shift \(l_1\) relative to pure iron for all types of treatments of the studied alloys is negative and amounts to a value of the order of \(-0.01\, \text{mm/s}\), comparable to the measurement error.

\(^2\) At the moment preceding the formation of the \(\gamma\)-phase.

Figure 3b shows the Mössbauer spectrum obtained from a sample of the Fe-7.25 at.% Mn irradiated with Ar\(^+\) ions in the initial (quenched) state in the same mode as the Fe-4.10 at.% Mn. The form of the spectrum shown in this figure is identical to the spectrum of the hardened sample. This means that short-term irradiation (for \(-3\) s) of the quenched Fe-7.25 at.% Mn, when heated by a beam no higher than 280 °C (Figure 1), does not cause intraphase processes of atomic redistribution in it, as well as the precipitation of new phases, similarly to the alloy Fe-4.10 at.% Mn.

At the same time, the formation of austenite enriched to 17.1 at.% Mn was found in \([41]\), in a cold-formed alloy of similar composition (6.29 at.% Mn) during short-term heating (for 4 seconds) of this alloy with a beam of Ar\(^+\) ions up to 299 °C without holding at the maximum temperature. One of the reasons for the absence of a similar effect in the quenched sample of Fe-7.25 at.% Mn, when heated by a beam no higher than 280 °C (Figure 1), does not cause intraphase processes of atomic redistribution in it, as well as the precipitation of new phases, similarly to the alloy Fe-4.10 at.% Mn.

The important role of the initial state of the material is confirmed by the fact that the Mössbauer spectrum of a sample of the same Fe-7.25 at.% Mn alloy subjected after quenching to two successive operations, (1) HPT and (2) irradiation with Ar\(^+\) ions in the same mode (including the conditions heating, by a beam, Figure 1), demonstrates noticeable changes (Figure 3c). A singlet appears in the center of the spectrum (which is similar to \([41]\)), whose area is 3.1% of the entire spectrum area. The isomeric shift of the singlet relative to the spectrum of pure iron is approximately \(-0.8\, \text{mm/s}\). The appearance of a single line with a measured shear value indicates the formation of a small amount of the \(\gamma\)-phase (austenite) in the alloy.

As you can see, the formation of austenite is accompanied by a change in the intensities (areas) of the \(H(H)\) peaks (Figure 3c). A similar result is obtained by a calculation based on the ratio (2) of the integral intensities (areas) \(S_0 - W(0), S_1 - W(1), S_2 - W(2), \ldots\) subspectra of the ferromagnetic phase corresponding to the presence of \(l_1 = 0, 1, 2\) etc. of Mn atoms in the closest environment of iron atoms. Their change (Table 1) indicates that the concentration of manganese in the solid solution decreases, and this, in turn, means that the concentration of manganese in the formed austenite is much higher than the average.

Relation (2) uses the additive bond \(H(l_1) = H_0 + \Delta H_1\) for the field strength at the nucleus of Fe atoms, which have \(l_1\) impurity atoms in the nearest environment. This relationship is typical for iron-rich (with \(<8-10\, \text{at.%}\)) single-phase alloys with substitutional impurities. If necessary, the role of the second and subsequent coordination spheres can also be considered. The additive effect of impurities makes it possible to obtain a linear dependence of \(<H>\) on the short-range order parameter \([39,43]\). Taking into account the data \([39,42]\), this dependence for Fe-Mn alloys can be written in the simplest form:
where $n_N$ is equal to or exceeds the value of the energy barrier ($\varepsilon_\beta$).

In [43], taking into account the transition from a homogeneous model of short-range order to a heterogeneous two-phase model, a relation was obtained for the manganese concentrations $c_1$ and $c_2$ in the $\alpha$- and $\gamma$-phases (see explanations to formula (2)): $n_F^{\gamma} = \frac{(c_2 - c)(1 - c_1)}{(c_2 - c_1)(1 - c)}$, from which the concentration of manganese in austenite can be expressed as

$$c_2 = \frac{n_F^{\gamma}c_1(1 - c) - c(1 - c_1)}{n_F^{\gamma}(1 - c) - (1 - c_1)},$$

where $n_F^{\alpha}$ and $n_F^{\gamma} = 1 - n_F^{\alpha}$ are the fractions of Fe atoms in the $\alpha$- and $\gamma$-phases (proportional to the areas of the subspectra of these phases, Figure 3c). For the analyzed alloy Fe-7.25 at.% Mn $c = 0.0725$ and, according to Table 1, $n_F^{\alpha} = 0.031$ ($n_F^{\gamma} = 1 - n_F^{\alpha} = 0.969$), $c_1 \equiv c^\prime = c(1 - \alpha_{\text{max}}) = 0.0573$. Taking into account these data and using relation (2), we obtain: $c_2 = 0.384$ (38.4 at.% Mn).

This result is in good agreement with extrapolation to the low-temperature region of the line of the limiting solubility of the $\gamma$-phase in the equilibrium phase diagram [33] constructed for temperatures above 400 °C. This indicates a full-fledged “instantaneous” radiation annealing of the Fe-7.25 at.% Mn alloy subjected to ion bombardment in a strongly nonequilibrium state (after high pressure torsion).

Note that shear under pressure without subsequent irradiation (Figure 3d) does not cause $\alpha \rightarrow \gamma$ transformation in the Fe-7.25 at.% Mn alloy.

Numerous facts of rapid radiation annealing of various alloys by ion beams, including those with precipitation and dissolution of phases at low temperatures, are given in reviews [1,3,16]. For example, the fact of nanocrystallization of an amorphous ribbon made of Fe$_{72.5}$Cu$_1$Nb$_2$Mo$_{1.5}$Si$_{14}$B$_9$ alloy with a thickness of 25 μm was discovered as a result of 2 s of irradiation with a continuous beam of argon ions at a temperature of 380 °C, much lower than the temperature of industrial annealing (570 °C, 1 h) and recrystallization threshold (500 °C).

Not only thermally activated, but also radiation-enhanced diffusion fails to explain the processes of instantaneous formation during ion irradiation of phases of significantly changed composition at anomalously low temperatures (see below the corresponding calculations).

In works [1,3,30,31] it is shown that thermo- and radiation-stimulated diffusion at low temperatures can be replaced by “radiation shaking” of the irradiated material. We are talking about radiation shaking during cascade-forming types of irradiation by powerful elastic and/or shock solitary waves emitted by rapidly expanding nanoscale (r~5 nm) regions of dense cascades of atomic displacements heated quasi-adiabatically (within about $10^{-12}$ s) to 3000–6000 K and higher (the temperatures were measured as a result of the analysis of the spectral composition of the thermal glow of the targets [1,44]). In metastable media, post-cascade waves, passing into a continuous propagation mode, can initiate structural-and-phase transformations at their front theoretically at an unlimited depth [1,30].

In order to explain the different effects of ion irradiation on the Fe-7.25 at.% Mn alloy after various preliminary treatments, we will use the results of works [1,30], in which a phenomenological theory of the formation of undamped postcascade powerful elastic and/or shock waves in metastable media under corpuscular irradiation is constructed.

According to the conclusions of this theory, a post-cascade solitary wave can initiate the transition of a medium from a metastable state 1 to a stable state 2 (Figure 4) if its energy $\varepsilon_0$ is equal to or exceeds the value of the energy barrier ($\varepsilon_0 \geq \Delta F$) separating these two states. In this case, the medium releases the energy $\Delta F' = -\Delta F = F_2 - F_1$ (per atom of the medium). It was shown [1,30] that an important parameter is the value $\varepsilon_\gamma = \frac{v\Delta F'}{2kG}$. Here $v$ is the wave velocity, $\delta$ (s$^{-1}$) is the absorption coefficient of the wave by the medium ($\beta = \delta/v$ (m$^{-1}$) is the attenuation coefficient), $k$ is the waveform coefficient (value of
the order of unity for a Gaussian profile), and \( G \) is the width wave front at half height. The velocity \( v \) of the shock wave, in contrast to the elastic, slightly exceeds the speed of sound in the medium. At \( \Delta F' > 0 \) depending on the ratio of the energies \( \varepsilon_0 \), \( \Delta f \), and \( \varepsilon^* \), the rearrangement initiated by the post-cascade wave may result in the following cases:

1. \( \varepsilon_0 < \Delta f \)—the transformation from metastable state 1 to stable state 2 or approaching a stable state does not occur, but the usual damping of the wave takes place (Figure 4a);
2. \( \varepsilon_0 \geq \Delta f \) and \( \varepsilon^* \geq \Delta f \)—undamped mode of the wave propagation (Figure 4a), which initiates a self-propagating phase (or intraphase) transformation at its front, at an unlimited depth \( x \) (or \( \rho \)) (the amplitude of the \( \varepsilon \) wave approaches \( \varepsilon^* \) either from below (grows) for \( \varepsilon_0 < \varepsilon^* \), or from above when \( \varepsilon_0 > \varepsilon \) (decays, but not to zero)),
3. \( \varepsilon_0 \geq \Delta f \), \( \varepsilon^* < \Delta f \)—the wave initiates the transformation of the medium at a limited depth \( x_0 \) (or \( \rho_0 \)), damping in amplitude to the value of \( \Delta f \); after this, the usual attenuation of this wave occurs in the absence of transformation.

\[
\varepsilon = \frac{v \Delta F'}{2 \delta k G}
\]

Intense external influences preceding irradiation can change the parameters \( \Delta f \) and \( \Delta F \) (determining the degree of metastability and resistance of the medium to external influences), Figure 4a,b. The foregoing can apply to both the medium as a whole and its microvolumes. This means that the change in the amplitude of the post-cascade wave and the effectiveness of the impact depend on the previous types of processing.

Thus, the results of experiments (Table 1) related to irradiation with ion beams and the data of [41] can be explained within the framework of the assumption about the decisive role of post-cascade waves, taking into account the difference in the initial state of the Fe-7.25 at.% Mn after various treatments: (1) quenching (2) cold deformation [41], and (3) hardening + HPT, which have different effects on the parameters \( \varepsilon_0 \), \( \Delta f \), and \( \varepsilon^* \).

Analysis of the spectrum of the alloy subjected to HPT, but not subjected to subsequent irradiation, shows that during HPT at 25 °C, only a slight redistribution of atoms \( (\alpha_1 = +0.04) \) occurs in the direction of separation of the solid solution into zones enriched
and depleted in manganese. This is confirmed by the absence of significant changes in the calculated functions \( P(H) \). The \( P(H) \) peaks areas are proportional to the probabilities of surrounding \(^{57}\)Fe with different numbers of the nearest manganese atoms (Figure 3c,d). This agrees with the data [2] on the destruction of atomic order at HPT in the temperature range \(-196\text{–}25\,^\circ\text{C}\) and an increase in the degree of order when HPT is performed at \( T > 100\,^\circ\text{C}\).

In [2], it is noted that in the course of HPT, two competing processes can occur: (1) the movement of dislocations, that destroys the short-range order, and (2) the formation and migration of nonequilibrium defects, which leads to an increase in the degree of short-range order. The relative contribution of the second process increases with increasing temperature. However, according to the available data [2,4], HPT, unlike radiation shaking, does not cause the formation of a \( \gamma \)-phase, which theoretically (according to the equilibrium phase diagram [33]) has a minimum free energy.

Thus, as shown by the performed experiments, the formation of the \( \gamma \)-phase with a very high Mn concentration takes place only under conditions of ion irradiation. This occurs at an extremely low temperature: \( T \leq 280\,^\circ\text{C} \) in a metastable alloy previously subjected to HPT and having an increased stored energy in the form of accumulations of dislocations and nonequilibrium point defects. As already noted, the obtained value of the manganese concentration in the \( \gamma \)-phase (38.4 at.%) is in qualitative agreement with the result of extrapolation to the region of low temperatures the line of limiting solubility from the side of the \( \gamma \)-phase [33].

It is known that at this temperature there is practically no thermal diffusion of substitutional impurities in iron-based alloys. The role of radiation-stimulated diffusion in the redistribution of Fe and Mn atoms can also be excluded. Indeed, according to calculations by the TRIM method, the predicted range of only an insignificant fraction of argon ions with energies \( E = 15\,\text{keV} \) in Fe-4.10 and 7.25 at.% Mn alloys exceeds 20 nm. Consequently, the region of formation of primary radiation defects is a thousand times smaller than the thickness (20 \( \mu \text{m} \)) of the samples subjected to the transformation (3.1% of the \( \gamma \)-phase), irradiated for only 3 s.

The advancement of excess radiation defects deep into the substance is limited by their intra-cascade recombination, low thermal diffusion due to the lowered temperature, and, in addition, absorption of defects by natural sinks. A rough estimate of the characteristic diffusion length of vacancies (without taking into account their recombination and absorption by sinks) \( L = \sqrt{D\tau} \) in Fe \( D = 8.49 \times 10^{-3}\,\text{exp}(-0.733/kT)\,\text{(m}^2\,\text{s}^{-1}) \) [45] at 280 \( ^\circ\text{C} \) for 3 s is 0.73 \( \mu \text{m} \). This means that during the irradiation time, vacancies cannot be delivered deep into the volume of the target. After turning off the beam, the temperature of the target drops very quickly.

As for the interstitial atoms formed during ion bombardment, the energy of their migration in metals is usually small in comparison with the migration energy of vacancies. However, as a result of recombination and absorption by sinks, the increased diffusion length decreases many times. A more accurate estimate of the size of the zone of influence of defects requires reliable data on the diffusion coefficient of intrinsic interstitial atoms and on the increase in the power of sinks of point defects in the alloys under study as a result of HPT and ion irradiation.

In this article, we do not focus on radiation damage in the zone of ion path, since we consider a three orders of magnitude more extended zone of exposure due to nanoscale dynamic effects [1,3,31,32] at low radiation doses. As already noted, the role of damage, alloying, and static stresses from embedded impurities should be considered under high-dose irradiation [13,14,18,21], when extreme static stresses accumulate, in some cases exceeding the theoretical yield strength of the material. Such stresses are capable of causing the formation of dislocation loops, which are shot into the depth of the substance by tens of micrometers and create in these layers a high density of dislocations that change the properties of the medium. The physics of the impact of pulse power energy flows is also specific [17,23,25].
Note that X-ray diffraction analysis, due to the factors noted above that reduce its sensitivity for the studied type of systems, did not reveal the presence of any new phases in alloys with both Fe-4.10 and 7.25 at.% Mn after all types of impacts. The results of processing the diffraction patterns indicate only the presence of textural changes after the application of the HPT, as well as an increase in the coherent scattering regions (i.e., the crystallite size) and a decrease in the crystal lattice parameter of the α-phase as a result of the action of Ar⁺ ions, which is consistent with the data [41]. The absence of reflections from the particles of the precipitated γ-phase for the Fe-7.25 at.% Mn alloy is apparently due to their small size ≤ 10–15 nm.

4. Conclusions

It is shown that the effect of accelerated ions on iron-rich ferromagnetic alloys of the iron-manganese system, Fe with 4.10 and 7.25 at.% Mn, significantly depends on their thermodynamic stability, determined by the concentration of manganese and the structural state formed as a result of previous treatments. This affects the ratio of the described parameters ε₀, Δf and ε*, which determine the result of radiation-dynamic exposure of post-cascade waves.

Indeed, an iron alloy with 4.10 at.% Mn, which belongs at low temperatures of irradiation (<300–500 °C) and at room temperature to the single-phase α-region, does not undergo structural phase transformations under the influence of HPT treatment and accelerated ion beams. The same applies to the absence of noticeable signs of short-range order formation (i.e., intra-phase rearrangements).

Alloy with 7.25 at.% Mn in the quenched state, which is a supersaturated solid solution of manganese in iron, is subject to an extremely insignificant degree of short-range stratification (α = +0.04) and does not undergo a phase α→γ transformation under short-term exposure (about 3 s) to a continuous beam of Ag⁺ ions (E = 15 keV, j = 200 mA/cm², F = 3.75·10¹⁵ cm⁻²) when heated by an ion beam up to 280 °C.

The same alloy in a highly nonequilibrium metastable state after HPT treatment undergoes an α→γ transformation at anomalously low temperatures (T ≤ 280 °C) with the formation of 3.1% high-manganese (38.4 at.% Mn) austenite in the sample volume 20 μm thick during short-term irradiation. Indeed, the zone of penetration of ions is only about 0.1% of the volume of the irradiated foil, which is many times less than the total volume of 3.1% of the formed austenite particles.

The high rate of transformation, within a few seconds of processing, indicates the initiation of a giant low-temperature mobility of atoms. The authors explain the fact of increasing the mobility of atoms at low temperatures by their previously proposed mechanism of cascade radiation shaking [1,3,30–32], which can be used to obtain thermally unattainable states of the irradiated media.

Note that the replacement of expensive iron-nickel alloys for the manufacture of cryogenic technology and equipment used in the Arctic and Antarctic latitudes, with cheaper ferromanganese alloys, is limited by the cold brittleness of the latter. The phenomenon of irreversible tempering brittleness of bcc α-ferrite in the range of 300 and 400 °C is also known [36], which is explained by the formation of short-range atomic order [36,38]. In this regard, it is of interest to find out in the future how the formation of austenite initiated by ion irradiation affects the embrittlement of iron-manganese alloys and steels based on them.

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