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Gamma-irradiation effect on heterogeneous short-range order in Fe+12 at.% Al alloy

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Abstract

The effects of γ-irradiation on heterogeneous short-range order (HSO) formation in a deformed Fe+12 at.% Al alloy and on the alloy structural stability were investigated in this work. It is established that HSO formation is accelerated under irradiation and the activation energy of this process is decreased by ~10% under the effect of γ-irradiation at 1500 R/s ($\sim 10^{-13}$ dpa/s). The efficiency of the γ-irradiation effect on HSO formation depends on the alloy heterogeneity and temperature under irradiation. Additional ordering is shown to take place under γ-irradiation in Fe+12 at.% Al alloy with preformed HSO. The possible mechanisms of the observed phenomena are discussed. Additional alloy ordering determined by increase of supplementary vacancy source efficiencies under γ-flux is proposed.

1. Introduction

Single-phase solid solutions based on transition metals (e.g., Fe–Al alloys) exhibit some property anomalies. These anomalies are connected with both the crystalline lattice structure of the solid solution and ordering processes in it. However, the short-range ordering mechanism in Fe–Al alloys has been studied insufficiently. There are different points of view about possible existing mechanisms [1]. The statistical model suggests that the short-range order in Fe–Al is homogeneous in the whole volume. According to the other opinion Fe–Al alloys contain atomic complexes (clusters), enriched by Al atoms (microdomain model). It has been established by direct methods that Fe–Al with Al content up to 19.6 at.% are heterogeneous in structure [2–4]. The heterogeneities in these alloys are connected with local areas with short-range order. This structure is formed by Fe atoms surrounded by Al atoms because of their chemical affinity. However, structural heterogeneities in single-phase disordered Fe–Al alloys ($Al \leqslant 19.6$ at.%) occur under low-temperature annealings only due to excess of vacancies (so-called K-state). Equilibrium chart of the Fe–Al system performed by means of electron microscopy is given in [3]. A thermodynamic area with the K-state is indicated on the chart. The heterogeneous DO_3-type short-range order appeared to be stable at room temperature and disordered at temperatures higher than 200°C, progressively being replaced by the B_2-type heterogeneous short-range order (HSO) in Fe+12 at.% Al alloy [2,5–7]. Deformed Fe–Al alloys have especially large structural and concentration heterogeneities [2]. This structure contains significant amounts of vacancies and is disordered and very unstable.

Formation of a stable HSO occurs due to an increase in vacancy mobility under alloy annealing. The HSO regions' maximum diameters in Fe–Al alloys are not more than 5 nm [3]. The areas with these dimensions appear to be additional scattering centers of conduction electrons. Therefore, HSO formation in Fe–Al alloy is accompanied by an electrical resistivity increase.

Neutron and γ-irradiation effects on the deformed Fe–Al alloys' electrical resistivity increase were shown by Konnov et al. and Danilchenko et al. [8,9]. The electrical resistivity of the Fe+12 at.% Al alloys was

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increased by 2% under γ-irradiation at temperatures of 40–50°C and fluence of $\sim 4.5 \times 10^9$ R in comparison with the initial value (without irradiation) [9]. This phenomenon was explained in Ref. [9] by the formation of the partial HSO in the completely disordered alloy due to atomic mobility increase under irradiation. However, such an explanation is ambiguous. The electrical resistivity increase under γ-irradiation can be caused by concentration heterogeneity growth before the local short-range order formation. One could also suppose that acceleration of diffusional processes by irradiation [10] would cause additional structural changes in the deformed Fe–Al alloy affecting its ordering under annealing.

Therefore, the aim of this investigation was to study the γ-irradiation effect on the HSO formation in the deformed Fe–Al alloy and on the alloy structural stability. The investigation of the HSO formation process under the γ-flux (in situ) appeared to be of great interest.

2. Material and investigation method

A Fe+12 at.% Al alloy was chosen for the investigation. The dependence of the configuration structure changes on annealing temperature in this alloy has been sufficiently studied under normal condition [2,5–7]. Long-range order is known to be absent within the whole temperature range in this alloy [11]. Fe+12 at.% Al alloy was preannealed at 1000°C within 1.5 h and cooled at the rate of 2°/min; then it was deformed to 300% by rolling, causing the formation of a completely disordered state [2]. Then the alloy samples were annealed at different temperatures and times for formation of HSO. The samples were investigated by the electrical resistance method. The electrical resistivity method has proved to be very sensitive and informative for investigations of structural and phase transformations in solid solutions under the γ-flux in particular. Moreover, the changes of the HSO rate in Fe–Al alloys are correlated with the electrical resistivity change [2,5–7]. The data obtained with this method allow a conclusion about HSO formation in the investigated alloy.

The electrical resistivity changes of the newly deformed both unirradiated (1-type) and irradiated (2) samples as well as samples aged at room temperature for one year after deformation (3) are studied in this paper. The samples were irradiated by γ-quanta with the energy of 1.2 MeV and with the γ-sources ^{60}Co intensity (I_γ) of 1500 R/s. The maximum fluence (F_{max}) was 9.5×10^9 R ($\sim 5 \times 10^{-7}$ dpa).

The kinetics of electrical resistivity changes of the samples 1–3 were studied at room temperature to get the information about structural stability in the deformed alloy. The residual electrical resistivity of all the samples investigated in this paper was measured at liquid nitrogen temperature in definite time intervals (sample 1) and after different fluences (F) at room temperature (samples 2 and 3).

The unirradiated sample 1 and samples 2 and 3, irradiated by 9.5×109 R at room temperature, were subjected to isochronal (10 min) step-by-step annealing at the temperature range 60–280°C. The residual electrical resistivity at liquid nitrogen temperature was measured at every annealing.

The kinetics of electrical resistivity change in the Fe+12 at.% Al alloy under its annealing was investigated on sample 1 both in normal condition and directly under irradiation in the following way: First, the residual electrical resistivity of every sample was measured. The sample with the welded Pt–PtRh thermocouple was placed in a furnace in the irradiation area. The sample was heated to the given temperature for 3–4 min. The temperature was maintained with the accuracy of ±0.1°C. The sample's electrical resistivity was measured at the given annealing temperature every 2 min with an accuracy of 0.1%. The same measurements of the alloy electrical resistivity were carried out without the ^{60}Co sources in the radiation area.

3. Experimental results and discussion

In Fig. 1 the kinetics of electrical resistivity changes $\Delta R/R_i$ at room temperature of samples 1–3 under γ-irradiation and in normal conditions (R_i is the initial residual electrical resistivity after deformation) are shown. As a result of the deformed state's instability, the value $\Delta R/R_i$ increases even without irradiation. However, this process is rather slow (curve 1). The value $\Delta R/R_i$ reaches $\sim 0.25\%$ in 850 h. In newly deformed samples under irradiation, $\Delta R/R_i$ (curve 2) also grows with time, first slowly (approximately 0.2% with $F = 1.8 \times 10^9$ R corresponding to 300 h of irradiation) and then faster (1.5% with the fluence of 3.5×10^9 R corresponding to ~ 630 h

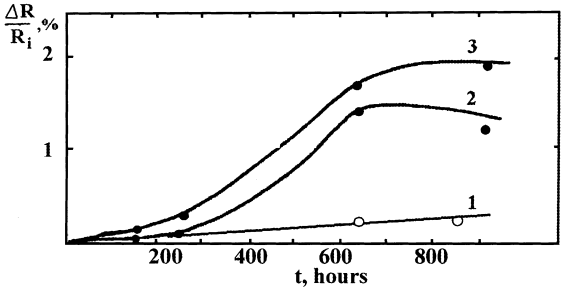

Fig. 1. The time-dependent residual resistance change of the alloy Fe+12% Al on exposition term at room temperature without γ-irradiation (○) and under γ-irradiation (●) (1, 2 – the newly deformed specimens, 3 – aged at room temperature for one year after deformation).

of irradiation). A further increase of fluence up to $F = 5 \times 10^9$ R ($\sim$ 900 h) results in a small decrease in $\Delta R/R_i$ (curve 2). The analogous results are observed for the sample 3 under irradiation: with $F = 5 \times 10^9$ R ($\sim$ 900 h) the $\Delta R/R_i$ value is $\sim$ 2% (curve 3).

Thus, γ-irradiation accelerates the electrical resistivity increase of the deformed alloy and the efficiency of this process depends on the alloy's initial state. It is known that at room temperature the HSO formation in Fe+12 at.% Al alloy does not happen practically [2–7]. Therefore, the data in Fig. 1 and also the theoretical representation [12] support the conclusion that the observed electrical resistivity changes of deformed samples are due to the amplification of concentration heterogeneities in them under γ-irradiation.

The Fe+12 at.% Al alloy's electrical resistivity behavior under isochronal annealing is demonstrated in Fig. 2. The investigated samples in the initial state had a different rate of the heterogeneity caused by the deformation and irradiation of $F_{max} = 9.5 \times 10^9$ R. Fig. 2 demonstrates that independent of the initial treatment of the samples all curves are of the similar character. The $\Delta R/R_i$ maximum increment as to R_i depends on the initial treatment of the samples (Fig. 2) and constitutes 5.3% (sample 3), 4.3% (sample 2) and 3.3% (sample 1), respectively. The saturation curves prove the formation of stable HSO in Fe+12 at.% Al alloy (according to [2–7]).

The initial stages of the HSO formation kinetics were investigated for estimation of the efficiency of the γ-irradiation effect on energetic parameters of this process. The kinetics dependence changes $\Delta R/R_0$ (t) (R_0 is the sample's initial electrical resistivity at given annealing temperature) under annealing at temperatures of 116°C, 129°C and 155°C under γ-flux and without irradiation is represented in Fig. 3. Irradiation clearly leads to a noticeable acceleration of HSO formation at 116°C and 129°C. The γ-flux has no effect at an annealing temperature of 155°C. So, as temperature increases the irradiation contribution to the HSO formation rate decreases.

The data in Figs. 3 and 4 were used for determination of the HSO formation activation energy (E_a). The slope of the curves of ln t vs. $(1/T_{ann})$ defines the value E_a (Fig. 4). The value E_a was obtained to be equal to 0.67 eV/at. under irradiation of $I_\gamma = 1500$ R/s and is equal to 0.74 eV/at. without irradiation. Therefore, γ-irradiation de-

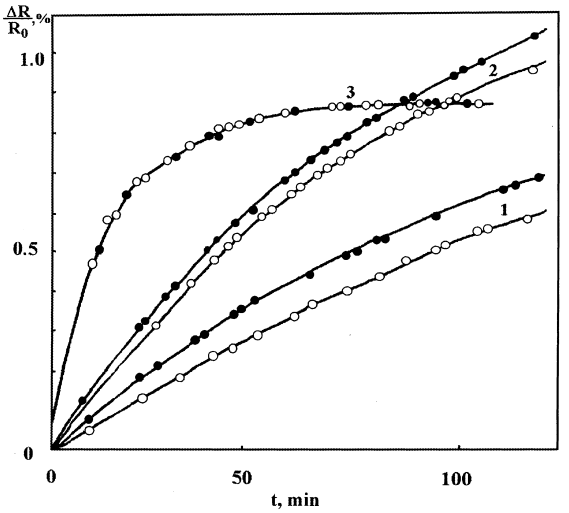

Fig. 3. The kinetic dependences $\Delta R/R_0$ of Fe+12% Al alloy at 116°C (1), 129°C (2) and 155°C (3) without irradiation (○) and under γ-flux of 1500 R/s (●).

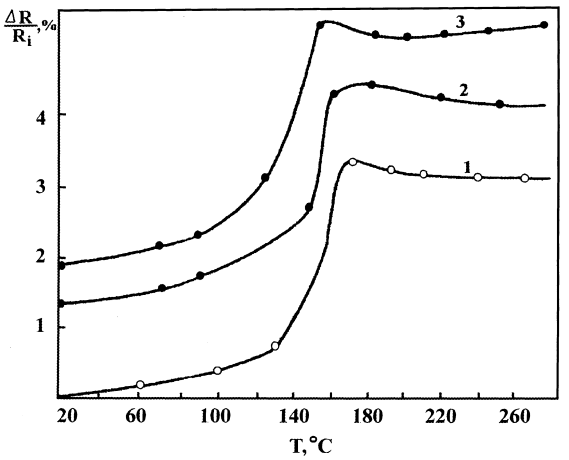

Fig. 2. The residual resistance change of the samples 1 (1) and irradiated to the maximum dose of the samples 2 and 3 (2, 3) under isochronal annealing.

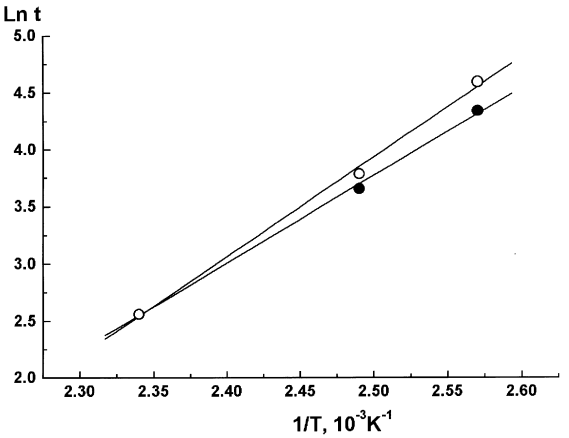

Fig. 4. Dependence of time of HSO same values formation vs. annealing temperature under normal condition (○) and under γ-flux (●).

creases the HSO formation activation energy by 10% in the temperature range 116–155°C. This activation energy decrease is equivalent to an increase in atomic jump frequency (v_{aT}) approximately by a factor of 7 assuming relation of $v_{aT} = v_o e^{-E_a/RT}$ [13], where v_o was the effective atomic oscillation frequency in the lattice.

The analysis of the data proves that the efficiency of the concentration heterogeneity change in the alloy Fe+12 at.% Al is determined both by the annealing temperature and the γ-irradiation flux. Apparently new areas of the short-range order arise in the alloy under γ-irradiation. These areas are distributed non-homogeneously in the unordered matrix.

The γ-irradiation was also found to affect alloy stability with established HSO. Samples 1 were heated to 240°C for 20 min without the ^{60}Co sources. The sample electrical resistivities were measured under heating and exposure at 240°C. The alloy's electrical resistivity was shown not to change during 60 min (Fig. 5) proving stable HSO formation in the investigated alloy. After the ^{60}Co sources input into the radiation zone the value $\Delta R/R_0$ (R_0 – initial electrical resistivity of annealing temperature at 240°C) was increased by 0.2% for 10 min. Further exposure at 240°C under γ-flux for 200 min, increased the value $\Delta R/R_0$ by 0.75% compared to the unirradiated state. After irradiation was stopped the value $\Delta R/R_0$ decreased by 0.2%, the same as the increase due to the onset of irradiation. However, the complete removal of the initial resistance value of R_0 did not occur. Thus, the additional irreversible $\Delta R/R_0$ increment in the γ-flux constitutes $\sim 0.55\%$. Further sample annealing without irradiation did not change the $\Delta R/R_0$.

The curve shape analysis (Fig. 5) indicated the following: The total increment of the value $\Delta R/R_0$ consists of two parts – the growth of $\Delta R/R_0$ at input of the ^{60}Co sources (0.2%) and under exposure to the γ-flux at a temperature of 240°C during ~ 200 min (0.55%). The evaluation of the temperature gradient due to the interior heating by absorption of γ-quanta by the sample cross-section shows that it is less than 0.01°C. So, the first part of the $\Delta R/R_0$ increment cannot be connected

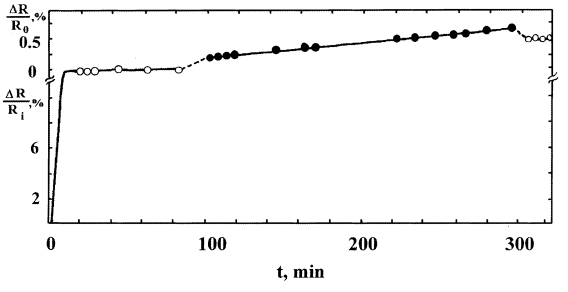

Fig. 5. The electrical resistivity change kinetics of the newly deformed specimens under annealing at 240°C without irradiation (○) and under γ-flux of 1500 R/s (●).

with the additional specimen heating under γ-irradiation. Since temperature fluctuations in the irradiation cell were ±0.1°C during the measurements, obviously, additional study is needed for unambiguous explanation of the reversible part of the $\Delta R/R_0$ change. The second irreversible part of the $\Delta R/R_0$ increase may be due to the increasing HSO rate in Fe+12 at.% Al alloy and appearance of the additional short-range ordered areas.

According to Refs. [12,14,15], HSO could be represented as a structural state with the heterogeneous distribution of both the short-range order and the composition in the alloy. This state of alloy is characterized by the local ordered areas in the disordered matrix. These areas are enriched with the Al atoms. As long as the atomic diameter of Al atoms is larger than the Fe ones the internal stresses appear in the local ordered areas. The model [16] proposed recently assumed the removal of internal stresses could occur due to the vacancy flows directed to the local stressed areas.

Two stages of high rate order area formation in Fe+12 at.% Al were suggested in [14]. The equilibrium with constant vacancy number is realized in the first stage. In the second stage, the vacancy sources which are grain boundaries in normal conditions (without irradiation) will begin to play the main role. However, total volume increase in ordered areas related to these source impacts occurs very slowly. Therefore, the second stage is not observed under normal thermal condition. The additional vacancies sources efficiency is apparently now under the γ-flux resulting in new areas with short-range order formation, that is to the alloy additional ordering (Fig. 5).

Vacancy number is determined proportionally to the irradiation time in the case if vacancies state conditioned by their origination and their absorption by sinks is assumed to be not able to become stationary due to the lack of time. Then it could be determined by the equation [17]: $n = N_0 \varphi t \sigma K$, where N_0 is the number of atoms per 1 cm^3; φ the γ-quantum flux ($\sim 10^{12}$ quantum/cm^2 s); t the time of irradiation; σ the cross-section of point defect formation; $K = 4 \times 10^3$ is the recalculation coefficient of polyenergetic beam of Compton electrons into a monoenergetic one. Taking into consideration that mainly light atoms are displaced (in our case it is Al), i.e., $\sigma = 2.5$ barn [18] then the concentration of the induced vacancies in 1 cm^3 due to 200 s γ-irradiation is about 10^{-9}, which is much less than the maximum vacancy concentration in the HSO areas, $c_v^0 \approx 10^{-3}$, as well as the average concentration of surplus vacancies in the hardened alloy, $\bar{c}_v \sim 10^{-6}$ [14]. Hence the observed effect of additional ordering under γ-flux in Fe+12 at.% Al cannot be explained by radiation-induced vacancies only but is apparently connected with the radiation defects recombination [19,20] and with atomic rearrangements under irradiation. This event could be explained by γ-irradiation ionization of inner atomic electron shells [21,22] resulting in a highly ionized state of atoms.

Life-time of the ionized state in the condensed environment is about 10^{-13} s, which can be compared to the period of atomic thermal oscillations in a lattice [21,22]. So, one could assume that thermal equilibrium atomic configuration around a vacancy is changed greatly with an ionized atom as this vacancy neighbor, resulting in possible decrease of potential barriers for atom rearrangement under γ-flux. The reduction of activation energy observed (Fig. 4) proves the above-mentioned event.

4. Summary

It is established that the HSO formation is accelerated in the deformed Fe+12 at.% Al alloy and the activation energy of this process is decreased by $\sim 10\%$ under the impact of γ-irradiation at 1500 R/s ($\sim -10^{-13}$ dpa/s). The efficiency of the γ-irradiation impact on HSO formation depends on the alloy heterogeneity and irradiation temperature.

Additional ordering is shown to take place under γ-irradiation in Fe+12 at.% Al alloy with the preformed HSO.

The possible mechanisms of the observed phenomena are discussed. An explanation for additional alloy ordering determined by an increase in supplementary vacancy source efficiency under γ-flux is proposed.

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