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Dissolution kinetics of intermetallics in aging austenitic steels during neutron irradiation

V.V. Sagaradze *, V.M. Koloskov, B.N. Goshchitskii, V.A. Shabashov

Institute of Metal Physics, Ural Branch RAS, 18 S. Kovalevskaya Str., 620219 Ekaterinburg, Russia

Abstract

The Mössbauer spectroscopy, X-ray diffraction analysis, and the electron transmission microscopy were used to study the dissolution kinetics of dispersed Ni_3Ti γ'-precipitates in displacement cascades at 340 and 530 K during neutron irradiation of the aged 35Ni3Ti austenitic steel (Fe + 34.2 at.% Ni + 3 at.% Ti). The dissolution was significantly intensified as the initial size of the particles decreased. At high neutron fluence and temperature, the dissolution was accompanied by competitive precipitation of the intermetallics. During irradiation at 340 K, the Ni concentration in the austenite matrix tended to some equilibrium value of about 32.2 at.%.

1. Introduction

Radiation-induced precipitation and dissolution of dispersed intermetallics retard the radiation-induced swelling of reactor steels and alloys [1,2]. Precipitation and dissolution of second phases in displacement cascades were studied, analyzed theoretically in Ref. [3]. Experimental studies dealing with dissolution of dispersed particles under ion and, especially, neutron irradiation are few however. The researchers [4,5] used the electron microscopy and showed that dissolution of coarse particles of the Ni_3Al γ'-phase was accompanied by formation of fine γ'-particles in nickel alloys exposed to a cascade-produced ion irradiation at temperature of 923 K. However, it is difficult to separate thermal-equilibrium, radiation-enhanced, and non-equilibrium radiation-induced processes. Low-temperature (298 K) dissolution of ordered Ni_3Al intermetallics estimated [4] from vanishing of superstructural reflections is also ambiguous and can only be related to radiation-induced disordering. The present study is mainly concerned with the Mössbauer analysis of neutron-initiated dissolution of dispersed particles of Ni_3Ti, a common phase in reactor steels with an fcc lattice.

2. Materials and methods

The subject of the present study was an aged model invar alloy 35Ni3Ti with an fcc lattice containing (at.%) 34.2 Ni, 3 Ti, 0.1 C, balance Fe. It is impossible to determine the quantity of the coherent ordered Ni_3Ti γ'-phase in the irradiated alloy by either the electron microscopy method because of a poor resolution of dispersed particles or the neutron diffraction method since the irradiation could lead to disordering of the Ni_3Ti phase without its dissolution. Thus, the quantitative phase analysis using superlattice reflections is difficult. Therefore the radiation-induced dissolution and precipitation of high-nickel Ni_3Ti phase, which lead correspondingly to the enrichment and the depletion of the austenitic matrix in nickel, and which largely alter magnetic properties of the model alloy, were analyzed by the Mössbauer spectroscopy technique. The Mössbauer measurements were made at 298 K using NGR spectrometer with a $^{57}Co(Cr)$ source. It is at room temperature that the shape of the spectra corresponding to $P(H)$ and $\widehat{H}$ exhibit a sharp dependence on the nickel concentration of fcc Fe–Ni alloys of the invar

* Corresponding author. Tel.: +7-3432 744214; fax: +7-3432 740003.

E-mail address: vsagaradze@imp.uran.ru (V.V. Sagaradze).

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range (29–38 at.% Ni). An analysis of the nickel concentration at low temperatures is less efficient because of the remoteness of the Curie point (and, hence, a low dependence of $P(H)$ and $\widehat{H}$ on the composition) and the presence of a $\gamma \rightarrow \alpha$ martensitic transformation in compounds containing less than 32 at.% Ni. The dispersed γ'-phase precipitated and dissolved in displacement cascades when the alloy was exposed to fast neutrons (the fluence of 5×10^{19}, 10^{20} and 5×10^{20} n/cm^2) in IVV-2M reactor at temperature of 340 and 530 K. Two to three mass % of titanium had negligible effect on the spectra of the alloy studied [6]. Strong variation of magnetic characteristics, in particular, the Zeeman location of the Mössbauer spectra was due to dissolution or precipitation of the high-nickel Ni_3Ti phase [6]. The concentration of nickel atoms in the matrix was determined from the distribution functions of the internal effective field at ^{57}Fe atom cores, $P(H)$. The density distribution functions $P(H)$ were reconstructed using algorithms proposed by Window [7] and Hesse-Rubartsch with normalization [8]. The quantitative analysis was performed using average values of Mössbauer parameters, for example, an average field calculated as a weighted average: $\widehat{H} = \sum HP(H)$. The quantitative analysis was possible due to strong dependence of Mössbauer parameters on the Fe–Ni alloy composition. The calculated $\widehat{H}$ values were used to determine the composition of the 35Ni3Ti alloy matrix from the $\widehat{H} = f(C_{Ni})$ dependences [9].

The 35Ni3Ti steel was examined in three states: after quenching from 1373 K; aging at 923 K (0.5 h); and cold-rolling deformation (reduction to 94%) at 298 K. The structure was examined in a JEM-200CX electron microscope. The X-ray technique was used to observe changes in the austenite lattice constant.

3. Results and discussion

3.1. Mössbauer analysis of dissolution of γ'-particles

When fcc Fe–Ni alloys of the 36Ni type are exposed to fast neutrons with an energy $E > 0.1$ MeV in an IVV-2M reactor, displacement cascades are 4–6 nm in size on average [10]. It is interesting to estimate the intensity of radiation-induced dissolution of dispersed intermetallic particles with size smaller and larger than the size of a displacement cascade. Finest coherent particles of the Ni_3Ti γ'-phase about 2 nm in size see [11,12] with the fcc structure, and the lattice constant close to that of the austenite matrix, were produced in the 35Ni3Ti alloy when it was partly quenched in water from 1373 K. These particles were poorly resolved in the electron microscope and produced a ripple-type diffraction contrast (Fig. 1(a)). Coarser particles (~6 nm in diameter) were formed after aging of quenched alloy at 923 K for 0.5 h (Fig. 1(b)). Cold-deformed samples of the 35Ni3Ti steel were examined too (Fig. 1(c)). The NGR spectra and corresponding probability densities of the magnetic field distribution $P(H)$ in samples containing γ'-particles of different size are shown in Fig. 2(a, a′, c and c′). The Mössbauer spectra and $P(H)$ changed dramatically after neutron irradiation at 340 K (Fig. 2(b, b′, d and d′)). The functions $P(H)$ for the initial and irradiated samples were characterized by some density peaks. The growth of H is associated with an increase in the number of Ni atoms predominantly in the first coordination sphere of the iron atoms. Irradiation caused a rise of the integral intensity of the peaks with high H. This corresponded to an increase in the nickel concentration of the alloy matrix. An average magnetic field $\widehat{H}$ at the core of a ^{57}Fe atom was used to estimate the nickel concentration and

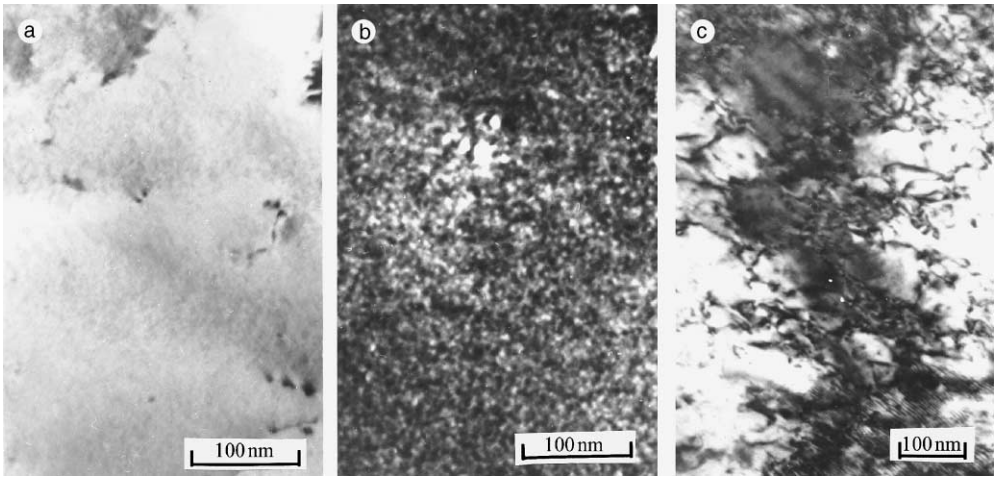

Fig. 1. Microstructure of the 35Ni3Ti steel: (a) quenching in water from 1323 K; (b) quenching + aging at 923 K for 0.5 h; (c) quenching + cold rolling with reduction to 94%.

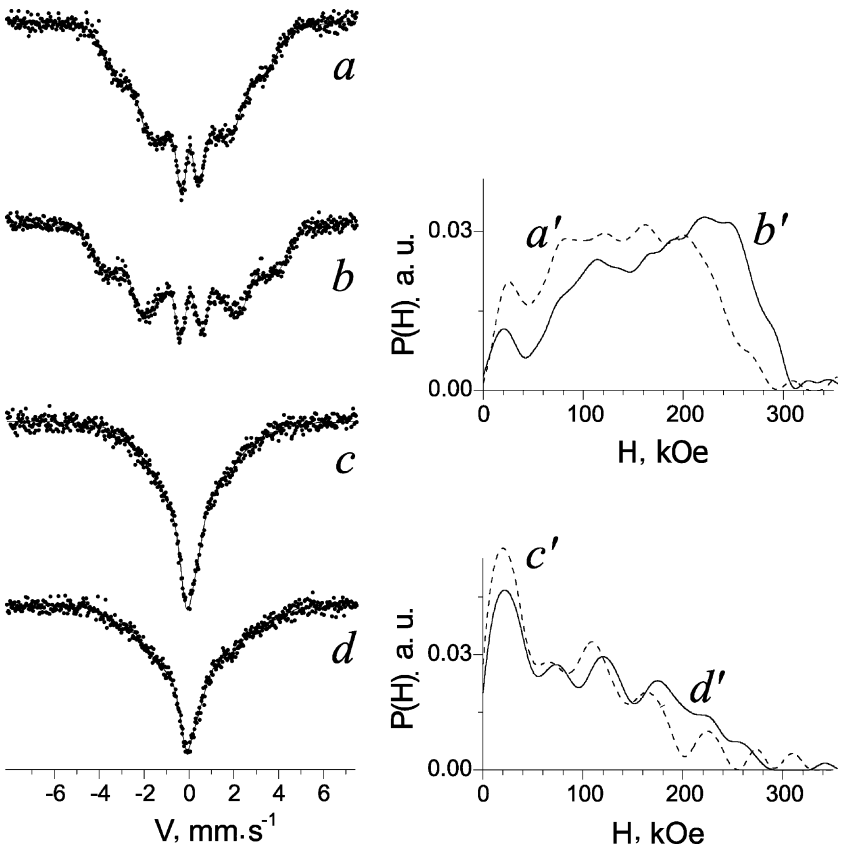

Fig. 2. Mössbauer spectra (a–d) and corresponding density distribution functions of the magnetic field $P(H)$ (a′–d′) of the 35Ni3Ti alloy after quenching from 1373 K (a, a′), aging at 923 K for 0.5 h (c, c′), and subsequent irradiation with fast neutrons at 340 K (to a fluence of 5×10^{19} n/cm^2) in quenched (b, b′) and aged (d, d′) samples.

the distribution of γ′-particles in the initial austenite after the following three treatments:

(1) Quenching in water from 1373 K. Considering experimental values of an average field $\widehat{H}$ (Fig. 2(a and a′)) and the $\widehat{H} = f(C_{\mathrm{Ni}})$ dependence [9], one might conclude that the nickel concentration in austenite dropped from 34.2 to 31.2 at.% during quenching (Fig. 3, curve 2). This corresponds [13] to precipitation of ~4 vol.% of Ni_3Ti particles with a size of 2 nm and a density of $\sim 4.5 \times 10^{18}$ cm^{-3} (the average center-to-center distance between the particles ~5 nm).
(2) Aging of the quenched 35Ni3Ti alloy at 923 K for 0.5 h. After this treatment, the nickel concentration of the austenitic γ-phase decreased to 30.5 at.% (Fig. 2(c and c′), curve 1 in Fig. 3) and ~5 vol.% of coarser (~6 nm) Ni_3Ti γ′-particles (Fig. 1(b)) precipitated. The latter particles had a density of $\sim 3 \times 10^{17}$ cm^{-3} (the center-to-center distance ~13 nm).
(3) Cold deformation at 298 K by rolling (reduction to ~94%) of the quenched 35Ni3Ti alloy. The γ′-precipitates dissolved partially during this treatment and the nickel concentration in the solid solution increased to ~32.9 at.% (Fig. 3, curve 3).

The spectrum of the neutron-irradiated sample (fluence of 5×10^{19} n/cm^2, 340 K) with initial particles 2 nm in size is a magnetic sextet having a considerably larger average field at a core ($\widehat{H} = 171$ kOe). This corresponds to an average nickel concentration in the austenite equal to 32.4 at.% (Fig. 2(b and b′), curve 2 in Fig. 3). The only explanation for this result is radiation-induced dissolution of the high-nickel γ′-phase. It is worth noting that no perceivable changes in NGR spectra of a non-aged Fe + 35 at.% Ni binary alloy after neutron irradiation were observed under similar conditions. The Mössbauer spectra and $P(H)$ of the aged 35Ni3Ti alloy with coarse (6 nm) γ′-particles before and after irradiation are shown in Fig. 2(c and d). An average field at a core, $\widehat{H}$, grows from 90 to 104 kOe after neutron irradiation (curve 1 in Fig. 3). This corresponds to an increase in an average nickel concentration [9] by 0.2% (from 30.5 to 30.7 at.%).

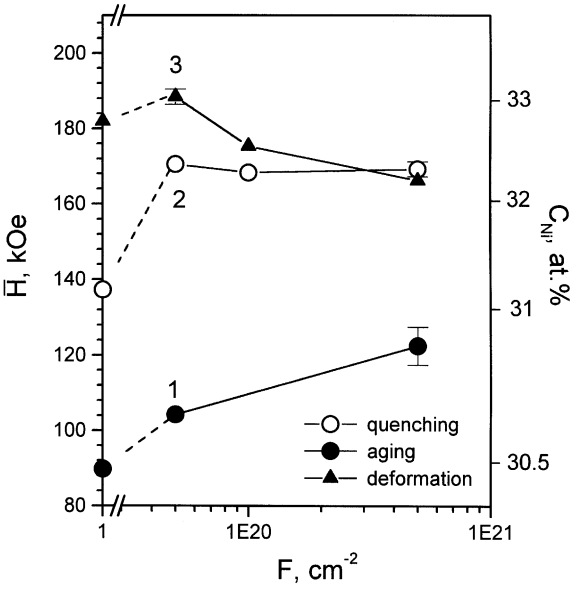

Fig. 3. Average magnetic field $\hat{H}$ and nickel concentration C_{Ni} of the austenitic matrix of the 35Ni3Ti alloy vs. fast neutron fluence. Initial treatment: (1) aging at 923 K for 0.5 h; (2) quenching in water from 1373 K; cold rolling (94%) of the quenched alloy.

An increase in the neutron fluence had a different effect on the stability of the precipitates. When the fluence was raised to 10^{20} and 5×10^{20} n/cm^2 and displacement cascades ~4–6 nm in size occupied the whole volume of the sample, dissolution of fine particles ~2 nm in size was interrupted (curve 2 in Fig. 3), while coarse (6 nm) particles continued dissolving (curve 1 in Fig. 3). It is clear that starting from 340 K, non-equilibrium dissolution of γ'-particles in displacement cascades was accompanied by a competitive equilibrium process of aging, caused by migration of vacancies and interstitial atoms. Probably, at this temperature the alloy accumulated a certain quasi-equilibrium concentration of nickel and the system tended to this concentration during irradiation, as predicted in [3]. This concentration is equal to ~32.2 at.% Ni (see curve 2) and did not change with the fluence. In samples with coarse (6 nm) and widely spaced (~13 nm) γ'-precipitates a significant fraction of displacement cascades was formed between the particles. As a result, the Ni_3Ti precipitates did not dissolve extensively (curve 1). Therefore the dissolution intensity of the particles was small, but dissolution rather than precipitation dominated (curve 1) perhaps because the 'quasi-equilibrium' nickel concentration (32.2 at.%) mentioned above has not been achieved yet.

An absolutely different situation was observed in the cold-deformed 35Ni3Ti alloy, where the nickel concentration in the matrix was nearly 33 at.% and a high density of dislocations was present. When the deformed 35Ni3Ti alloy was exposed to a fluence of 5×10^{19} n/cm^2, the concentration of nickel in solid solution increased a little (curve 3 in Fig. 3). However, at a higher neutron fluence, precipitation of particles started dominating over their dissolution and the nickel concentration in the matrix decreased to the 'equilibrium' level of 32.2 at.% (see Fig. 3, curve 3). A similar aging of the 35Ni3Ti alloy under 'cascade-free' electron irradiation was observed earlier [9].

When the irradiation temperature of the aged alloy was increased from 340 to 530 K (at a fluence of 5×10^{20} n/cm^2), the direction of the phase transformation was reversed: dissolution of particles in displacement cascades was replaced by radiation-induced aging (Fig. 4). It is seen from Fig. 4(a and b) that the shape of the Mössbauer spectrum approaches the singlet of the paramagnetic low-nickel austenite. An average magnetic field diminishes from 90–42 kOe (Fig. 4(a′ and b′)). This corresponds to a decrease in nickel concentration from 30.5 to 29 at.%.

3.2. X-ray diffraction of the irradiated 35Ni3Ti alloy

The X-ray was used to examine the lattice constant of the austenite. It strongly depends on titanium concentration in the fcc Fe–Ni–Ti matrix. Table 1 gives values of the lattice constant a of the austenite in the 35Ni3Ti alloy for different thermal and irradiation conditions. As seen from Table 1 the initial lattice constant of the austenite quenched in water from 1373 K was equal to 0.3596 mm. Aging at 923 K (0.5 h) led to additional precipitation of the Ni_3Ti γ'-phase and the lattice constant decreased to 0.3590 mm. Cold-rolling deformation of a quenched sample caused partial dissolution of the dispersed γ'-precipitates and a increased to 0.3600 mm.

The behavior of the Ni_3Ti γ'-phase during neutron irradiation at 340 K as determined by X-ray method (Table 1) did not differ qualitatively from that as seen from the Mössbauer data. For example, irradiation of the alloy aged at 923 K caused a progressive increase of the lattice constant from 0.3590 mm in the initial state to 0.3595 mm after exposure to a neutron fluence of 5×10^{20} n/cm^2. This fact points to dissolution of the γ'-phase in displacement cascades. Radiation-induced dissolution of dispersed γ'-phase ($d_{particle} \simeq 2$ nm) in the quenched alloy was observed at a fluence of 5×10^{19} n/cm^2 either. The lattice constant remained unchanged ($\simeq$0.3598 mm) as the fluence was increased further. This observation shows that dissolution and aging proceeded concurrently. The lattice constant of the austenite first decreased considerably and then increased a little in the cold-deformed alloy. This indicates that titanium leaves the solid solution in the form of the Ni_3Ti phase.

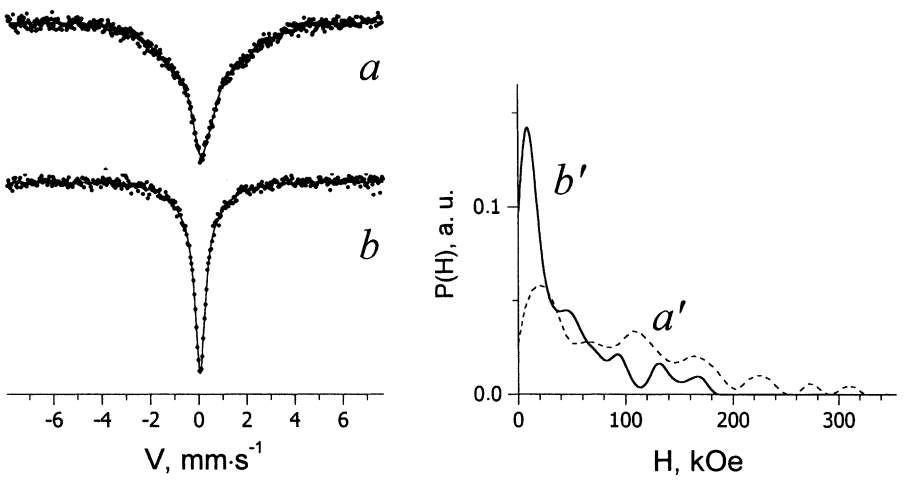

Fig. 4. Mössbauer spectra (a, b) and corresponding density distribution function of the magnetic field $P(H)$ (a′, b′) of the 35Ni3Ti alloy after aging at 923 K for 0.5 h (a, a′) and subsequent irradiation with fast neutrons at 530 K for 300 h in an IVV-2M reactor (b, b′).

Table 1
Lattice constant a (mm) of the austenitic matrix of 35Ni3Ti alloy under different conditions

Treatment	F (n/cm^2)			
	0	5×10^{19}	10^{20}	5×10^{20}
Quenching in water from 1373 K	0.3596	0.3598	0.3600	0.3598
Quenching + aging at 923 K (0.5 h)	0.3590	0.3594	–	0.3595
Quenching + cold deformation, rolling (94%)	0.3600	0.3592	0.3593	0.3597

The same conclusion was drawn from the Mössbauer data.

4. Conclusion

The Mössbauer and X-ray analyses showed that dispersed Ni_3Ti γ'-particles present in an aged austenitic 35Ni3Ti alloy exposed to neutron irradiation at 340 K may either dissolve in displacement cascades or precipitate depending on the fluence and the density and size of these particles. Intermetallic aging is facilitated when the irradiation temperature is raised to 530 K. The fcc matrix has a quasi-equilibrium nickel concentration of about 32.2 at.% at 340 K and the irradiated Fe–Ni–Ti system tends to this concentration.

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