Conditions for the Violation of Concentrational Homogeneity of Fe–Ni Invar Alloys

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Abstract—Conditions for the formation of microconcentration inhomogeneities in Fe–Ni alloys, which can decrease their invar characteristics, are determined. The nickel separation can be reached in the course of short-term annealing as a result of deformation-induced nickel segregation, nickel redistribution between martensite and austenite and between ferrite and austenite as well.

Keywords: austenitic alloy, invar, martensitic transformation, ferrite, deformation, nickel segregation, electron microscopy, magnetometry

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INTRODUCTION

The retained structural and concentrational stability of austenitic invar Fe–Ni alloys is the important condition for reaching the required low values of the thermal expansion coefficient (TEC) over a given temperature range (below the Curie temperature of austenite). Available data on the effect of thermal and thermodeformation action on intragrain concentration changes of austenite allow one to find optimum treatment conditions for the Fe–Ni invars. The separation of Fe–Ni austenite into low-nickel and high-nickel components in the Fe–32Ni alloys allows their TEC values to be substantially increased [1, 2]. In order to realize the nickel redistribution between the α and γ phases in the invars in accordance with the equilibrium Fe–Ni phase diagram, very prolonged holdings at 300–400°C are required [3, 4]. The nickel separation for a relatively short time within the two-phase (α + γ) region of the Fe–Ni phase diagram at 300–300°C can be realized only in the course of annealing of two-phase austenite–martensite mixture [1, 2]. The prolonged annealings of the Fe–Ni invars in the single-phase γ state with the fcc lattice do not lead to a marked separation of austenite into the low-nickel and high-nickel components [5]. Only the introduction of a great amount of point defects via irradiation of single-phase Fe–Ni invars with high-energy particles (electrons) [6, 7] allows one to observe diffusion redistribution processes of nickel at low temperatures. Thus, the efficient redistribution of nickel can be realized mainly in metastable Fe–32Ni invars that form the second α-martensite phase upon γ → α transformation. In highly alloyed Fe–Ni invars, no martensite forms, and it is difficult to expect nickel segregation. However, in recent studies [8–10], the diffusion decomposition with the formation of α ferrite phase was found in the Fe–36Ni alloys subjected to preliminary severe deformation. The expected nickel redistribution upon the formation of ferrite in the Fe–36Ni alloys (in accordance with the equilibrium Fe–Ni phase diagram) indicates the possibility of obtaining the concentration inhomogeneity even in relatively stable invars. In this study, main conditions for the realization of nickel concentration segregation in stable and metastable Fe–Ni invars are considered. This should be taken into account upon treatment of the similar alloys in order to prevent worsening the properties of invars.

EXPERIMENTAL

The austenitic Fe–32Ni, Fe–32.5Ni, and Fe–36Ni invar alloys containing 0.02 wt % C are studied. For comparison, the high-alloyed austenitic Fe–36Ni–3Cr and Fe–13Cr–30Ni alloys were also analyzed, which are the most stable with respect to the formation of martensite and ferrite. The alloys were melted in an induction furnace, homogenized at 1200°C for 2 h, forged to rods 10 × 10 mm in section, and subsequently water-quenched from 1050°C. Chromium was introduced into steel in order to increase the stability against the formation of strain-induced martensite. Samples were subjected to shear deformation under a high pressure of 8 GPa using Bridgman anvils and rolling. The true strain ε under the high-pressure shear (at a distance of r from the
The magnetization at temperatures above room temperature is in the saturated ferromagnetic state. Upon transition into the paramagnetic state, the relationship of magnetizations becomes equal to the relationship of the fields, namely $3:2$. The volume fraction of the ferromagnetic phases with the bcc lattice (martensite and ferrite) was estimated by magnetometry. The analysis of the atomic redistribution was performed using Mössbauer spectroscopy. As the source of resonance $\gamma$ radiation with an energy of 14.4 keV, $^{57}$Co(Cr) was used. The microstructure was studied on a JEM 200CX microscope using dark- and bright-field images and electron diffraction mode.

RESULTS AND DISCUSSION

Nickel Redistribution upon $\alpha \rightarrow \gamma$ Transformation

The nickel segregation between martensite and austenite upon the $\alpha \rightarrow \gamma$ transformation in the metastable Fe–Ni invar was studied in [1, 2, 12]. For example, upon cooling of the Fe–32Ni alloy with a martensite point of $-70^\circ$C in liquid nitrogen, to 80% of the $\alpha$ martensite forms. The development of the reverse $\alpha \rightarrow \gamma$ transformation with the formation of fine $\gamma$-phase plates in slow heating at a rate of 0.2–0.3 deg/min in a temperature range of 300–490$^\circ$C is accompanied by enrichment of the formed $\gamma$ phase in nickel and depletion of the initial $\alpha$ phase of nickel in accordance with the equilibrium Fe–Ni phase diagram [4]. At the end of the $\alpha \rightarrow \gamma$ transformation region, the globular austenite forms, which takes the concentrationally inhomogeneous $\alpha$- and $\gamma$-phase mixture and retains the nickel segregation within a $\gamma$ globule. Figure 1 shows the structure of concentrationally inhomogeneous globular austenite grain characterized by different etching in the Fe–32Ni alloy, which was obtained after the above treatment. A dark band diffraction contrast within the globule corresponds to thin-plate areas of nickel-enriched $\gamma$ phase that was taken up by growing globular austenite.

The concentration changes in the Fe–32Ni alloy were analyzed by Mössbauer spectroscopy. Figure 2 shows Mössbauer spectra of the Fe–32.5Ni alloy in the initial homogeneous (Fig. 2a) and concentrationally inhomogeneous austenitic (Fig. 2b) states after nickel segregation upon the $\alpha \rightarrow \gamma$ transformation in the course of slow heating to 450$^\circ$C. An analysis of atomic distribution in the Fe–32.5Ni alloy matrix was performed using a physical model of Fe–Ni invar suggested in [13–15]. The effect of nearest atoms on the hyperfine field at $^{57}$Fe nucleus was taken into account via their effect on the projection of magnetic moment $\mu_z$ in assuming the proportionality of values of the hyperfine field and molecular field. This model allows one to describe the Mössbauer spectrum based on the distribution of $p(H)$ hyperfine field at $^{57}$Fe nuclei in a crystal with the noncollinear magnetic structure [14, 15]. The analysis of atomic distribution in the alloy matrix was performed based on the $p(H)$ distribution function using concept on the correlation between the inhomogeneity of the magnetic structure of the Fe–Ni alloys and composition fluctuations [13, 15, 16]. To perform quantitative estimations of the Ni content in the fcc matrix of the Fe–32.5Ni alloy,
we used the \( p(H) \) distribution function and dependence of average field \( \langle H \rangle \) on the Ni content in the binary Fe–Ni alloys in the composition range 29.5–43.5 at \% Ni [17, 18]:

\[
C_{\text{Ni}} = 29.6 + 0.3\exp\left(\frac{\langle H \rangle}{80}\right).
\]

The spectrum of the quenched austenitic Fe–32.5Ni alloy and the \( p(H) \) distribution are typical of the relaxation structure of the Fe–Ni invars (Fig. 2a). The sextet corresponds to the \( p(H) \) distribution characterized by several peaks. It is assumed that the distribution peaks at high magnetic fields correspond to areas of the austenite structure with the higher nickel content. In a portion of the spectrum, component characterized by zero or near-zero field is present, which corresponds to areas of invar structure with the low nickel content (\( \leq 29 \) at \%). The performed heat treatment cardinally changes the spectrum (see Fig. 2b). Along with the peaks in \( p(H) \), which correspond to the initial quenched austenite (\( \sim 50\% \) integral intensity), an additional component \( p(M) \) (\( \sim 20\% \)) characterized by enhanced magnetic field (290–300 kOe) and component \( p(0) \) (\( \sim 30\% \)) with zero magnetic field appear. Based on the spectra and \( p(H) \) of model alloys [17], it is possible to state that the spectrum obtained after heat treatment indicates the presence of three structural areas with different nickel contents. In terms of superimposed integral spectrum, it consists of subspectrum close to the initial spectrum with \( C(\text{Ni}) \sim 32 \) at \% (the intensity is \( \sim 50\% \)) and additional subspectra corresponding to the increased nickel content with \( C(\text{Ni}) \sim 40 \) at \% (the intensity is \( \sim 20\% \)) and nickel content \( C(\text{Ni}) \leq 29 \) at \% (the intensity is \( \sim 30\% \)). In such a model of spectrum, the nickel material balance is retained, \( 0.5 \times 32 + 0.2 \times 40 + 0.3 \times 29 = 32.7 \) at \%, which corresponds to the total nickel content in the austenite matrix.

The use of the slow heating to different temperatures upon \( \alpha \rightarrow \gamma \) transformation (for example, to 430, 470, and 490°C) leads to the different nickel redistribution in accordance with the Fe–Ni phase diagram [3, 4]. The subsequent rapid heating of samples from these temperatures to 600°C stabilizes different concentrational inhomogeneity in the single phase austenitic state and allows us to cardinally change the TEC of the Fe–32Ni alloy from \( 2.5 \times 10^{-6} \) to \( 10.5 \times 10^{-6} \) deg–1 [1, 2].

In the high-alloyed invar alloys, in particular, the Fe–36Ni alloy, the \( \alpha \) martensite does not form after cooling to negative temperatures and no decomposition into ferrite and austenite occurs after quenching and heating to the two-phase (\( \alpha + \gamma \)) region of the Fe–Ni phase diagram. Figure 3a shows the specific magnetization curves for the Fe–36Ni alloy measured on heating to 590°C and cooling to 25°C. The curves measured on heating and cooling almost coincide; this fact indicates the retained austenitic structure and absence of any first-order phase transformations. The stability of the austenitic structure in the Fe–36Ni alloy is retained in the course of cooling to negative temperatures and deformation at 25°C. However, the severe shear deformation of sample under torsion with
three revolutions under a pressure of 8 GPa at a low temperature $-196^\circ$C increases the specific magnetization to 150 G cm$^3$ g$^{-1}$; this is related to the formation of $\sim$30% of fine ferromagnetic $\alpha$ martensite. Crystals of the martensite are clearly observed in the dark-field image taken in the $(200)_{\alpha}$ reflection (Fig. 4a). The heating of deformed alloy at a rate of 3 deg/min causes the development of the reverse $\alpha \rightarrow \gamma$ transformation in a temperature range of 350–500°C (see Fig. 3b, curve 1). In this case, instead of the martensite, first fine $\gamma$-phase crystals enriched in nickel and the depleted $\alpha$ phase and, after that, concentrationally inhomogeneous globular austenite appear [1, 2]. The concentrational inhomogeneity of such a structure is characterized by anomalous arrangement of the specific magnetization curve of the Fe–36Ni alloy measured on cooling from 500°C (Fig. 3b, curve 2). Curve 2 in Fig. 3b is arranged substantially above curve 3 (Fig. 3b) corresponding to the concentrationally homogeneous nondeformed alloy with the Curie temperature below 300°C. In the deformed and transformed austenite in the Fe–36Ni alloy, there are $\gamma$-phase areas enriched in nickel with the Curie temperature above 350–400°C. Thus, in the sufficiently-alloyed invar Fe–36Ni alloy, it is possible to obtain the nickel segregation upon $\alpha \rightarrow \gamma$ transformation when the initial martensite structure was obtained after severe deformation at cryogenic temperatures.

Redistribution of Nickel with the Participation of Ferritic Transformation

It is of great interest to obtain the nickel concentrational inhomogeneity in the Fe–Ni invars, for example, in the Fe–36Ni–3Cr alloy additionally alloyed with chromium, which are stable with respect to the martensitic transformation. The earlier found [8–10] diffusive formation of the $\alpha$ phase (ferrite) in a temperature range of 330–370°C in the highly deformed austenitic Fe–36Ni–3Cr alloy allows us to expect the nickel redistribution between the $\alpha$ and $\gamma$ phases. In accordance with the Fe–Ni phase diagram [4], the nickel content in the ferrite should be substantially lower than that in the austenite. The severe deforma-

![Fig. 3. Temperature dependences of the specific magnetization (in a field of 2 kOe) of the Fe–36Ni alloy measured upon (curves 1) heating and (curves 2 and 3) subsequent cooling at a rate of 3 deg/min (a) after quenching from 1050°C and annealing at 370°C for 168 h and (b) after quenching and torsion at $-196^\circ$C with 3 revolutions ($e = 6.5$) under a pressure of 8 GPa; curve 3 corresponds to the specific magnetization of the homogeneous quenched Fe–36Ni alloy.](image)

![Fig. 4. Dark-field images (taken in (002)$_{\alpha}$ reflection) of (a) martensite and (b) ferrite in the (a) Fe–36Ni and (b) Fe–36Ni–3Cr alloys subjected to (a) torsion (with 3 revolutions $e = 6.5$) under a pressure of 8 GPa at $-196^\circ$C and (b) torsion (with 4 revolutions $e = 6.8$) under a pressure of 8 GPa at 25°C; annealing at 370°C for 24 h.](image)
Condition for the Violation of Concentrational Homogeneity

The formation of the austenitic Fe–36Ni–3Cr and Fe–36Ni alloys by rolling or high-pressure torsion at room temperature does not lead to the formation of $\alpha$ martensite but substantially accelerates the diffusion processes that determine the ferritic decomposition. Figure 5 shows the increase in the specific magnetization in accordance with the holding time (to 168 h) at temperatures 320–370°C for the deformed Fe–36Ni and Fe–36Ni–3Cr alloys, which is related to the formation of the ferromagnetic ferrite with the bcc lattice. Figure 4b shows the dark-field image of ferritic crystals in the Fe–36Ni–3Cr alloy. The maximum volume fraction of ferrite in the similar alloys is 15% [10]. Figures 6a, 6b show the temperature dependences of the specific magnetization of the preliminarily deformed alloys subsequently annealed at temperatures corresponding to the ferritic decomposition region of the Fe–36Ni (Fig. 6a) and Fe–36Ni–3Cr (Fig. 6b) alloys, which were measured upon heating (curves 1) and cooling (curves 2) at a rate of 3 deg/min. The reverse ferrite to austenite transformation on heating in a temperature range of 300–550°C is observed for both the alloys and is fixed based on a bend in curves 1 (Figs. 6a, 6b). The specific magnetization curves (2) of transformed alloys in the austenitic state, which were measured on cooling, are arranged markedly above curves (3) related to the quenched nondeformed austenitic Fe–36Ni and Fe–36Ni–3Cr alloys in the homogeneous state (Figs. 6a, 6b). This indicates the existence of concentrational inhomogeneity of the transformed austenite in both the alloys, in which nickel-enriched areas are present; their Curie temperature is higher than that of homogeneous nondeformed materials. The concentrational inhomogeneity results from the fact that the austenite inherits the nickel concentration from the low-nickel ferrite and high-nickel $\gamma$ component upon $\alpha \rightarrow \gamma$ transformation.

The nickel segregation occurs in accordance with the equilibrium phase diagram not only in the ferrite upon its formation, but also in the course of reverse $\alpha \rightarrow \gamma$ transformation at the higher temperatures.

It should be noted that the formation of a small amount of ferrite and its reverse transformation into the concentrationally inhomogeneous austenite can occur directly upon heating of deformed alloys at a rate of 3 deg/min without preliminary prolonged treatment ensuring the ferrite formation. As the degree of preliminary deformation increases, the nickel segregation is intensified. The homogenization of concentrationally inhomogeneous austenite in the similar invar alloys occurs as a result of recrystallization annealing at 800°C [1].

**Nickel Redistribution in the Austenitic State**

The possibility of the realization of the nickel segregation in the stable austenitic invars in which neither $\alpha$ martensite nor ferrite forms is of substantial interest. In accordance with the equilibrium Fe–Ni phase diagram, this can be realized in the Fe–36Ni alloys in the
upon the ferrite formation and nickel redistribution high strained Fe–36Ni and Fe–36Ni–3Cr alloys transformation. The similar situation takes place in the nickel concentrational inhomogeneity is inherited by transformation in the course of slow heating. The invars with 32–36 wt % Ni is observed upon the induced martensite and austenite in the metastable redistribution between the cooling-induced (strain-decrease in their invar characteristics. The nickel decrease in the TEC of the Fe–Ni invars, i.e., the increase in the TEC of the alloy under a high pressure of 8 GPa.

Fig. 7. Temperature dependences of the specific magnetization of the austenitic Fe–13Cr–30Ni alloy (in the field $H = 3$ kOe) in the (1) initial quenched state, after cold ($T = 25^\circ$C) rolling by (2) 92.5%, $e = 2.6$ and (3) 98%, $e = 3.9$ and (4) torsion with 5 revolutions ($e = 7.3$) under a pressure of 8 GPa.

two-phase ($\alpha + \gamma$) region at temperatures of 200–500°C. However, it is likely that such a process takes place only at very prolonged holdings or in the case of abrupt increase in the amount of point defects under irradiation of alloys with high-energy particles [1, 6]. The analogous increase in the concentration of point defects can be ensured upon severe cold deformation that causes the formation of deformation-induced segregation of alloying elements, in particular, nickel [19]. As the alloy stable with respect to the martensitic and ferritic transformations, we used the high-alloyed austenitic Fe–13Cr–30Ni alloy. The cold shear deformation of the alloy under a high pressure of 8 GPa ($e = 7.3$) leads to the increase in the specific magnetization from 1 to 6 G cm$^3$ g$^{-1}$ at 25°C (Fig. 7), which is related to the formation of high-nickel areas with the higher Curie temperature. The observed effect is explained, as in the case of the formation of radiation-induced segregations [20–22], by the migration of point defects of deformation origin to sinks (boundaries, grains, subgrains, etc.) with their enrichment in or depletion of elements with different atomic radii.

CONCLUSIONS

Conditions for the realization of the nickel segregation process and formation of microconcentrational inhomogeneities were determined, which can result in the increase in the TEC of the Fe–Ni invars, i.e., decrease in their invar characteristics. The nickel redistribution between the cooling-induced (strain-induced) martensite and austenite in the metastable invars with 32–36 wt % Ni is observed upon the $\alpha \rightarrow \gamma$ transformation in the course of slow heating. The nickel concentrational inhomogeneity is inherited by formed globular austenite at the final stage of the $\alpha \rightarrow \gamma$ transformation. The similar situation takes place in the highly strained Fe–36Ni and Fe–36Ni–3Cr alloys upon the ferrite formation and nickel redistribution between the ferrite and austenite. In the more stable austenitic alloys, which do not form secondary phases, the nickel segregation takes place as a result of the formation of strain-induced atomic segregations at sinks of point defects. The nickel segregation can not only worsen the properties of invars, but also ensures the preparation of alloys with given increased values of TEC.

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