Abstract

The crystal structure and magnetic properties of Fe_{51.1}Ni_{23.5}Al_{23.7}Si_{1} alloy underwent three different heat treatments were investigated by scanning (SEM) and transmission (TEM) electron microscopy, X-ray diffraction, Mössbauer spectroscopy and magnetostatic methods. The heat treatments were (1) quenching from 1200 °C; (2) cooling with the critical rate V = 2 deg/s; (3) additional aging of the cooled sample at 780 °C for 10 min. TEM investigation revealed the intermixed heterogeneous nanostructure with similar morphology but finer features for quenched sample. The Mössbauer study showed the coexistence of ferromagnetic (α_{1}) and paramagnetic (α_{2}) phases in all samples under study. The first heat treatment resulted in low coercive force Н_{с} < 4 Oe and led to coexistence of α_{2} phase (B2 structure type) and strongly disordered α_{1}-phase (L2_{1} structure type). After cooling with the critical rate the coercive force grew up to Н_{с} = 650 Oe along with the increase of L2_{1} superstructure reflections intensity. Additional aging reduced Н_{с} of high-coercivity sample to 320 Oe without visible changing of phase composition.

1. INTRODUCTION

The Fe_{2}NiAl based alloys are known as hard magnetic alloys with coercive force Н_{с} ≈ 700 Oe. These materials belong to a group of alloys with insolubility region on phase diagram (Fig. 1). It is known that on cooling below the solubility curve α-solid solution decomposes into a mixture of two isomorphic cubic phases α → α_{1} + α_{2} [1].

Maximum of Н_{с} attainable at intermediate stage of solid solution decomposition is related with non-equilibrium microstructure forming during two modes of heat treatment (HT): i) cooling of α-solid solution with critical rate and ii) aging of previously quenched α-solid solution below the solubility limit. But the value of Н_{с}
reached by HT-i is 1.5 times as large as \( H_c \) value reached by HT-ii [3, 4]. It was supposed that on slow cooling the solid solution decomposition is a two-stage process [5]. At the first step the reaction \( \alpha \rightarrow \alpha_1 + \alpha_2 \) proceeds and then at lower temperature the \( \alpha \) and \( \alpha_2 \) products decay once again with change of their composition.

It was supposed also that high coercivity of heat treated alloy is explained by separation of single domain ferromagnetic \( \alpha_1 \)-precipitates from each other by layers of nonmagnetic matrix \( \alpha_2 \)-phase [6-9]. In spite of numerous investigations the available data on the correlation between structure and coercivity are very contradictory [6-11].

This work summarizes our studies of micro- and crystal structure of Fe\(_2\)NiAl-based alloy on different heat treatments and contributes to understanding of the correlation between structure and coercivity.

2. EXPERIMENTAL PROCEDURES

The samples Fe\(_{51.1}\)Ni\(_{23.5}\)Al\(_{23.7}\)Si\(_{1.7}\) were prepared by induction melting in Ar atmosphere. Three modes of heat treatment were used (Fig. 2). All samples were aged at 1200°C for 20 min and then:

- **N1** - sample was quenched in water (\( H_c < 4 \) Oe);
- **N2** - sample was cooled with critical rate \( V_{cr} = 2^\circ/s \) (\( H_c = 650 \) Oe)
- **N3** - sample after the same heat treatment as **N2** was subsequently annealed at 780°C for 10 min and then quenched in water (\( H_c = 320 \) Oe).

Phase identification was carried out by X-ray diffraction using CoK\(_\alpha\) radiation. Simplified Rietveld method was used for quantitative phase analysis [12]. The room temperature Mössbauer studies were carried out at powder samples. Microstructural observations were performed by scanning electron microscopy (SEM) and atomic force microscopy (AFM) after electroetching of the specimens. TEM investigations were performed on thin foils prepared by ion beam milling. Magnetic measurements were carried out on cylindrical magnets of 10 mm diameter, using hysteresisgraph.

![Fig. 2 Schemes of heat treatment regimes](image)
2. RESULTS

Snoek [4] has examined the behaviour of coercitivity $H_c$ of the sample firstly cooled with critical rate $V_{cr}$ from $1200\, ^\circ C$ to temperature $T_q$ and then quenched in water (Fig. 3, curve 1). When the high coercivity samples N2 were aged at different temperatures $T_{ag}$ followed by quenching in water, the dependence of $H_c$ on $T_{ag}$ was received in [13] (Fig. 3, curve 2) which was the same as curve 1 (the point $T_{ag}=780\, ^\circ C$ in curve 2 corresponds to N3-sample). Hence, the microstructural changes during slow cooling from $T_q$ to room temperature annihilate by short aging at $T_{ag} = T_q$. On the base of these data one can conclude that the reversible changes of $H_c$ may be determined by the reversible changes of microstructure or the ordering-disordering process in decayed phases.

It is significant that slow cooling from $T_{ag} \leq 970\, ^\circ C$ to RT partly restores $H_c$ (Fig. 3, curve 3). However, only after aging at $T_{ag} \geq 970\, ^\circ C$ the homogeneous $\alpha$-solid solution is formed and the following cooling with critical rate to RT increase coercive force of the samples up to the highest level.

![Fig. 3](image)

Fig. 3 Dependence of $H_c$ on temperature $T$ and regimes of the heat treatment:

1 - cooling with critical rate $2^\circ/s$ from $1200^\circ C$ down to $T_q$ and then quenching;

2 – aging the sample N2 at $T_{ag}$ for 10 min followed by quenching in water;

3 – aging the sample N2 at $T_{ag}$ for 10 min followed by slow cooling to RT

Quenching from $1200^\circ C$ in water (N1) fixes non-homogeneous solid solution with low coercive force ($H_c < 4$ Oe). X-ray structure analysis showed the superposition of two phases (Fig. 4): i) $\alpha_2$-phase which is partly ordered in CsCl-manner structure (B2 phase) and ii) $\alpha_1$-phase with bcc-structure (A2 phase), which can be partly ordered in Cu$_2$MnAl-like structure (L2$_1$). Both phases have practically equal lattice parameter $a = 0.2877$ nm.
The cooling with critical rate (N2) transforms the alloy to the high-coercivity state \((H_c = 650 \text{ Oe})\). The diffraction pattern shows peaks broadening (for example, integrated width of (220)-line changed from 2.83° to 3.48°) and increase of intensity of additional superstructural reflections belonging to L2₁ phase. The mean lattice parameter of alloy is \(a \approx 0.2879 \text{ nm}\) (or twice of it as regards L2₁ phase). Aging of high-coercivity sample (N2) at 780 °C for 10 min (N3) reduces coercive force to \(H_c = 320 \text{ Oe}\) and leads to additional broadening of peaks (integrated width of (220)-line increased from 3.48° to 4.28°) together with decrease of the intensity of superstructural reflections of L2₁ phase. The mean lattice parameter of alloy is \(a \approx 0.2878 \text{ nm}\). It seems that aging leads to full disordering of L2₁-phase and its transformation into A2 phase.

The RT Mössbauer effect measurements shows the coexistence of ferromagnetic and paramagnetic phases in all samples N1-N3 (Fig. 5). According to X-ray data these phases correspond to A2/L2₁ and B2 type phases, respectively. The hyperfine field distribution of the ferromagnetic compounds indicates to atomic disorder of the crystal structure. After HT N2 the Fe₂NiAl alloy consists of B2 and L2₁ phases with volume fractions \(v\) and \((1-v)\) and compositions \(\text{Fe}_x\text{Ni}_{0.5-x}\text{Al}_{0.5}\) and \(\text{Fe}_y\text{Ni}_z\text{Al}_{1-w}\), respectively, where \(w = 1 - y - z\). The Mössbauer data give not only the fraction of ferromagnetic phase \((1 - v)\) and Al-content \(w = (0.25-v/2)/(1-v)\) in it but also the concentrations \(x\), \(y\), \(z\) due to the shift of hyperfine field caused by substitution of Fe atoms for Al and Ni in the 1-st coordination sphere.
Table 1 The fraction of Fe atoms in ferro- and paramagnetic phases

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The calculations produce values $v \approx 0.43 \div 0.45$ and $w \approx 0.05$. For $v = 0.45$ the composition of B2 and L2₁ phases must be near Fe_{20}Ni_{30}Al_{50} and Fe_{74}Ni_{21}Al_{5}, respectively. But the experimentally observed value of ratio $I(111)/I(220)$ ($I_{HKL}$ is integral intensity of HKL reflection of L2₁ phase) for N2 sample may be received only for partly ordered L2₁ phase which composition is near Fe_{65}Ni_{25}Al_{10}.

TEM image of the quenched sample N1 (Fig. 6a) reveals two-phase nanostructure constituting the fine mixture of black and white precipitates of size $5 \div 10$ nm, forming at the initial stage of solid solution decomposition. After cooling with critical rate (Fig. 6b) the features of nanostructure becomes noticeably coarser. The sample contains lamellar precipitates with an average size of $80 \div 150$ nm and pronounced preferred orientation inside a single grain.

![Fig. 6 TEM images of quenched N1 (a) and slow cooled N2 (b) samples](image)
Figure 7 shows TEM (a) and SEM (b) images of the high coercivity sample aged at 780°C for 10 min (N3), which indicate a visible increase of precipitates size up to 200÷250 nm. Further using the atomic force microscopy it was found in aged sample N3 that there exists an influence of aging on the internal structure of precipitates and hence on the magnetic properties. Fig. 7c indicates the fragmentation of elongated α₁-phase precipitates to fine spherical particles.

3. DISCUSSION

The hypothetic projections of cross sections of (α₁+α₂) cupola at different temperatures are drawn at the triangle Fe-Ni-Al (Fig. 8). According to [1], at room temperature the conoda, determined the compositions of α₁ and α₂-phases, agrees with the line Fe–NiAl. We supposed that a slightly below the temperature of decomposition of solid solution (< 940°C) the direction of conoda parallel to the Fe-Ni line. In this case, the formation of Guinier-Preston zones enriched by Fe and Ni atoms takes place during slow cooling below the solubility curve.

The hypothetic dependences of α₁- and α₂-phase compositions during slow cooling below 940°C are shown in Fig. 8 by dotted lines. Because of asymmetric form of the solubility curve, in a range of 900–750°C α₂ phase is enriched by Ni and Al atoms and the fraction of α₁ phase quickly increases. On the contrary, below 750°C the α₁ phase is impoverished by Ni and Al atoms and the quantity of α₂ phase grows up. Owing to slow rate of diffusion below 750°C this process may be realized via the “secondary decomposition” of α₁ phase by formation of thin layers of α₂-phase at the surface of α₁ precipitates. The formation of nonmagnetic α₂ shells at the surface of α₁ precipitates leads to increase of coercivity.
Fig. 8 Polythermal section of solubility cupola of Fe-Ni-Al diagram along the line Fe–NiAl [6]. X is the composition of investigated alloy

Firm lines with arrows show the changes of $\alpha_1$ and $\alpha_2$ phase compositions in N2 sample during aging at 780°C. Three observations could explain the reduction of Hc after short aging at 780°C: (i) a dissolution of $\alpha_2$ shells at the surface of $\alpha_1$ precipitates leads to deterioration of magnetic isolation of $\alpha_1$ precipitates, (ii) a disordering transformation of L2₁ phase and (iii) the fragmentation of elongated $\alpha_1$-phase precipitates into fine spherical particles which may be easily remagnetized.

ACKNOWLEDGMENTS

This work was supported by Russian Federal Agency of Education under 2.1.2/7264 grant.

LITERATURE REFERENCES