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FORMATION OF STRUCTURE IN AN ALNI ALLOY UPON COOLING FROM THE RANGE OF SINGLE-PHASE SOLID SOLUTION AND ANNEALING

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The methods of transmission electron microscopy, x-ray diffraction and magnetic measurements are used to study the laws of formation of microstructure and magnetic properties of an AlNi alloy during cooling from the range of single-phase solid solution (1240°C) in water at a critical rate ($v \sim 2$ K/min) and after 10-min additional annealing of the cooled specimens at 780°C.

Key words: AlNi alloy, heat treatment, periodic modulated structure, coercivity.

INTRODUCTION

Hard magnetic alloys of the Fe – Ni – Al system (alni) discovered in 1932 [1] have been used widely for making permanent magnets until the appearance of magnets based on compounds of rare-earth metals (REM) with metals of the iron group in the 1970 – 1990s. Today the monopolistic position of China in the market of REM and the marked growth of prices for Nd and Dy have stimulated an intense search for sparingly alloyed and/or not bearing REM hard magnetic materials alternative to Nd-Fe-B magnets. Alloys of the Fe – Ni – Al system are also included into the wide range of the research. These studies are aimed at solution of the problem of raising the magnetic properties of alloys of the Fe – Ni – Al system with the help of the latest advancements in the field of magnetic materials. In addition, alni alloys remain a convenient object for studying the structural transformation behavior and formation of a modulated structure in other iron-base materials.

The highly coercive state of alni alloys is connected with decomposition of supersaturated solid solution into two isomorphic cubic phases represented by an iron-base bcc solid solution (a β-phase) and a NiAl-base solid solution ordered by type B2 (a β_2-phase). The optimum structural state is characterized by the presence of Fe-enriched precipitates of a β-phase anisotropic in shape and surrounded with a nonmagnetic β_2-phase enriched with Ni and Al. When the size of the particles of the strongly magnetic β-phase does not exceed the critical single-domain size, the coercivity H_c grows together with the anisotropy of the shape of β-particles and with the difference in the values of saturation magnetization of the β- and β_2- phases [2]. The degree of decomposition of solid solution in alloys of the Fe – Ni – Al system required for the morphology and composition of the forming β- and β_2-phases to be optimum from the standpoint of the hysteresis properties is provided either in the process of isothermal annealing of the single-phase solid solution quenched from 1200 – 1250°C (HT I) or by cooling of the solid solution from these temperatures at the critical rate (HT II) [3, 4]. After cooling at the critical rate the coercivity is 1.5 times higher than the value of H_c provided by HT I. The results of an x-ray diffraction analysis and of electron microscope studies of the decomposition of the solid solution in the process of annealing of quenched alloys reflect a spinodal mechanism of the decomposition and formation of a periodic modulated structure in the stage corresponding to a high coercivity H_c [5 – 9]

It has been noted in [7 – 11] that the cooling rate of alni alloys from 1200 – 1250°C in water is not sufficient for fixation of a single-phase solid solution. The inhomogeneous structure of quenched alloys is characterized by the presence of randomly arranged equiaxed zones 5 – 10 nm in size. These inhomogeneities can affect substantially the decomposition behavior of the solid solution under subsequent heating and annealing of the alloys. However, this problem has not been studied in detail.

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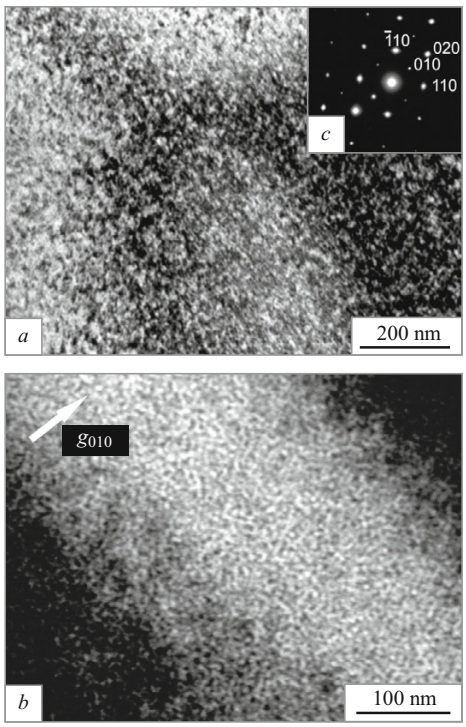

Fig. 1. Microstructure of the cast alni alloy cooled from 1240°C in water (H_c = 4 Oe): *a*) light-background image; *b*) dark-background image in superstructural reflection (010) of phase B2; *c*) electron diffraction pattern of the same region with the axis of zone [001].

The aim of the present work was to study and compare the microstructures formed in a cast alni alloy after a treatment by the following two variants: HT I involving quenching from the single-phase range in water and additional annealing at 780°C followed by water quenching and HT II involving cooling from the single-phase range at a critical rate to 780°C (with subsequent water quenching), cooling at the critical rate to room temperature, and additional annealing at 780°C followed by water quenching.

METHODS OF STUDY

We studied specimens of an alni alloy with composition $Fe_{51.1}Ni_{23.5}Al_{23.7}Si_{1.7}$ [58Fe – 28Ni – 13Al – 1Si (in wt.%)]. The alloy was melted in an induction furnace in an argon atmosphere. The melt was cast into a finger copper mold. Specimens of the cast magnets 12 mm in diameter and 25 mm long were subjected to a heat treatment by the following regimes: (*1*) water quenching of a cast specimen from 1240°C (after a 20-min hold), (*2*) the same + annealing at 780°C for 10 min followed by water quenching, (*3*) cooling of a cast specimen from 1240°C (after a 20-min hold) at a critical rate (v ~ 2 K/min) to 780°C followed by water quenching and (*4*) cooling of a cast specimen from 1240°C (after a 20-min hold) at a critical rate (v ~ 2 K/min) to 20°C + annealing at 780°C for 10 min followed by water quenching.

We studied the structure of the heat treated specimens by the methods of x-ray diffraction and transmission electron microscopy (TEM). The x-ray diffraction analysis (RDA) was performed with the use of a DRON-4-07 diffractometer, cobalt K_α radiation and a graphite monochromator. The diffractograms were obtained for powders of cast specimens milled to a particle size $d \le 100$ μm. The specimens for the TEM were prepared by electrolytic polishing using a Struers TenuPol 5 device in an $HClO_4$-ethanol-butoxyethanol electrolyte at a temperature of –20°C and a voltage of 23 V. The foils obtained were studied under a JEM-1400 transmission electron microscope at an accelerating voltage of 120 kV. The magnetic properties of the cast specimens were measured by a standard method using an AMT-4 hysteresigraph in a magnetizing field of up to 25 kOe.

RESULTS AND DISCUSSION

Figure 1 presents light-background (*a*) and dark-background (*b*) images of the structure of the cast alloy quenched in water from 1240°C and the corresponding electron diffraction patterns (*c*) of the same region with orientation [001]. The microstructure of the quenched specimen obviously does not match the state of a homogeneous solid solution. The light-background micrograph exhibits concentration inhomogeneities (zones) with a size of about 10 nm, which allows us to assume that the process of water cooling from 1240°C was accompanied by partial decomposition of the solid solution into β- and β_2-phases at a temperature below the boundary of insolubility. The coercivity H_c of the water-quenched specimen is only 4 Oe. The hypothesis of partial decomposition of the solid solution allows us to treat the electron diffraction pattern in Fig. 1*c* as a superposition of two structures, i.e., a disordered A2 phase (a β-phase, an iron-base solid solution) and a B2-ordered phase (a β_2-phase based on NiAl), which corresponds to superstructural reflections (010).

The dark-background photograph (Fig. 1*b*) of the microstructure of the quenched alloy gives a more detailed picture of the morphology of the products of decomposition of the solid solution in the image-forming superstructural reflection (010) of phase B2 (Fig. 1*c*). The B2-ordered precipitates of the β_2-phase in Fig. 1*b* look light and the precipitates corresponding to the β-phase look dark. It can be seen that the alternating precipitates of the β- and β_2-phases form a labyrinth structure.

Figure 2 presents the microstructure of a cast alni alloy cooled from 1240°C (after a 20-min hold) at a critical rate of about 2 K/min to 780°C and then quenched in water against a light background (*a*) and against a dark background (*b*) and an electron diffraction pattern corresponding to the same region with axis of zone [001].

During the cooling to 780°C at the critical rate the alni alloy acquires a periodic modulated structure represented by

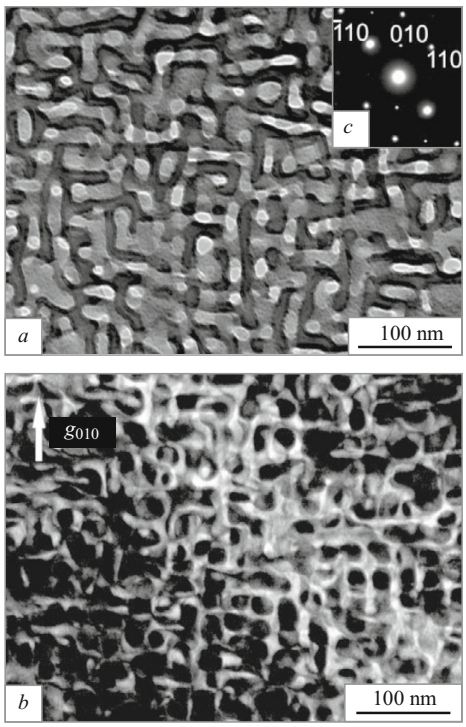

Fig. 2. Microstructure of the cast alni alloy after cooling at the critical rate from 1240°C to 780°C + water quenching (H_c = 580 Oe): *a*) light-background image; *b*) dark-background image in superstructural reflection (010) of phase B2; *c*) electron diffraction pattern of the same region with the axis of zone [001].

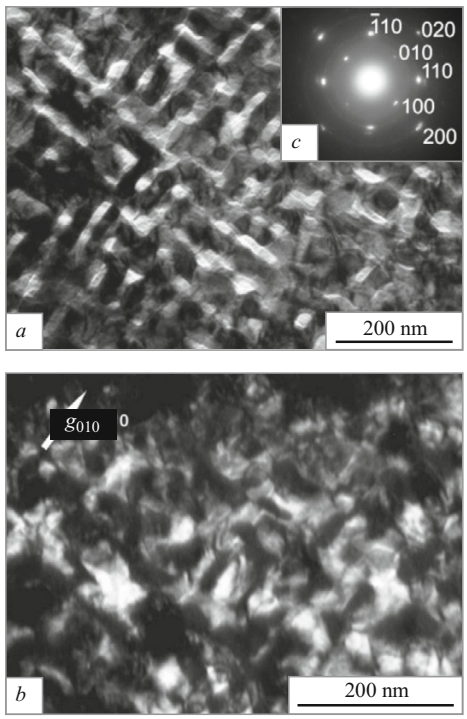

Fig. 3. Microstructure of the cast alni alloy after water quenching from 1240°C and additional annealing at 780°C for 10 min and subsequent water quenching (H_c = 350 Oe): *a*) light-background image; *b*) dark-background image in superstructural reflection (010) of phase B2; *c*) electron diffraction pattern of the same region with the axis of zone [001].

stretched particles of β-phase oriented chiefly over directions of type ⟨100⟩ and separated by dark regions of the matrix β_2-phase. The coercivity of the alloy after this treatment H_c = 580 Oe. It can be seen from the dark-background image of the microstructure obtained in superstructural reflection (010) of the B2 phase that the light precipitates of the β_2-phase form a virtually continuous net separating the dark particles of the β-phase. The size of the particles of the β-phase fluctuates from 20 to 80 nm, and their oblongness l/d varies from 1 to 4. It seems that the combination of such structural factors as the small size, the anisotropic shape and the magnetic insulation of the particles of the β-phase provides the high coercivity (H_c = 580 Oe) of the specimens after cooling at the critical rate in the temperature range between the boundary of insolubility and 780°C.

According to the data of the x-ray diffraction analysis, the experimental spectrum of the specimen cooled from 1240°C at the critical rate to 780°C followed by water quenching virtually does not differ from that of the specimen water-quenched from 1240°C. In both cases the x-ray spectra are describable by superposition of the spectra of two structures A2 (β-phase) and B2 (β_2-phase) with very close values of the crystal lattice parameters. The lattice parameters of the quenched specimen are a = 0.28776 nm (A2) and a = 0.28782 nm (B2). For the specimen cooled at the critical rate the difference in the lattice parameters of the phases is more noticeable, i.e., a = 28729 nm (A2) and a = 0.28760 nm (B2), which means that the components have been redistributed between the β- and β_2-phases in the process of cooling at the critical rate.

Figure 3 presents micrographs of the structure of the alni alloy quenched from 1240°C in water and annealed additionally at 780°C for 10 min with subsequent water quenching, which were obtained against light (*a*) and dark (*b*) backgrounds, and an electron diffraction pattern of the same region (*c*) with axis of zone [001]. According to the diffraction data the lattice constants of the phases after the annealing of the quenched specimen at 780°C are a = 0.28746 nm for A2 and a = 0.28782 nm for B2. As a result of the annealing the coercivity of the quenched specimen increases from 4 to 350 Oe, but is still much lower than the coercivity of the specimen cooled at the critical rate to 780°C with subsequent water quenching (H_c = 580 Oe).

It can be seen from Fig. 3 that the annealing of the quenched specimen at 780°C causes formation of a modulated structure that differs considerably from the microstructure of the specimen cooled from 1240°C at the critical rate to 780°C with subsequent water quenching (Fig. 2). The mean size of the precipitates of the strongly magnetic β-phase attaining 100 – 150 nm is almost twice larger than

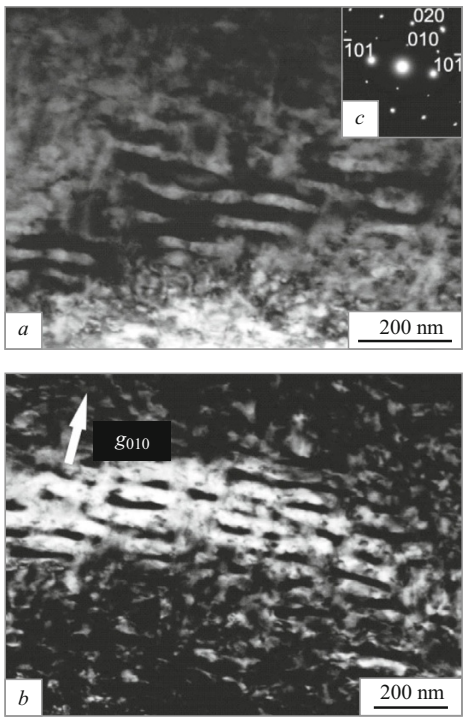

Fig. 4. Microstructure of the cast alni alloy after water quenching from 1240°C to 20°C and additional annealing at 780°C for 10 min and subsequent water quenching (H_c = 320 Oe): *a*) light-background image; *b*) dark-background image in superstructural reflection (010) of phase B2; *c*) electron diffraction pattern of the same region with the axis of zone [001].

the mean size of the precipitates in the specimen cooled at the critical rate (Fig. 2). In addition, it follows from the dark-background image of the microstructure (Fig. 3*b*) obtained in superstructural reflection (010) of phase B2 that the light precipitates of the β_2-phase do not already form a continuous net separating the dark particles of the β-phase. This worsens the magnetic insulation of the strongly magnetic particles and causes decrease in the coercivity.

The microstructure of the optimally treated specimen of the alni alloy cooled from 1240°C at the critical rate (about 2 K/min) to 20°C is identical to the microstructure presented in Fig. 2. The coercivity of the optimally treated specimen is 690 Oe. Figure 4 presents micrographs of the structure of the optimally treated specimen, which has been subjected to additional annealing at 780°C for 10 min and then quenched in water. The micrographs have been obtained against a light background (*a*) and against a dark background (*b*), as well as the electron diffraction pattern of the same region with the axis of zone [101] (*c*). The coercivity of the optimally treated specimen after annealing at 780°C decreases to 320 Oe.

After cooling at the critical rate to 20°C the crystal lattice parameters of the β- and β_2-phases are a = 0.28712 for A2 and a = 0.28791 for B2. After annealing at 780°C difference in these parameters deceases, namely a = 0.28720 for A2 and a = 0.28786 for B2, which means that the components have been redistributed between the β- and β_2-phases in the direction contrary to that of their redistribution in the process of cooling at the critical rate.

The nature of the microstructure in the light and dark backgrounds in Fig. 4 shows hat the short-term annealing at 780°C of the optimally treated specimen causes partial degradation of the modulated structure formed earlier due to cooling at the critical rate to 20°C, which is accompanied by a noticeable growth (by a factor of 2 – 3) in the size of the precipitates of the strongly magnetic β-phase and their partial decomposition into smaller fragments.

When the size of the precipitates increases above the single-domain critical size, the coercivity should decrease; therefore, we may assume that the decrease in H_c after annealing at 780°C in the water-quenched specimen (Fig. 3) and in the optimally treated specimen (Fig. 4) is connected primarily with coarsening of the components of the modulated structure and violation of the criterion of single-domain state for particles of the strongly magnetic β-phase. Another cause of decrease in H_c may be a change in the composition of the precipitates of the β-phase and of the β_2-matrix in accordance with the phase diagram. Heating of the alloy to the annealing temperature of 780°C narrows the two-phase $\beta + \beta_2$ range, and hence the β_2-phase should be enriched with iron, which may transfer it from a paramagnetic state to a ferromagnetic one. This should worsen the magnetic insulation of the precipitates of the strongly magnetic β-phase and, as a consequence, should lower the coercivity of the alloy.

CONCLUSIONS

1. The rate of decomposition of the solid solution of the alni alloy into phases β and β_2 below the boundary of insolubility is so high that water cooling from the single-phase region (1240°C) does not provide suppression of the decomposition and fixation of a homogeneous solid solution. The quenched specimens are characterized by a zonal structure with a mean size of the concentration inhomogeneities of about 10 nm, the presence of which affects the formation of structure under subsequent annealing.

2. The optimum periodic modulated structure formed due to cooling of the alni alloy at the critical rate from the single-phase range (1240°C) to a temperature of 780 – 20°C provides a high coercivity H_c = 580 – 690 Oe.

3. The periodic modulated structure formed in the specimen preliminary quenched in water from 1240°C due to annealing (780°C, 10 min) is characterized by a large size of the precipitates of strongly magnetic β-phase, which seems to exceed the single-domain critical size and thus promotes magnetization reversal and lowers the coercivity.

4. The optimum periodic modulated structure formed due to cooling of the alni alloy at the critical rate to 20°C undergoes changes under an additional annealing (780°C, 10 min), which are accompanied by a marked (by a factor of

2 – 3) growth in the size of the precipitates of the strongly magnetic β-phase and their partial decomposition into small fragments, and this lowers the coercivity.

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REFERENCES

1. J. Mishima, *Ohm*, **19** (July), 353 (1932).
2. E. C. Stoner and E. P. Wohlfarth, "A mechanism of magnetic hysteresis in heterogeneous alloys," *Phil. Trans. Roy. Soc.* (London), **240**, 599 – 642 (1948).
3. J. Snoek, *Probleme der Techn. Magnetisierungskurve*, Berlin (1938), 73 p.
4. B. G. Livshits, "Internal transformations in Fe – Ni – Al alloys," *Zh. Teor. Fiz.*, **23 – 24**, 1981 – 1985 (1940).
5. L. M. Magat, "About the initial stages of decomposition of supersaturated solid solution in alloys based on the Fe – Ni – Al system," *Fiz. Met. Metalloved.*, **15**, 478 – 480 (1965).
6. Yu. D. Tyapkin and I. G. Yaroshenkova-Lukanina, "About modulated periodic structure in magnetic alloys based on Fe – Ni – Al with cubic body-centered lattice," *Dokl. Akad. Nauk SSSR*, **160**, 325 – 328 (1965).
7. N. N. Buynov and R. M. Lerinman, "Submicroscopic structure of an alni alloy," *Dokl. Akad. Nauk SSSR*, **79**(1), 69 – 73 (1951).
8. Yu. A. Skakov, "Structure of iron-nickel-aluminum alloys for permanent magnets," *Dokl. Akad. Nauk SSSR*, **79**, 77 – 81 (1951).
9. K. J. De Vos, "Mikrostrukturen von Alnico-Legierungen," *Z. Angew. Phys.*, **21**(5), 381 – 385 (1966).
10. E. G. Povolotskii, "Superstructural defects in single crystals of alnico-type alloys," *Fiz. Met. Metalloved.*, **33**(1), 167 (1972).
11. V. P. Menushenkov, T. A. Sviridova, and V. V. Shelehov, "X-ray, TEM and Mossbauer studies of hard magnetic Fe_2NiAl alloy," in: *Proc. 19th Int. Metallurgical and Materials Conf., 2010, 18 – 20 May, Roznov pod Radhostem, Czech Republic, EU* (2010), p. 284.