Local structure of high-coercivity Fe-Ni-Al alloys

A P Menushenkov[1]**, V P Menushenkov**[2]**, R V Chernikov**[1,3]**, T A Sviridova**[2]**,
O V Grishina**[1]**, V V Sidorov**[1]

[1] National Research Nuclear University "MEPhI", 115409 Moscow, Russia
[2] National University of Science and Technology «MISIS», 119049 Moscow, Russia
[3] HASYLAB at DESY, D-22603 Hamburg, Germany

E-mail: menushen@htsc.mephi.ru

Abstract. Results of hard magnetic Fe-Ni-Al alloys after various thermal processing local structure researches by method of EXAFS-spectroscopy with use of synchrotron radiation at temperature 77 K are presented. It is established, that during cooling a firm solution with critical speed reorganization of a local environment of nickel relative to quickly tempered sample owing to stratification of a firm solution is observed. The subsequent aging at 780°C practically restores local structure, characteristic for quickly tempered sample, keeping thus rather high coercitive force.

1. Introduction

Hard magnetic Fe-Ni-Al alloys belong to a group of alloys with insolubility field at state diagram. On cooling below the solubility curve solid solution decomposes to a mixture of two isomorphic cubic phases $\beta \rightarrow \beta + \beta_2$ [1]. Maxima of coercive force H_c achieved at intermediate decomposition stage is related with nonequilibrium microstructure which is formed at aging of homogeneous solid solution (heat treatment I), or at solid solution cooling with critical rate (heat treatment II). H_c value reached by heat treatment II is 1.5 times as large as H_c value reached by heat treatment I.

X-ray studies of Fe-Ni-Al solid solutions decomposition (see [2] and references therein) do not reveal any changes in shapes and positions of diffraction lines of spectra for samples prepared by quenching or cooling with critical rate. This is probably connected with the proximity of the lattice parameters of precipitating phases or strong diffusion of the β-phase diffraction lines. Available data on the structure of high-coercivity alloys are very contradictory. According to electron microscopic studies hetero-phase structure is formed by $\beta \rightarrow \beta + \beta_2$ decomposition, this structure consists of fine-grained (10-100 nm) β-phase precipitations enriched by iron and matrix β_2-phase enriched by Ni and Al. In fact no direct measurements of phase composition have been made. β-phase equated particles were observed in high-coercivity sample. On the contrary it was observed in [3] that microstructure consists of intermittent plates of β- and β_2 phases. Anisotropic shape of single-domain particles seems to be the main reason for high coercitive force in Fe-Ni-Al alloys. Improvement of magnetic insulation of β-particles increases H_c due to the process of second decomposition below 750°C related with Ni and Al precipitation from β-phase [2].

Thus data on structural transformations in Fe-Ni-Al alloys are contradictory and need to be specified. This work summarizes our studies of crystal structure and local environment of iron and

nickel in Fe-Ni-Al alloy after different heat treatment by means of X-ray absorption spectroscopy (EXAFS).

2. Experimental

The samples with nominal composition of $Fe_{46.4}Ni_{24.5}Al_{26.7}Si_{2.4}$ were prepared by induction melting in Ar atmosphere followed by casting in a copper mould. Three schemes of heat treatment were used: sample N1 was aged at $1200^{o}C$ for 20 min and quenched in water ($H_c < 4$ Oe); sample N2 was aged at $1200^{o}C$ for 20 min and cooled in air atmosphere with critical speed V = 2°/s ($H_c = 650$ Oe) and sample N3, heat treated in similar manner as N2, was aged at $780^{o}C$ for 10 min and then quenched in water ($H_c = 320$ Oe).

Phase identification was carried out at powder samples by X-ray diffraction using Co-Kα radiation. EXAFS measurements above iron and nickel K-edge absorption were performed at E4 beamline of HASYLAB synchrotron centre (DESY, Hamburg, Germany) at temperatures of 77 K and 300 K. Spectra were measured for powder samples (d < 100 microns) in transmission mode. EXAFS spectra processing and modelling was performed in VIPER [4] software environment. The background in the experimental spectra was removed as described in [5], taking care to remove the low-frequency oscillations. The EXAFS functions $\chi(k)k^2$ obtained from the absorption spectra were Fourier transformed (FT) in the range of wave-number k from 2 to 12 Å^{-1}, using the Kaiser-Bessel windowing function. Fourier back-transformation (BFT) was carried out using a Hanning window over the range of 1.2 – 2.0 Å for K-Fe and 1.1 – 2.9 Å for K-Ni edges. BFT modelling was performed according to formula:

$$\chi(k) = -S_0^2 \sum_j \frac{\left| f_j(k,\pi) \right|}{kR_j^2} \exp(-2k^2\sigma_j^2) \sin(2kR_j + \varphi_j(k,\pi)) \qquad (1)$$

where R_j - mean radius of j-th sphere, σ_j^2 - Debye-Waller factor (mean-square deviation of interatomic distance), S_0^2 - many-body reduction factor, $f_j(k,\pi)$ and $\varphi_j(k,\pi)$ - back-scattering amplitude and phase shift calculated by FEFF [6].

3. Results

Quenching from $1200^{o}C$ in water (N1) fixes solid solution with low coercitive force ($H_c < 4$ Oe). X-ray structure analysis showed the superposition of two phases: β2-phase which is partly ordered in CsCl-manner structure (B2) and β-phase with bcc-structure (A2), which can be partly ordered in Cu_2MnAl-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 ($H_c = 650$ 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 L2$_1$ phase. The mean lattice parameter of alloy is a ≈ 0.2879 nm (or twice of it as regards L2$_1$ phase). Aging of sample N2 at 780°C for 10 min (N3) reduces coercitive force to $H_c = 320$ 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 L2$_1$ phase. The mean lattice parameter of alloy is a ≈ 0.2878 nm. It seems that aging leads to disordering of L2$_1$-phase and its transformation into A2 phase.

Transmission electron microscopy (TEM) image of the quenched sample N1 (fig. 1a) reveals two-phase nanostructure constituting the fine mixture of black and white precipitates of size 5÷10 nm, forming at the initial stage of solid solution decomposition. After cooling with critical rate (N2) the features of nanostructure becomes noticeably coarser (fig. 2a). The sample contains lamellar precipitates with an average size of 80÷150 nm and pronounced preferred orientation inside a single grain. The diffraction pattern (fig. 2b,c) reveals the superposition of reflections of two phases: β-phase

with bcc-structure (A2) and β_2-phase with CsCl structure (B2). Figure 1b shows TEM image of the sample aged at 780°C for 10 min (N3), which indicate a visible increase of precipitates size up to 200÷250 nm.
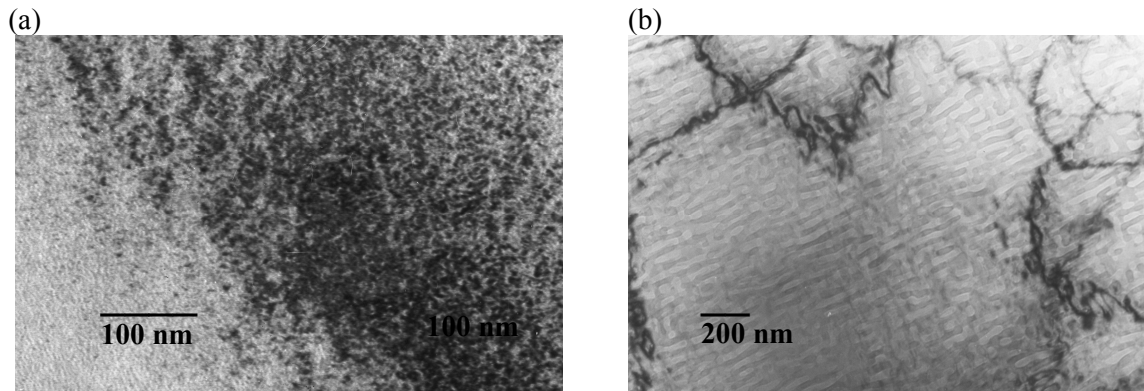

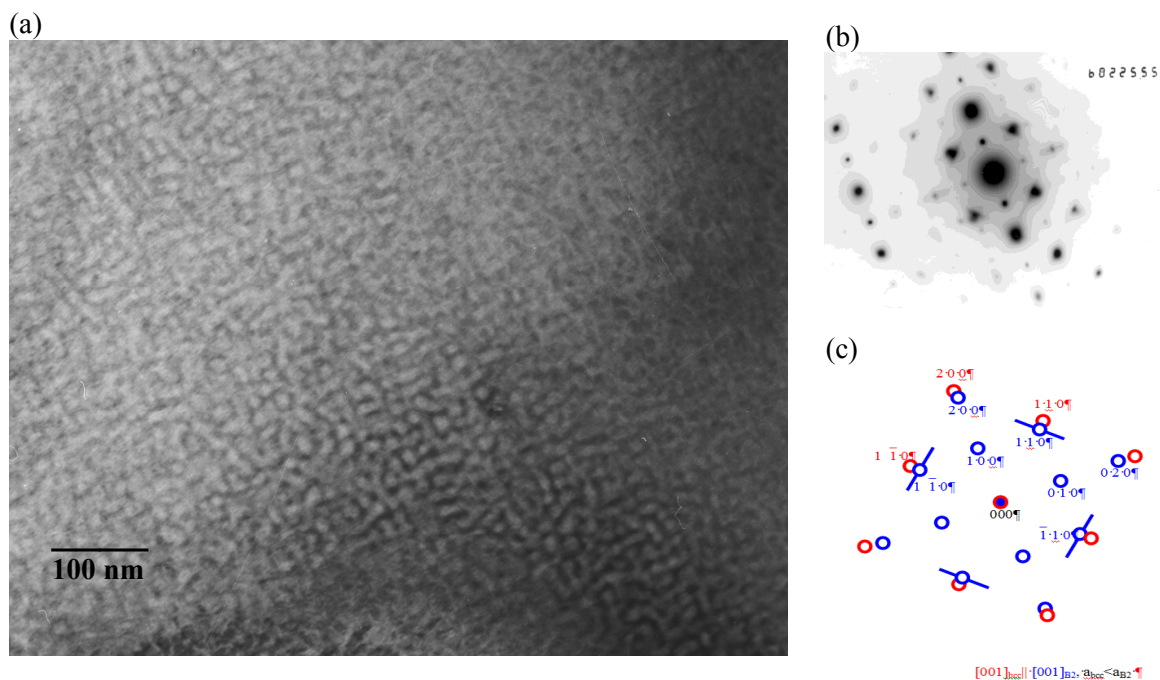**Figure 1.** TEM images of quenched sample N1 (a) and sample N3 aged at 780°C for 10 min (b).

Figure 2. (a) TEM image of sample N2.   (b,c) Diffraction pattern for the region depicted in (a).

According to EXAFS spectra analysis, iron local environment is the same for both L2$_1$ and B2 types of ordering, so parameters of coordination shells around iron atoms are practically identical in all samples N1-N3. However analysis of the EXAFS-function measured above K-Ni edge showed the strong difference of the nickel local environment in sample N2 from the environment in sample N1 and N2. One can observe similar picture for BFT of EXAFS functions measured above K-Ni absorption edge for N1 and N3 samples (fig. 3a,b). EXAFS spectra modelling showed that local environment corresponds to B2 type of ordering in both N1 and N3 samples.

At the same time modelling of high-coercivity sample N2 EXAFS functions showed that it is impossible to fit experimental spectrum with single phase (B2 or L2$_1$) model due to samples heterogeneity (fig. 3c). Good results were obtained by modelling the spectrum assuming the

simultaneous existence of two ordering types. Thus the local structure analysis confirms appearance of $L2_1$ phase in addition to B2 phase in the structure of sample N2 after cooling with critical rate. Apparently this transformation is the main reason of the high-coercivity state in Fe-Ni-Al alloys.

According to X-ray diffraction data aging of sample N2 at 780°C (N3) returns the alloy to A2+B2 phase state. EXAFS data analysis shows that parameters of coordination shells around Fe and Ni as well as BFT shapes are restored to values corresponding to sample N1 (fig. 3b). It seems that aging at 780°C leads to disordering of $L2_1$-phase and its transformation into A2 phase [2]. As a result the coersivity decreases.
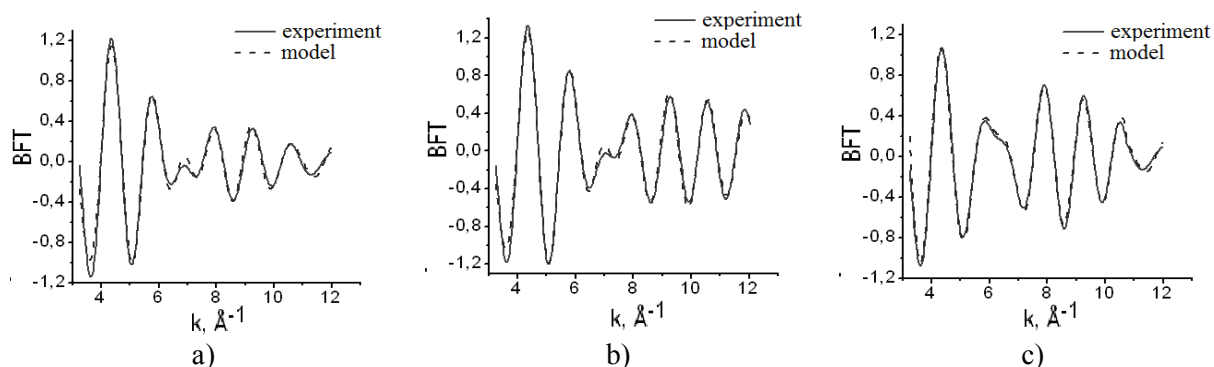

Figure 3. BFT of the nearest shells, obtained from treatment of EXAFS function measured above K-Ni absorption edge for samples N1 (a), N3 (b) and N2 (c).

4. Conclusions

Quenching from 1200°C (N1) fixes initial stage of solid solution decomposition into two phases: β_2-phase which is partly ordered in CsCl-manner structure (B2) and β-phase with bcc-structure (A2). The cooling with critical rate (N2) transforms the alloy to high-coercivity state with β-phase partly ordered in Cu_2MnAl-like structure ($L2_1$). Annealing at 780°C (N3) transfers the alloy to initial phase state: parameters of coordination spheres around Fe and Ni are restored to values corresponding to sample N1 (A2+B2 structures) due to disordering of $L2_1$-phase and its transformation into A2 phase.

Acknowledgments

References

[1]   Bradley A J, Taylor F 1938 *Proc. Roy. Soc.* (A) **166** 353
[2]   Menushenkov V P, Sviridova T A, Shelekhov EV 2010 *Proceedings of the 19-th Int. Metallurgical and Materials Conference "Metal-2010" (Roznov pod Radhostem, Czech Republic, 18-20 May 2010)* pp 807-811
[3]   Cahn J W 1962 *Acta Met.* **10** 179
[4]   Klementev K V 2001 *J Phys D: Appl. Phys* **34** 209
[5]   Newville M, Līviņš P, Yacoby Y, Rehr J J and Stern E A 1993 *Phys. Rev.* B **47** 14 126
[6]   Rehr J J, Mustre de Leon J, Zabinsky S I et al. 1991 *J. Am. Chem. Soc.* **113** 5135