Proceedings of the European Conference Physics of Magnetism, Poznań 2014

Phase Transitions in Fe–Rh Alloys Induced by Temperature

V. Rodionov[a,*], V. Rodionova[a,b] and M. Annaorazov[a]

[a]Innovation Park and Institute of Physics and Technology, Immanuel Kant Baltic Federal University, Nevsky 14, Kaliningrad 236041, Russia

[b]National University of Science and Technology MISiS, Leninsky 4, 119049, Moscow, Russia

This research work was aimed to find the composition of equiatomic Fe–Rh alloy and to find the way of preparation of samples with extremely narrow thermal hysteresis and repeatable results. Alloys with content of Fe from 48 up to 52 at.% were examined. Fe–Rh alloys were prepared in forms of bulk piece, plate and wire. The plates of alloys were found to be more perspective for further investigations. The influence of parameters of ingot and samples treatments on antiferromagnetic-ferromagnetic transition was studied. The ways of narrowing of temperature hysteresis were established.

DOI: 10.12693/APhysPolA.127.445

PACS: 64.60.Cn, 75.30.Kz, 64.70.K–

1. Introduction

The nearly equiatomic Fe–Rh alloys when heated without an external influences to critical temperature suffer the first-order antiferromagnetic (AFM)–ferromagnetic (FM) transition. The reverse transition takes place at lower temperature. The width of thermal hysteresis can be varied by the changing of alloy's chemical content, preparation technique of the samples, heat- and mechanical treatment in wide range of temperatures [1, 2]. To decrease the hysteresis — it is important for technical applications. Moreover, each subsequent measurement leads to change of the antiferromagnetic-ferromagnetic transition temperature. The details of perspective applications and other fundamental tasks can be found, for example, in [3–5].

This research work was aimed to find the composition of equiatomic Fe–Rh alloy and to find the way of preparation of samples with extremely narrow thermal hysteresis and repeatable results.

2. Experimental details, samples preparation, and selection of sample form

Fe–Rh alloys were prepared by induction melting in argon atmosphere. For production of alloys the powder of Rh and chips of Fe with 99.99% and 99.98% purity, respectively, were used. Blend melting was performed in annealed (air, 1273 K — to eliminate a possibility of alloy pollution) alundum crucibles. Homogenization of alloy was achieved by the mixing of melt owing to electromagnetic interaction of eddy currents in this alloy with alternating magnetic field. Fe–Rh alloys with content of Rh from 48 to 52 at.% have been produced. The composition of alloys was examined by means of X-ray fluorescent analysis.

Ingots of alloys were subjected to mechanical cleaning and chemical etching in the following solutions sequentially: (i) nitrohydrochloric acid (20% of nitric acid and 80% of hydrochloric acid) — to remove slags from the surface of ingot, (ii) solution, containing eight parts by volume of sulphuric acid and three parts by volume of aqua — to remove the iron oxide (rhodium oxide dissociates at heating in vacuum above 1070 K). Then, the ingots were annealed in vacuum at 1273 K for 45 h to remove the stresses, acquired during after-melting quenching and to increase the degree of homogenization.

From all Fe–Rh alloys the samples with the sizes of $10\times2\times2$ mm^3 were cut. Then samples were mechanically polished, etched in solution (ii), annealed in vacuum at 1273 K for 2 h and slowly cooled with the rate of 100 K/h.

The following circumstance was taken into account during the choosing the samples form, too. One of most important point is to obtain the samples, exhibiting the AFM-FM transition as much as possible approximated to the isothermal process. It is well known that the sharper transition occurs in quenching samples than in slowly cooled [6]. Therefore, the preparation of thin samples is more advanced way — increase of the area of surface in thin samples in comparison with bulk materials leads to increase of the rate of heat exchange with the environment. Moreover, the AFM-FM transition in FeRh alloy is the first order transition that is why the gradient of temperatures (appeared during the melting artefact) influences on the kinetics of transition via appeared inelastic deformation and other non-doped defects. In this connection plate-shape and wire-shape samples were prepared.

The set of the samples in form of plate was prepared from $Fe_{49}Rh_{51}$ alloy by flatting. The sizes of the samples were $14\times4\times0.25$ mm^3. After cutting the samples were mechanically polished and corroded in concentrated hydrochloric acid.

The samples in the form of wire with 1 mm diameter and 50 mm in length were obtained by means of drawing into alundum tubes from alloy with Rh content of 52 at.%. These wires were mechanically polished, etched, annealed, and cooled in the same sequence as previous samples. However, the measurements of resistance depending on temperature demonstrate that the region of AFM-FM transition in wire lies lower in comparison

*corresponding author; e-mail: rodionov_vlad@mail.ru

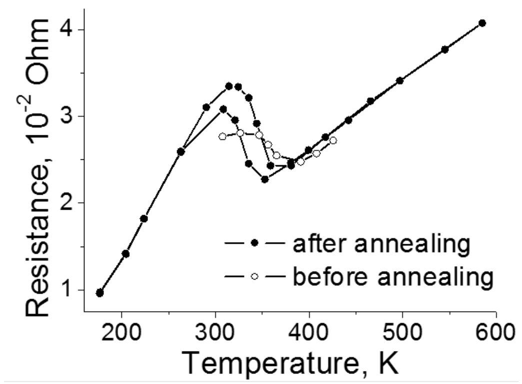

Fig. 1. Temperature dependence of resistance of wire from Fe-Rh alloy before annealing and after annealing at 1273 K for 2 h.

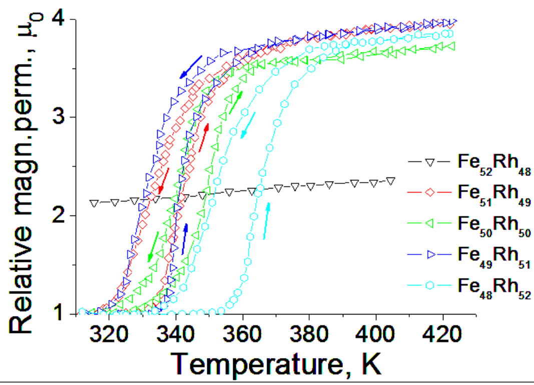

Fig. 2. Temperature dependences of relative initial magnetic permeability of samples: $Fe_{52}Rh_{48}$, $Fe_{51}Rh_{49}$, $Fe_{50}Rh_{50}$, $Fe_{49}Rh_{51}$, and $Fe_{48}Rh_{52}$ alloys.

with the temperatures of transition in base alloy. This fact can be explained by distinction of wire and alloy compositions and by contamination with impurities at interaction with alundum tube during drawing. Temperature dependence of wire resistance both before and after annealing is shown in Fig. 1.

Comparison of temperature dependences of resistance of wire before and after annealing (the same sample) exhibits the larger jump of resistance during AFM-FM transition in annealed state. It means that the larger value of sample is not involved in transition process in annealed wire to compare with as-prepared wire. Since the specific resistance of alloy is lower in ferromagnetic state than in antiferromagnetic state near transition region, lower resistance of the sample testifies to presence of significant value of ferromagnetic phase in sample, which is not involved in transition.

Thus, the cut and plate samples, as more perspective in compare with wire-shape samples, were selected for further measurement.

Measurements of magnetic properties depending on temperature were performed by induction method. Temperature was changed in the range from 170 to 700 K.

3. Experimental results and discussion

Temperature dependences of relative initial magnetic permeability, μ_0 (maximum change of initial magnetic permeability in the temperature range), for Fe–Rh alloys with different composition are presented in Fig. 2.

The temperatures where μ_0 is undergoing the largest changes during heating or cooling — is the temperatures of AFM-FM and FM-AFM transitions, respectively. The $Fe_{52}Rh_{48}$ alloy (see Fig. 2) is found to be ferromagnetic and it has no AFM-FM transition in the temperature range from 170 to 700 K. The transition in $Fe_{51}Rh_{49}$ and $Fe_{49}Rh_{51}$ alloys occurs roughly in the same temperatures range. The transition in $Fe_{50}Rh_{50}$ and $Fe_{48}Rh_{52}$ alloys takes place at higher temperatures. But the most perfect transition is found to be in $Fe_{49}Rh_{51}$ alloy. This is manifested in the facts that transition in this alloy is sharper, curves $\mu_0(T)$ are more monotonic, heating curve coincides with cooling curve in the range of FM phase. The jump of permeability during the transition in $Fe_{51}Rh_{49}$ alloy and the jump of permeability during the transition in $Fe_{49}Rh_{51}$ alloy are almost coincident bot jump for last mentioned alloy is higher in comparison with $Fe_{50}Rh_{50}$ and $Fe_{48}Rh_{52}$ alloys. That is why we conclude that transition in $Fe_{49}Rh_{51}$ alloy is near model transition and we chose this alloy for further experiments.

To exclude randomness selection of the place of samples cutting from ingot, we have measured the $\mu_0(T)$ curves of ingot remainder (see Fig. 3). The transition in the ingot is found to be in temperature range from 293 to 367 K with temperature hysteresis of 12 K, while in the sample — in the temperature range of 316–378 K with temperature hysteresis of 11 K. This indicates the inhomogeneity of the ingot. That is why the ingot was few times remelting. During each melting the alloy was kept in liquid state for 1 h and then slowly cooled for 1 h in inductor. The temperature range of transition becomes narrower — down to 29–370 K after remelting process, the jump of magnetic permeability becomes higher, the transition exhibits sharper form and temperature hysteresis increases up to 18 K. The temperature hysteresis decreases down to 14 K and the permeability jump increases in 1.5 times (in regard to non-annealed ingot) after annealing at 1273 K for 7 h and slow cooling down to room temperature with rate of 200 K/h. However, $\mu_0(T)$ curves during the heating and cooling at the temperatures of 333 and 319 K, respectively, undergo the breaks. These breaks are found to be independent of the number of subsequent heating-cooling cycle. The jump increase of μ_0 after annealing can be explained by homogenization of annealed ingot and removing of mechanical stresses, with the result that the larger part of ingot is involved in the transition. This explanation is confirmed by the following experimentally observed fact. The samples are ferromagnetic and show only poor signs of AFM-FM transition during quenching process. Magnetization of alloys at room temperature decreases and the transition becomes more prominent with relatively slow cooling. The presence of breaks in $\mu_0(T)$ curves testifies to the inhomogeneity of alloy and to the existence of at least two compositions in the alloy. Transition of the part of alloy with higher content of Rh occurs at higher temperature in comparison with transition of other part of alloy with lower comment of Rh. Thus, the few times remelting of alloy — it is necessary process for obtaining of the alloys with high degree homogeneity.

All the described features during remelting and set of annealing are presented in Fig. 3.

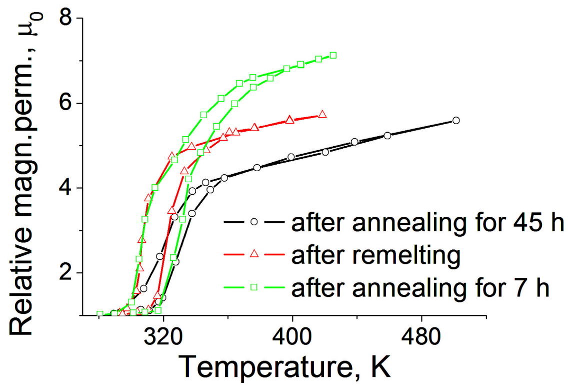

Fig. 3. Temperature dependence of relative initial permeability of ingot of $Fe_{49}Rh_{51}$ alloy: after annealing at 1273 K for 45 h, after remelting and after annealing at 1273 K for 4 h sequentially.

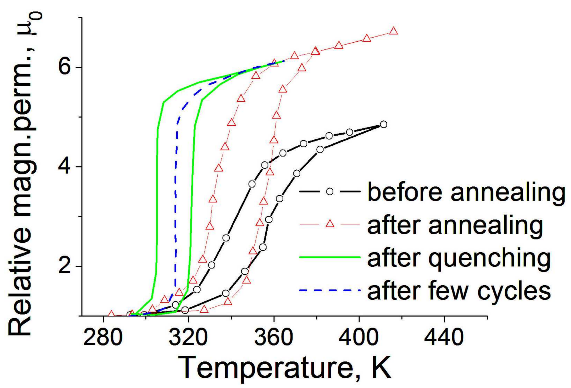

Fig. 4. Temperature dependence of relative initial permeability of sample of $Fe_{49}Rh_{51}$ alloy: before annealing (as-prepared flatted sample), after annealing at 1273 K for 72 h, after quenching from 1273 K in ice water and after few heating-cooling cycles in temperature range 273–513 K.

To compare the properties of ingot with the properties of sample in plate shape, the temperature dependences of relative initial permeability of plate-shape sample were measured. The influence of different treatments on magnetic properties was investigated. $\mu_0(T)$ curves for as-prepared, annealed and quenching samples are presented in Fig. 4.

The AFM-FM transition in as-prepared sample takes place in the temperature range from 314 to 415 K with temperature hysteresis of 20 K. It is on record that plastic deformation affects the AFM-FM transition in Fe–Rh alloy and the mechanical stresses and mechanical treatments dramatically affects the magnetic properties of alloys. First one leads to decrease of the transition jump and second one leads to decrease of the initial magnetic permeability. Co-existing of these two factors leads to small change of relative initial magnetic permeability of as-prepared flatted sample (see Fig. 4). We can explain presence of transition in this sample by heating of the plate during flatting up to red heat. Reaching of this temperature is enough condition to back this alloy to the state in possession of AFM-FM transition. The annealing of this sample in vacuum at 1273 K for 72 h with subsequent slow cooling results in narrowing of transition temperature range, increase of transition sharpness and widening of the temperature hysteresis up to 23 K. Changing of μ_0 increases 1.5 times. The control quenching of the sample from temperature of annealing demonstrates that this process significantly shifts the temperature range of transition toward low temperatures and approaches the transition to isothermal one. Moreover, a significant influence of thermo cycling on the parameters of AFM-FM transition has been found.

3. Conclusion

We have studied the temperature dependences of magnetic properties of Fe–Rh alloys with different content of Fe and prepared in different forms. The plate-form sample of $Fe_{49}Rh_{51}$ alloy prepared by quenching and flatting was found to be with narrow temperature hysteresis. The thermo cycling for this sample leads to narrowing of temperature hysteresis.

Acknowledgments

This work was carried out with financial support from the MES of the RF in the framework of Increase Competitiveness Program of MISiS and in the framework of government assignment (No. 3.2582.2014/K). M.A. greatly acknowledges grant RFBR, project No. 14-32-50892.

References

[1] M.P. Annaorazov, M. Unal, S.A. Nikitin, A.L. Tyurin, K.A. Asatryan, *J. Magn. Magn. Mater.* **251**, 61 (2002).

[2] M.P. Annaorazov, H.M. Guven, K. Barner, *J. Alloys Comp.* **397**, 26 (2005).

[3] R. Sindhunil Barman, *J. Phys. Condens. Matter* **25**, 183201 (2013).

[4] D.W. Cooke, F. Hellman, C. Baldasseroni, C. Bordel, S. Moyerman, E.E. Fullerton, *Phys. Rev. Lett.* **109**, 255901 (2012).

[5] X. Marti, I. Fina, C. Frontera, J. Liu, P. Wadley, Q. He, R.J. Paull, J.D. Clarkson, J. Kudrnovský, I. Turek, J. Kuneš, D. Yi, J.-H. Chu, C.T. Nelson, L. You, E. Arenholz, S. Salahuddin, J. Fontcuberta, T. Jungwirth, R. Ramesh, *Nature Mater.* **13**, 367 (2014).

[6] L. Pal, T. Tarnoczi, P. Szabo, E. Kren, J. Toth, in: *Proc. Int. Conf. on Magnetism, Nottingham 1964*, p. 158.