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Hard magnetic nanocrystalline alloys of Fe-O system

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The structure and magnetic properties of nanocrystalline Fe-O alloys produced by high-energy ball milling and subsequent low-temperature annealing were investigated. The Fe_2O_3, FeO and Fe powders as well as their mixtures were used as starting materials. The structure was studied by X-ray diffraction analysis, Mössbauer spectroscopy and scanning electron microscopy. The magnetic properties were measured in vibrating sample magnetometers at room temperature and 4.2 K. The nanocrystalline composite alloys obtained as a result of the milling contained FeO and α-Fe with an average crystallite size of 15–20 nm as well as an amorphous phase, which was identified as a solid solution of oxygen in iron. However, alloys subjected to subsequent annealing contained only α-Fe and Fe_3O_4 with an average crystallite size of about 20 nm. Unlike the starting materials the produced powders had properties which are characteristic of hard magnetic materials. For example, the powder produced by the milling of $Fe_2O_3 + 50\%$ α-Fe mixture followed by annealing had the following properties at 300 K: intrinsic coercive force $\mu_0 H_c = 0.067$ T, remanence $B_r = 0.48$ T, energy product $(BH)_{max} = 9$ kJ/m^3.

1. Introduction

Recently, considerable attention has been drawn to the investigation of nanocrystalline hard magnetic materials [1–4]. These materials are produced by various techniques, in particular, by high-energy milling and subsequent annealing. Previously, it was shown that nanocrystalline hard magnetic Fe-O alloys could be produced by high-energy milling of Fe_2O_3 powder [4]. This fact is of both scientific and technical interest. Indeed, ore bodies containing practically pure hematite are sufficiently abundant [5] and the problem of manufacturing materials with high consumer properties from these ores is very actual. The present work is a continuation of our investigations of nanocrystalline alloys produced from different powders of the Fe-O system [4, 6].

2. Experimental

The Fe_2O_3, FeO and Fe powders as well as their mixtures ($Fe_2O_3 + 25\%$Fe, $Fe_2O_3 + 50\%$Fe, FeO + 38.5%Fe) were used as starting materials. High-energy milling was carried out in hermetic vessels with ShKh15 steel balls using an AGO-2U planetary ball mill [7]. The milling time was varied from 0.5 up to 7 h. According to the estimations given in [7, 8], the milling process power was about 20 W/g. Computer-controlled diffractometers were used for X-ray diffraction study of the samples. Phase composition and average crystallite sizes ($\langle D \rangle$) were determined by a reduced Rietveld method. In addition, the powders were investigated by ^{57}Fe Mössbauer spectroscopy and scanning electron microscopy. Magnetic properties were measured at room temperature and 4.2 K with an accuracy of 3% using vibrating sample magnetometers and external fields up to 14 T.

3. Results and discussion

According to X-ray diffraction analysis, the starting Fe_2O_3 powder was α-Fe_2O_3 (hematite) with D5.1-type lattice and the Fe powder was α-Fe (A2-type lattice). The powder called FeO contained 67% pure FeO (wustite), 20% α-Fe_3O_4 (H1.1-type lattice), and 13% α-Fe_2O_3. All starting powders had a coarse-grain structure and a low intrinsic coercive force ($\mu_0 H_c <$ 0.005 T). The phase composition of all starting materials (except that of the Fe powder) was changed considerably during the milling process. These variations of the phase composition may be described in

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the following way (crystal structure types of the phases are indicated in parenthesis):

$$\begin{aligned}\mathrm{Fe_2O_3(D5.1) + Fe(A2)} &\rightarrow \mathrm{Fe_2O_3(D5.1)}\\ &\quad + \mathrm{Fe_3O_4(H1.1) + FeO(B1) + Fe(A2)}\\ &\rightarrow \mathrm{FeO(B1) + Fe(A2) +}\ \text{amorphous phase.}\end{aligned}$$

When pure α-Fe_2O_3 was used as the starting material, the transformations mentioned above were caused by interaction of Fe_2O_3 with Fe polluting the treated powder as a result of steel ball and vessel wall unavoidable wear. The same conclusion was drawn by Novikov *et al.* [9] from the data of Mössbauer investigation. The similar process took place when FeO powder was subjected to the milling.

The variations of the phase composition were already observed after 0.5 h milling. As an example, the phase composition variations as a function of milling time of the Fe_2O_3 + 50% (39 vol%) Fe mixture are presented in Fig. 1. The final product (the mixtures of amorphous phase + FeO + α-Fe with amorphous phase with the average size of crystallites of 15–20 nm) was obtained after 5 h milling of Fe_2O_3 powder and after 2 h milling of Fe_2O_3 + α-Fe or FeO + α-Fe mixtures. One should note that after 3 h milling, the average particle size of the powders (determined by scanning electron microscopy) was below one micrometer. The abundance of α-Fe and FeO in the milled powders depended on Fe content in the starting material, but the amount of the amorphous phase was practically the same (about 30 vol%) in all milled mixtures [6]. The average crystallite size decreased strongly after relatively short milling time to a value of $\langle D\rangle \approx 15$–$20$ nm (Fig. 2).

Room temperature ^{57}Fe Mössbauer spectra of Fe_2O_3 + Fe milled mixtures could be decomposed into one sextet with hyperfine field $H_{\mathrm{hf}} = 330$ kOe, which was attributed to α-Fe, two doublets with isomer shift (relative to ^{57}CoRh at 300 K) $\delta \approx 0.81$ mm/s, and a superposition of several sextets with practically equal isomer shifts ($\delta \approx 0.10$ mm/s) representing a component exhibiting a hyperfine field distribution (180 kOe $< H_{\mathrm{hf}} <$ 390 kOe). The two doublets may be attributed to FeO [6] taking into account that the lattice parameter of this phase ($a \approx 0.428$ nm) points to a considerable oxygen enrichment compared to the stoichiometric composition. The hyperfine field distribution is attributed to the amorphous phase. The considerable difference of δ compared to the one of α-Fe ($\delta \approx -0.15$ mm/s) permits to assume that this phase is a solid solution of oxygen in iron. The Mössbauer spectrum of a powder obtained after 3 h milling of a mixture of Fe_2O_3 + 50% Fe is presented in Fig. 3. Assuming that the Debye-Waller factors are the same in all above-mentioned phases, the relative amount of the phases was calculated from the line intensities. The obtained results are in satisfactory agreement with the X-ray data [6].

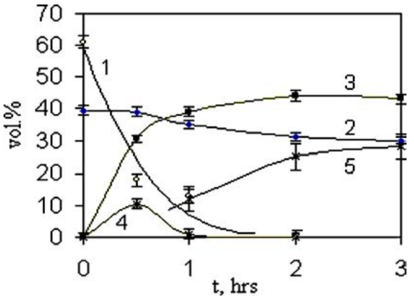

Figure 1 Phase composition variations as a function of milling time (t) of the Fe_2O_3+50% (39 vol%) Fe mixture: 1—Fe_2O_3; 2—α-Fe; 3—FeO; 4—Fe_3O_4; 5—an amorphous phase.

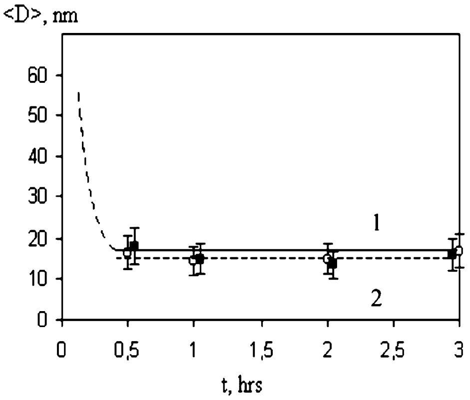

Figure 2 Average crystallite size as a function of the milling time of the Fe_2O_3 + 50% Fe mixture: 1—α-Fe; 2—FeO.

Unlike the starting materials the milled powders had properties, which are characteristic of hard magnetic materials. An intrinsic coercive force $\mu_0 H_{\mathrm{c}} \geq 0.05$ T at 300 K (Fig. 4) was achieved for the Fe_2O_3 + 50% Fe mixture already after 1 h milling. (Following [10, 11], intrinsic coercive forces of hard magnetic materials should exceed 0.01 T.) After 3 h milling, B_{r} and $(BH)_{\max}$ of this powder were about 0.38 T and 6 kJ/m^3, respectively. In the other powders these values were lower, what may be explained by a lower content of nanocrystalline α-Fe.

The relatively high values of the coercive force may be caused by the formation of α-Fe single-domain particles in the milled powders. Magnetization reversal of these particles occurs by flipping of the magnetic moment only. According to the estimation of [12] the size of single-domain particles for α-Fe is 10–30 nm, what is in good agreement with the above-mentioned results (Fig. 2). Note that nanocrystalline hard magnetic materials should be regarded as materials consisting of the single-domain particles (crystallites).

An analysis of the magnetic properties, in particular, the saturation magnetization, allows to assume that FeO oxide and the amorphous phase have no considerable influence on the magnetic behavior of the milled powders. Moreover, the remanence of these powders was approximately equal to one-half of the saturation magnetization. Thus, in spite of the cubic crystal structure of α-Fe, the milled powders behaved as a uniaxial magnetic material. This conclusion is in agreement with [13] where the magnetic properties of nanocrystalline Fe powders were measured.

One should note that we did not observe any solid state reactions during the high-energy milling of Fe powder. The treatment has not led to formation of a nanocrystalline structure in the Fe powder. Even after

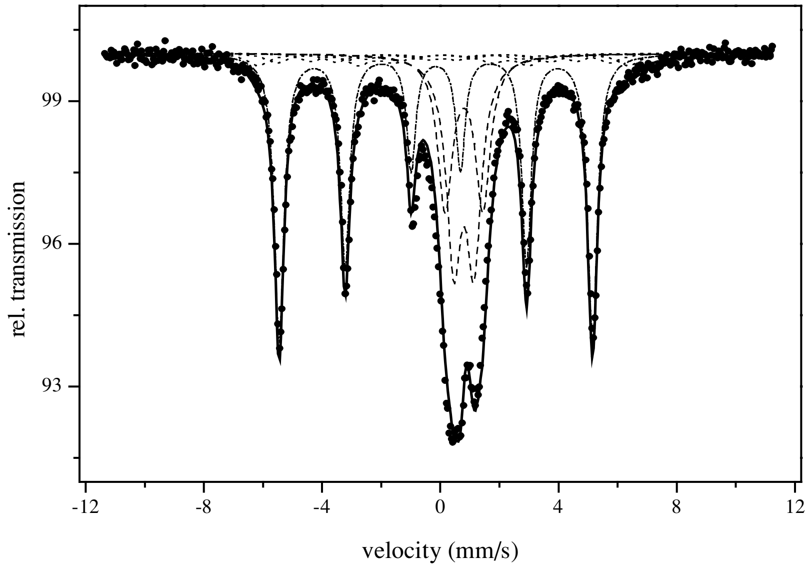

Figure 3 Room temperature ^{57}Fe Mössbauer spectrum of the $Fe_2O_3 + 50\%$ Fe mixture taken after 3 h milling.

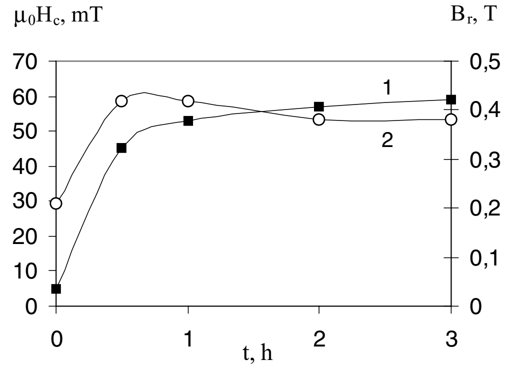

Figure 4 $\mu_0 H_c$ (1) and B_r (2) at room temperature as a function of a milling time.

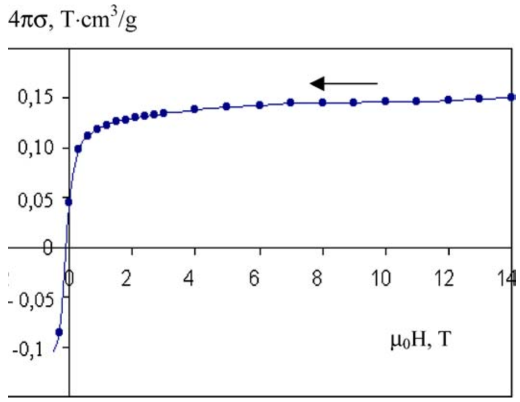

Figure 5 Demagnetization curve at 4.2 K of the α-Fe + Fe_3O_4 powders obtained by milling and the subsequent annealing.

3 h milling the average size of the crystallites was still greater than 50 nm. As a consequence, the hard magnetic properties of the milled α-Fe powder at 300 K were very poor: $\mu_0 H_c < 0.004$ T and $B_r \approx 0.035$ T.

According to X-ray and Mössbauer investigations a low-temperature annealing of the milled powders led to dissociation of FeO and the amorphous phase into α-Fe and α-Fe_3O_4. For example, the milled $Fe_2O_3 + 25\%$ Fe mixture after annealing contained 26 ± 1% (19 ± 1 vol%) of α-Fe and 74 ± 2% of Fe_3O_4. Note that the crystallite size decreased when the annealing temperature was reduced. The intrinsic coercive force of the powders after annealing increased with a decrease of the phase crystallite size.

The annealing helps to increase the remanence, the energy product and to retain the high coercive force. For example, the $Fe_2O_3 + 50\%$ Fe mixture after the milling and annealing contained 47 ± 2% of α-Fe, 53 ± 2% of Fe_3O_4 with the crystallite sizes of about 20 nm and had the following properties at 300 K: $\mu_0 H_c = 0.067$ T, $B_r = 0.48$ T, $(BH)_{max} = 9$ kJ/m^3.

A demagnetization curve at 4.2 K of the annealed powder, which contains $25 \pm 2\%$ (18 ± 2 vol%) of α-Fe and $75 \pm 3\%$ of Fe_3O_4 with $\langle D \rangle \approx 20$ nm, is presented in Fig. 5. The coercive force ($\mu_0 H_c$) of the powder at 4.2 K reached approximately 0.1 T. The specific saturation magnetization was equal to $\sigma_s \approx 0.15\ \mathrm{T \cdot cm^3/g}$, what corresponds to $4\pi I_s \approx 0.85$ T. Even at high fields the magnetization is not saturated, that is characteristic for nanocrystalline materials. Possible reasons of this phenomenon are discussed in [14]. One should note that the coercive forces of about 0.1 T at 4.2 K were observed earlier in nanocrystalline Fe-powders with the crystallite size of 20–30 nm [15], what is in good agreement with the results of the present investigation.

4. Conclusions

Nanocrystalline composite alloys containing FeO, α-Fe and an amorphous phase were obtained as a result of high-energy ball milling of Fe-O powdered system. The average size of crystallites in the produced composite was 15–20 nm. The amorphous phase was a solid solution of oxygen in iron. Unlike the starting materials, the milled powders had properties, which are characteristic of hard magnetic materials. Further improvement of the magnetic properties was achieved by low-temperature annealing of the milled powders. The annealed powders consisted only of α-Fe and Fe_3O_4 with average crystallite size of about 20 nm. The amount of these constituents depended on composition of the starting materials.

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