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Mössbauer and X-ray diffraction investigation of nanocrystalline Fe–O alloys

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Abstract

X-ray and Mössbauer investigations were carried out on powders produced by milling of $Fe_2O_3 + \alpha$-Fe mixtures in a high-energy ball mill and subsequent low-temperature annealing. 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. Alloys subjected to subsequent annealing contained, however, only α-Fe + Fe_3O_4 with an average crystallite size of about 20 nm. Unlike the starting materials the produced powders had properties, which are characteristic for hard magnetic materials.

Keywords: Nanocrystalline alloys; Fe–O powders; Mössbauer spectroscopy; X-ray diffraction analysis

1. Introduction

It is possible to manufacture nanocrystalline composite Fe–O alloys by milling of Fe + Fe_2O_3 mixtures in a high-energy ball mill and subsequent low-temperature annealing [1]. Unlike the starting materials the produced powders had properties (intrinsic coercive force of 40–50 kA/m and a remanence up to 0.6 T) which are characteristic for hard magnetic materials. The aim of the present paper was the determination of phase composition and structural characteristics of the phases present in the milled powders by X-ray and Mössbauer investigations to gain a better understanding of the appearance of the hard magnetic properties.

2. Experimental

Powders of Fe_2O_3 + 25% α-Fe (mixture A) and Fe_2O_3 + 50% α-Fe (mixture B) were chosen as starting materials.

The treatment was carried out using an AGO-2U planetary ball mill and sealed vials with hardened steel balls. The longest milling times were 3 h. According to the estimation of Shelehov et al. [2] at the applied conditions the milling process power was about 0.05 W/g. Computer-controlled diffractometers were used for X-ray examination of the samples. Phase composition and crystallite sizes were determined by a reduced Rietveld method [3]. In addition, the phase composition of the powders was investigated by ^{57}Fe Mössbauer spectroscopy at room temperature. The magnetic properties were measured at room temperature in maximum fields of 1300 kA/m with an accuracy of 3% using a vibrating sample magnetometer.

3. Results and discussion

According to the X-ray diffraction analysis, the starting powders contained Fe_2O_3 phase (with D5.1-type lattice) and α-Fe (with A2-type lattice). They had a coarse-grain structure and a low intrinsic coercive force ($_{I}H_c < 4$ kA/m). Treatment in the high-energy ball mill led to a change of the powder phase composition in the following way (crystal structure types of the detected phases are indicated in parenthesis): Fe_2O_3(D5.1) + Fe(A2) → Fe_2O_3(D5.1) + Fe_3O_4(H1.1) + FeO(B1) + Fe(A2) → Fe_3O_4(H1.1) + FeO(B1) +

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Fe(A2) + amorphous phase → FeO(B1) + Fe(A2) + amorphous phase.

The variations of the phase composition were observed after 0.5 h milling of the powders. The final state of FeO + α-Fe + amorphous phase with average size of crystallites, determined from X-ray-line broadening, of 15–20 nm was reached after 3 h milling of mixture A and after 2 h milling of mixture B. As an example the X-ray pattern of mixture B after 3 h milling is presented in Fig. 1. One should note that the average particle size after milling (determined by Scanning Electron Microscopy) was 0.3–0.4 μm. Thus, one can assume that macroparticles containing nanocrystallites of Fe and FeO as well as amorphous phase, which are formed as a result of solid state transformations, were produced at the milling process.

The abundance of α-Fe and FeO in the milled powders depended on Fe content in the starting mixture, but the amount of the amorphous phase was practically the same in both mixtures (about 30 vol%, Table 1). As a result of the milling the intrinsic coercive force of the powders increased up to 45–50 kA/m.

^{57}Fe Mössbauer spectra recorded at 300 K could be decomposed into a sextet with hyperfine field $H_{hf} = 330$ kOe, which was attributed to α-Fe and two doublets with isomer shift (relative to ^{57}CoRh at 300 K) $\delta \approx 0.81$ mm/s, which may be attributed to FeO [4]. Note that the lattice parameter of the FeO phase ($a \approx 4.28$ Å) points to a considerable oxygen enrichment in comparison to the stoichiometric composition. In addition, the Mössbauer spectra were fitted with 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 $< H_{hf} <$ 390 kOe). This contribution may be 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 mixture B is presented in Fig. 2. Assuming that the Debye–Waller factors are the same in all the above-mentioned phases, the relative amount of the phases was calculated from the Mössbauer data. The results were in satisfactory agreement with the X-ray data (Table 1).

According to X-ray investigations, the annealing of the milled powders led to dissociation of FeO and the amorphous phase into α-Fe + Fe_3O_4 (H1.1). The average crystallite size was about 20 nm. For example, the powder obtained by the milling of the mixture A contained after annealing 19 ± 1% of α-Fe and 81 ± 2% of Fe_3O_4. In this case the analysis of the Mössbauer spectra confirmed completely the results of the X-ray phase composition determination. Note that the annealing helps to increase the remanence (B_r), the energy product ($(BH)_{max}$) and to retain the high coercive force. For example, the mixture B after the milling and annealing contained 37 ± 2 vol% of α-Fe, 63 ± 2 vol% of Fe_3O_4 and had the following properties: $_{I}H_c = 56$ kA/m, $B_r = 0.48$ T, $(BH)_{max} = 9$ kJ/m^3.

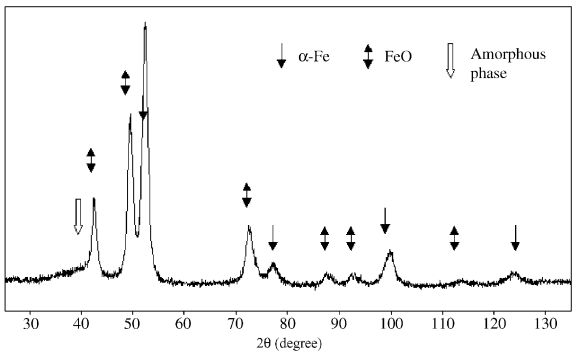

Fig. 1. X-ray diffraction pattern of mixture B after 3 h milling (Co K_α radiation).

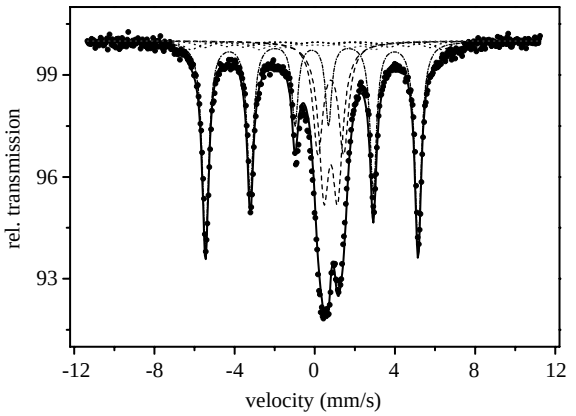

Fig. 2. ^{57}Fe Mössbauer spectrum of mixture B after 3 h milling.

Table 1
Phase composition of the mixtures A and B (vol%)

Method	Mixture A			Mixture B		
	α-Fe	FeO	Amorphous phase	α-Fe	FeO	Amorphous phase
X-ray diffraction analysis	9 ± 2	58 ± 12	33 ± 14	30 ± 2	42 ± 3	28 ± 5
Mössbauer spectroscopy	14	77	9	32	49	19

4. Conclusions

As a result of high-energy ball milling of Fe_2O_3 and Fe mixtures nanocrystalline composite alloys containing FeO, α-Fe and the amorphous phase were obtained. The average size of crystallites was 15–20 nm. The amorphous phase is a solid solution of oxygen in iron. However, the alloys subjected to milling and subsequent annealing contained only α-Fe and Fe_3O_4 with average crystallite size of about 20 nm. Unlike the starting materials, the produced powders had properties, which are characteristic for hard magnetic materials.

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