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Hard magnetic nanocrystalline alloys of Fe–Fe_2O_3 system

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Abstract

The structure and magnetic properties of Fe_2O_3 and Fe powders as well as their mixtures, subjected to treatment in a high-energy ball mill, were studied. It was shown that the phase composition of all the starting materials (except that of the Fe powder) was changed in the milling process. The nanocrystalline composite alloys, containing FeO and α-Fe with an average crystallite size of 10–20 nm as well as an amorphous phase, were obtained as a result of the milling. Phase content in the milled powders depended on the composition of the starting materials. Unlike the starting materials, the milled powders (except of the milled Fe powder and $Fe_2O_3 + 90\%$ Fe mixture) had the properties, which are characteristic for hard magnetic materials. Further improvement of the properties was achieved by low-temperature annealing of the milled powders. The annealed powders of the mixtures contained only nanocrystallites of α-Fe and Fe_3O_4. The amount of these constituents and the magnetic properties of the annealed powders depended on the composition of the starting materials. The sufficiently high properties of the produced powders may be explained by the formation of α-Fe and Fe_3O_4 single-domain particles.

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Keywords: Nanocrystalline alloys; Magnetic powders; Structure; Coercive force

1. Introduction

Hard magnetic materials are widely used in technics. Therefore, production and investigation of new hard magnetic materials are urgent and important. Recently, considerable attention has been drawn to the investigation of nanocrystalline hard magnetic materials [1–4]. These materials are produced by various methods, in particular, by mechanochemical technique. We have previously showed that nanocrystalline hard magnetic Fe–O alloys could be produced by mechanochemical technique from a Fe_2O_3 powder or a mixture of Fe and Fe_2O_3 ($Fe_2O_3 + X\%$Fe where $X \leqslant 50$) [4,5]. The goal of the present work was to study the structure and magnetic properties of nanocrystalline Fe–O alloys in dependence on their composition.

2. Experimental

The Fe_2O_3 and Fe powders as well as their mixtures ($Fe_2O_3 + X\%$Fe where $X = 25,50,65,75,90$) were used as starting materials. High-energy milling was carried out in hermetic vessels with ShKh15 steel balls using an

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AGO-2U planetary ball mill [6,7]. The milling time was varied from 0.5 up to 7 h and the milling process power was 15–20 W/g. Computer-controlled diffractometers were used for X-ray diffraction examination of the samples. Phase composition and average crystallite sizes ⟨D⟩ were determined by X-ray diffraction analysis of the samples. In addition, the powders were investigated by scanning electron microscopy. Magnetic properties were measured at room temperature with an accuracy of 3% using vibrating sample magnetometer.

3. Results and discussion

According to X-ray diffraction analysis the 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). All the starting powders had a coarse-grain structure and a low intrinsic coercive force ($\mu_0 H_c < 5$ mT). The phase composition of all the starting materials (except that of the Fe powder) was changed considerably in the milling process. The final state (mixture of amorphous phase + FeO + α-Fe) was reached after 5 h milling of Fe_2O_3 powder and after 2 h milling of $Fe_2O_3 + X\%$ α-Fe mixtures for $X \leqslant 75$. As an example, the phase composition variations as a function of the milling time of Fe_2O_3 + 50% (39 vol%) Fe mixture are presented in Fig. 1.

The phase abundance of the milled powders almost did not depend on Fe content in the starting material for $X \leqslant 25$ (Fig. 2). These powders contained about 60 vol.% of FeO, 10 vol% of α-Fe and 30 vol% of the amorphous phase. With an increase of Fe content in the starting materials, the amount of FeO and the amorphous phase decreased while α-Fe concentration increased. Moreover, the amorphous phase was not observed in a powder, obtained by the milling of the Fe_2O_3 + 90% α-Fe mixture. One should note that the structure in the studied powders was formed as a result of solid state transformations (mechanochemical reactions). In contrast to this we did not observe any solid state reactions during the high energy milling of the Fe powder.

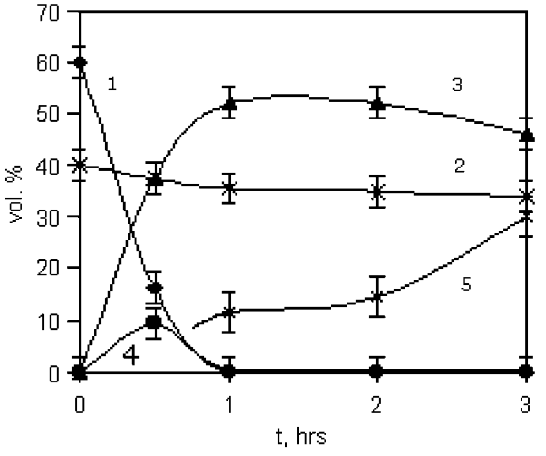

Fig. 1. Phase composition variations as a function of milling time (t) of Fe_2O_3 + 50% Fe mixture: (1) Fe_2O_3; (2) α-Fe; (3) FeO; (4) Fe_3O_4, and (5) an amorphous phase.

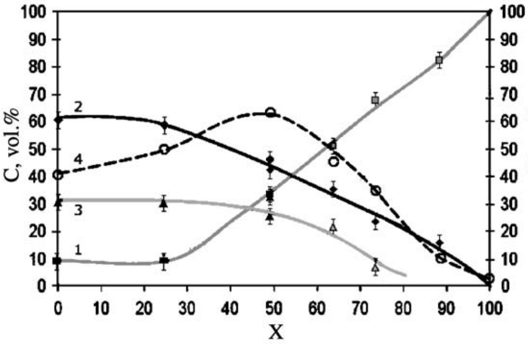

Fig. 2. Phase amount (1) α-Fe, (2) FeO, and (3) an amorphous phase and $\mu_0 H_c$ (4) of the milled powders as a function of the starting material composition.

Note, that when pure α-Fe_2O_3 was used as the starting material the transformations mentioned above were caused by an 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. [8] from the data of Mössbauer investigation only.

The average crystallite size in the powders, determined from a X-ray-line broadening, decreased strongly after relatively short milling time to a constant value of $\langle D \rangle \approx 10$–20 nm (for α-Fe and FeO) [3,4]. At the same time, the average particle size in the milled powders, determined by scanning electron microscopy, was less than a micrometer. Thus, one can assume that macroparticles containing nanocrystallites of α-Fe and FeO as well as amorphous phase (for $X \leqslant 75$) are produced during the milling process.

Analysis of room temperature ^{57}Fe Mössbauer spectra of Fe_2O_3 + Fe mixtures (for $X \leqslant 50$) carried out earlier in Refs. [4,5] allows to assume that the amorphous phase is a solid solution of oxygen in iron. This result is in a good agreement with the X-ray data. Indeed, it is seen from Fig. 1 that the amount of the amorphous phase increased at $t \geqslant 2$ h at the expense of FeO amount decrease, i.e. one can suppose that the composition of the amorphous phase is close to FeO.

Unlike the starting materials, the milled powders (for $X \leqslant 75$) had properties, which are characteristic for hard magnetic materials. An intrinsic coercive force $\mu_0 H_c = 53$ mT was achieved for the Fe_2O_3 + 50% Fe mixture already after 1 h milling and after 3 h milling it was equal to 60 mT. (Following [9], intrinsic coercive forces of hard magnetic materials should exceed 10 mT.) After 3 h milling, the remanence (B_r) and the energy product ($(BH)_{max}$) of this powder were about 0.38 T and 6 kJ/m^3, respectively. The intrinsic coercive force of the milled powders as a function of a starting material composition is presented in Fig. 2. The milling time of all the powders (except that of Fe_2O_3) was 3 h. In the case of the Fe_2O_3 powder it was 7 h.

The sufficiently high values of the coercive force of the powders ($\mu_0 H_c = 35$–60 mT at $X \leqslant 75$) 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 [10] the size of single-domain particles for α-Fe is about 25 nm, what is in good agreement with the above-mentioned results. Note that nanocrystalline hard magnetic materials should be regarded as materials consisting of the single-domain particles (crystallites). One should note, that the milling has not led to formation of a nanocrystalline structure in the Fe powder. Even after 3 h milling the average size of the crystallites was $\langle D \rangle \geqslant 40$ nm. As a consequence, the hard magnetic properties of the milled α-Fe powder were very poor ($\mu_0 H_c < 4$ mT).

According to X-ray and Mössbauer investigations, a low-temperature annealing of the milled powders led to a dissociation of FeO and the amorphous phase into α-Fe and α-Fe_3O_4 [4,5]. The powders (except for the Fe powder) after the annealing contained only α-Fe and α-Fe_3O_4 with the average crystallite size of 15–20 and 10–15 nm, respectively. (Note that the size of the single-domain particles for Fe_3O_4 is about 50 nm [11].) The amount of these constituents depended on the composition of the starting materials (Fig. 3). For example, the milled Fe_2O_3 + 50% Fe mixture after the annealing contained 47 ± 2% (37 ± 2 vol.%) of α-Fe and 53 ± 2% of Fe_3O_4.

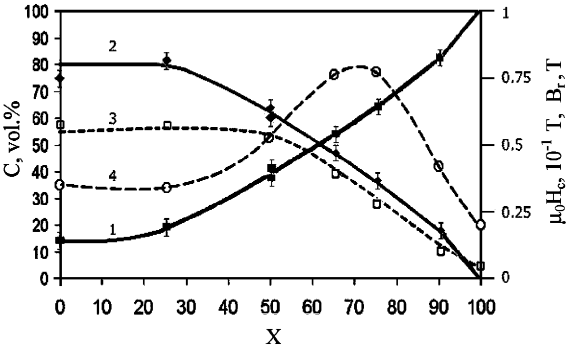

Fig. 3. Phase amount (1) α-Fe, (2) Fe_3O_4 and magnetic properties, (3) $\mu_0 H_c$, and (4) B_r of the annealed powders as a function of the starting material composition.

The annealing helps to increase the remanence, the energy product and to retain the high coercive force. The magnetic properties of the powders after the annealing also depended on the composition of the starting materials (Fig. 3). The powders for $X \leqslant 50$ had the highest values of $\mu_0 H_c \approx 60$ mT. For higher X the coercive force decreased and the annealed Fe-powder ($\langle D \rangle \geqslant 40$ nm) had $\mu_0 H_c \leqslant 5$ mT. The powders for $X = 50 \ldots 75$ had the remanence $B_r \approx 0.5$–0.8 T and the energy product $(BH)_{max} \approx 9$–14 kJ/m^3. In the other powders these values were lower and $(BH)_{max}$ was close to zero in the annealed Fe-powder.

4. Conclusions

Nanocrystalline composite alloys containing FeO, α-Fe (with the average crystallite size of 10–20 nm) and an amorphous phase were obtained as a result of high-energy ball milling of Fe_2O_3 powder and $Fe_2O_3 + X\%$Fe mixtures for $X \leqslant 75$. The milling has not led to variation of the phase composition and formation of a nanocrystalline structure in Fe powder. Unlike the starting materials, the milled powders (for $X \leqslant 75$) had properties, which are characteristic for hard magnetic materials. Further improvement of the magnetic properties was achieved by low-temperature annealing of the milled powders. The annealed powders (except for the Fe powder) after the annealing contained only α-Fe and α-Fe_3O_4 with the average crystallite size of 15–20 and 10–15 nm, respectively. The amount of these constituents and the magnetic properties of the annealed powders depended on composition of the starting materials. The sufficiently high properties of the produced powders may be explained by the formation of α-Fe and Fe_3O_4 single-domain particles.

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