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Hyperfine interactions in nanocrystalline Fe–Al alloys

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Abstract. Nanocrystalline powder samples of Fe–30 at.% Al, Fe–40 at.% Al and Fe–50 at.% Al alloys were prepared by the mechanical alloying method. X-ray diffraction studies indicated that the solid solution with bcc structure was formed with increasing milling time for all investigated compositions. The magnetic ordering temperature T_c of the nanocrystalline mechanically synthesized alloys was larger than that of the corresponding alloys on a micrometric scale. The magnetization curves as well as the Mössbauer spectra revealed that the Fe–Al alloys formed during the low energy ball milling process contained different magnetic phases.

1. Introduction

Nanocrystalline materials characterized by crystallite sizes of a few nanometres and a high grain boundary density (typically 10^{19} per cm^3) have been intensively investigated in the last years. Some magnetic properties of nanocrystals are remarkably different than those of the bulk material. A very sharp decrease of the saturation magnetization in fine ferrite particles has been observed by Sato *et al* [1] when the sizes of the particles were reduced below about 10 nm. The magnetic coercivity of nanoparticles achieves high values, for example in 4 nm grains of Fe_3C those values are three orders of magnitude higher than ones of the bulk cementite [2]. Some distinctions in hyperfine interactions, i.e. hyperfine field of nanocrystalline iron, have been observed by Schaaf *et al* [3] in comparison with α -Fe.

In this paper, we present some structural and magnetic properties of nanocrystalline Fe–Al alloys prepared by mechanosynthesis. Mechanical alloying (MA) extends the solubility of Al in the Fe lattice up to 50 at.%. It is known that the average magnetic moment per Fe atom in the disordered Fe–Al alloys decreases to zero for 40 at.% of Al and the hyperfine magnetic field reaches zero at a critical concentration of 47.5 at.% Al [4]. In our research, nanocrystalline Fe–Al alloys are still ferromagnetic for Al concentration of 50 at.%.

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2. Experiment

The powders of crystalline Fe and Al with a purity of 99.9% and particles sizes of 100 and 40 μm respectively, were mixed to give the starting Fe–30, 40 and 50 at.% Al compositions. The mechanical alloying processes were performed in a conventional horizontal low energy ball mill rotated at a speed of 120 rev min^{-1} . Stainless steel vials and balls were used. The total weight of the powders was 20 g and the ball-to-powder weight ratio was 50:1. The vials were loaded under an argon atmosphere and all powder handling was performed in a glove box. Small quantities of the powders were withdrawn at different time intervals to evaluate the extent of alloying.

During the studies several experimental techniques were applied for the structure characterization. X-ray investigations were performed on a Philips PW 1830 diffractometer in a continuous scanning mode using Cu $K\alpha$ ($\lambda = 0.154$ nm) and Co $K\alpha$ ($\lambda = 0.179$ nm) radiations. Differential scanning calorimetry (DSC) measurements were carried out in a Perkin Elmer DSC 7 unit within the temperature range 320–1000 K at a continuous heating rate of 20 K per min.

Magnetization, $\sigma(T)$, of the alloy samples of the mass of 1 to 2 mg was measured by means of a Faraday balance in magnetic fields up to 1.5 T. Relative accuracy was better than 0.5%. Measurements were performed in the high-temperature furnace. The temperature was stabilized within ± 0.5 K. The heating rate was up to 3 K per min.

Mössbauer spectroscopy studies in the standard transmission geometry were carried out for the powder samples at room temperature using a constant acceleration drive. The source was ^{57}Co in an Rh matrix with an activity of about 50 mCi.

Determinations of Ni and Cr impurities in the tested materials were made using an AAS-3 spectrometer with a deuterium-lamp background corrector, equipped with EA-3 electrothermal atomizer and MPE autosampler. The relative accuracy of the analysis was up to 5%. As the chemical analysis proved the total contamination of the alloy by Ni and Cr from the milling medium was below 0.1 at.% and the final composition of the longest milled alloys was the same as the initial one within the limit of the experimental error.

3. Results and analysis

For all compositions investigated the final products of the milling process were disordered Fe(Al) solid solutions with bcc structure as the x-ray diffraction analysis proved. The diffraction patterns of Fe–30 at.% Al, Fe–40 at.% Al and Fe–50 at.% Al were similar in shape, however they differed from each other in the intensity of the lines and their angular positions. The example of the diffraction spectra for equiatomic FeAl alloy is shown in figure 1 for various milling times. For all studied compositions the superstructure lines were not registered. The disordered bcc Fe(Al) solid solutions for Al concentration up to 50 at.% have been also observed in DC sputtered alloys [5, 6] and for high energy ball milled Fe–Al alloys [7]. For Al concentration above 50 at.% Fe–Al alloys are amorphous up to 90 at.% Al as reported in [6, 8–10].

The changes of the lattice parameter a of the mechanically alloyed Fe–Al (figure 2) were calculated from the shift of the Fe(211) diffraction line with the accuracy of 0.2%. The lattice constant increases monotonically from 0.2867 nm to 0.2915 nm, 0.2925 nm and 0.2935 nm for 30 at.% Al, 40 at.% Al and 50 at.% Al, respectively. The larger atomic size of the Al atom in comparison with the Fe atom is responsible for the increase of the lattice parameter with Al concentration and with the increasing milling time. The obtained final values of a are in good agreement with the data reported in [4–6, 11, 12].

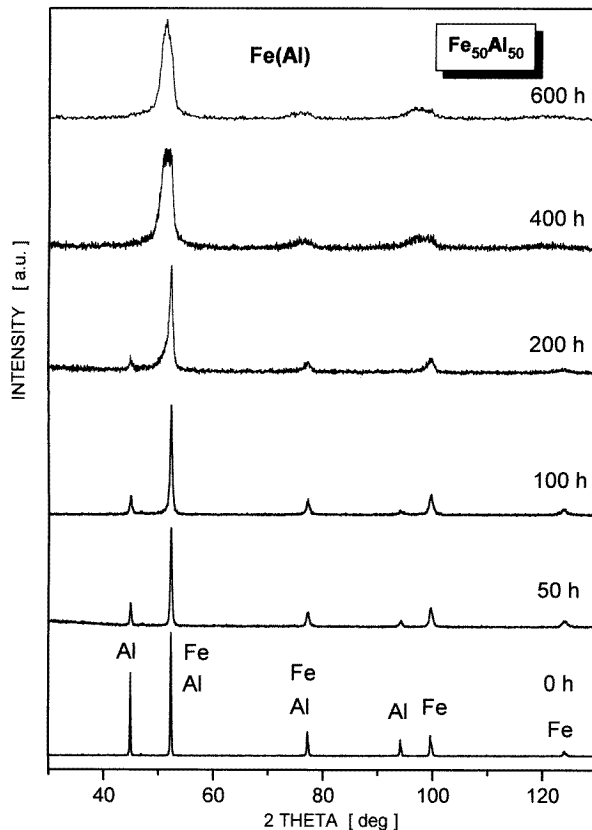


Figure 1. X-ray diffraction patterns of mechanically synthesized Fe–50 at.% Al alloy as a function of milling time.

The Williamson–Hall approach [13] was adopted to calculate the crystallite size D (figure 3(a)) and the level of internal strains e (figure 3(b)). The accuracy of the D and e parameters was $\Delta D = \pm 1$ nm and $\Delta e = \pm 0.05\%$, respectively. It may be observed that both D and e parameters depend weakly on the Al concentration while the dependences on milling time are stronger and the decrease of the crystallite sizes is accompanied by the increase of the lattice strain level when milling time increases. The milling period of 200 h seems to be the crucial time after which the grain sizes and strain level reach the saturation values.

Heating treatment performed on the final products of the mechanical alloying process in the calorimeter up to 1000 K resulted in the increase of the crystallite sizes up to 15 nm and 18 nm for Fe–30 at.% Al and Fe–40 at.% Al alloys, respectively. Significant reduction of the lattice strain was observed at the same time. X-ray diffraction analysis carried out after heating proved that the phase composition of the mechanically alloyed Fe–30 at.% Al and Fe–40 at.% Al did not change. In case of the Fe–50 at.% Al alloy an ordered FeAl intermetallic compound with a crystallite size of 10 nm was formed after heating [14].

Magnetization measurements revealed a strong ferromagnetic interaction in all studied alloys. The example of the magnetization curves for Fe–50 at.% Al alloy is shown in figure 4. It may be observed that the slope of the curves changes with rising temperature

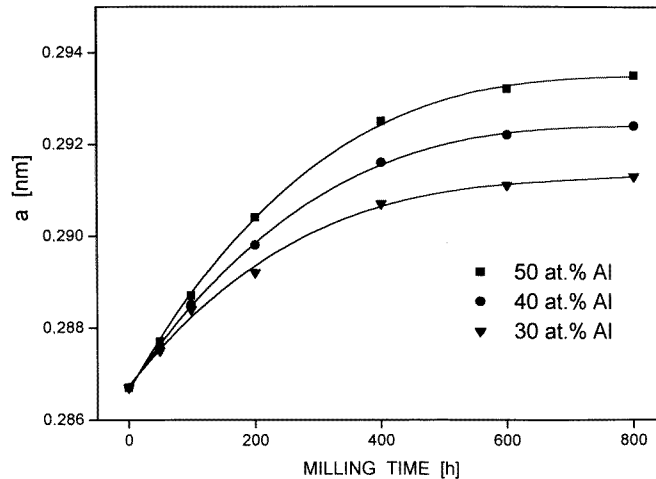


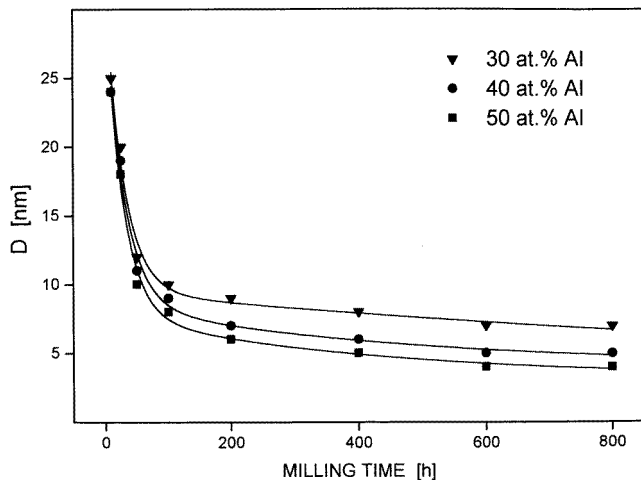
Figure 2. The changes of the lattice constants versus milling time for various Al concentration.

and for milling periods up to 200 h the intermediate phase with the Curie temperature T_c of about 650–700 K is formed during the MA process (figure 4(a)). After 400 h of milling the magnetization curves become smooth giving the magnetic ordering temperature T_c over 1000 K (figure 4(b)). Similar behaviour was observed for Fe–30 at.% Al and Fe–40 at.% Al alloys. In case of the Fe–40 at.% Al alloy the intermediate phase with T_c about 630–640 K was detected up to 200 h, while for Fe–30 at.% Al alloy a phase with T_c about 750–850 K has been registered for milling periods up to 100 h [15]. The intermediate phases arose most probably due to the moderately fast diffusion of the Al atoms into the surface layer of nanograins. These phases disappeared after 400 h of milling.

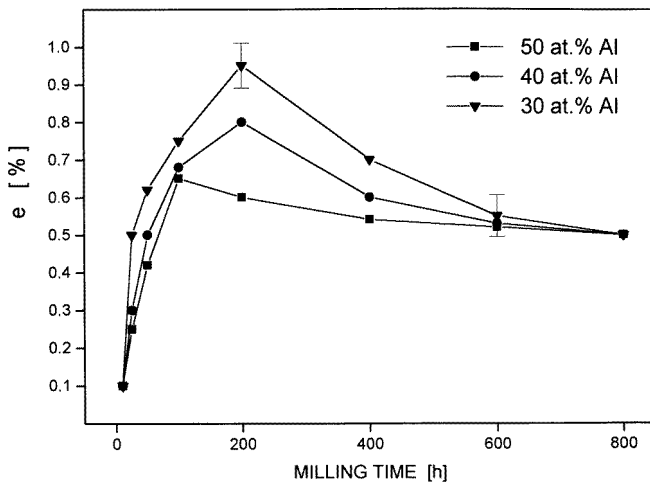
The final products of MA process have the magnetic ordering temperature T_c above 1000 K and T_c seems to be independent of the Al concentration. This is a quite different phenomenon than that observed for disordered Fe–Al alloys with the average size of particles of 1–2 μm [12], where the magnetic ordering temperature T_c decreases nonlinearly with the Al concentration. It is also worth emphasizing that T_c of nanocrystalline Fe–Al alloys is significantly larger than that of the corresponding micro-sized alloys. In the crumbled material each grain may be treated as a single magnetic domain and the change of the spontaneous magnetization of nanocrystalline powder requires a larger thermal energy supply than in the microcrystalline sample.

The room temperature magnetization σ measured for the 800 h milled Fe–30 at.% Al and Fe–40 at.% Al alloys was about 10% smaller as compared with the corresponding micro-sized alloys [11]. We observed the opposite behaviour for 800 h milled Fe–50 at.% Al alloy, where σ was about three times larger than that of the alloy with grains on the micrometric scale [11].

Mössbauer measurements allow us to observe the alloy formation at every stage of the mechanical alloying process. Figure 5 shows the Mössbauer spectra of MA equiatomic FeAl alloy for various milling times together with the hyperfine magnetic field (HMF) distributions $p(B)$ obtained by the Hesse–Rübartsch method [16]. A small peak close to zero velocity can be seen for short milling times, which could be related to the diffusion of Fe into Al. After 200 h the component with low magnetic field (B) of about 3 T can be



(a)



(b)

Figure 3. (a) Average crystallite sizes and (b) mean levels of lattice strain as a function of milling time for Al concentration of 30 at.%, 40 at.% and 50 at.%.

seen in the HMF distribution and the contribution of this component increases with milling time. Unfortunately, after prolonged milling time of 800 h a small quantity of α -Fe still exists in the sample, which is indicated by the peak within the range of 31 to 35 T in the HMF distribution. Moreover, the broad maximum between 6 and 30 T can be seen.

The Mössbauer spectra for Fe–30 at.% Al and Fe–40 at.% Al 800 h milled alloys and the corresponding distributions of the hyperfine fields are shown in figure 6 together with the data for equiatomic FeAl alloy. In case of the Fe–40 at.% Al alloy the contribution of α -Fe component is still relatively high and the HMF distribution is very broad. However, in the case of the Fe–30 at.% Al alloy the α -Fe component is completely reduced. The broad HMF distributions are result of the high grain boundary density, defects and the relatively high strain level in the longest milled alloys. For the Fe–30 at.% Al alloy the local environment

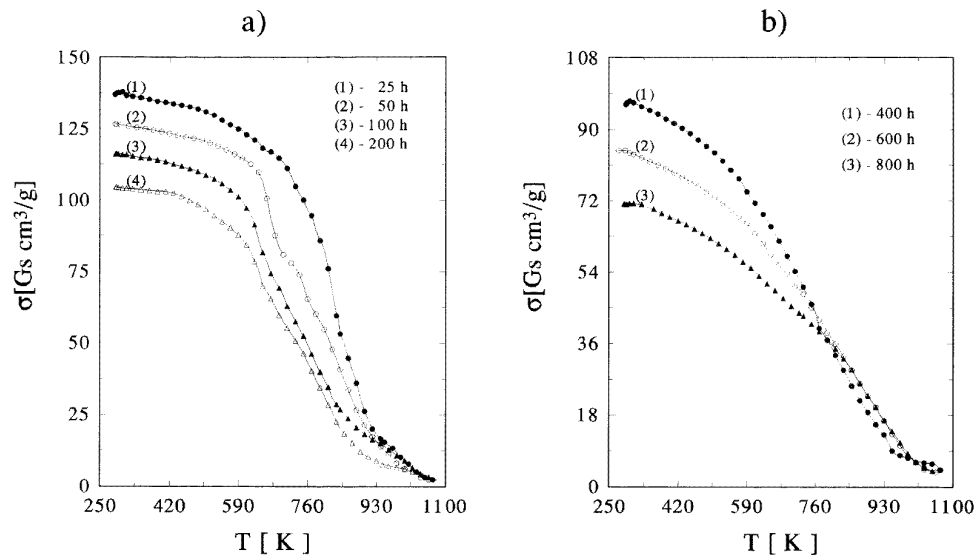


Figure 4. Temperature dependence of magnetization of mechanically synthesized Fe-50 at.% Al alloy (a) for milling times up to 200 h, (b) for 400, 600 and 800 h of milling.

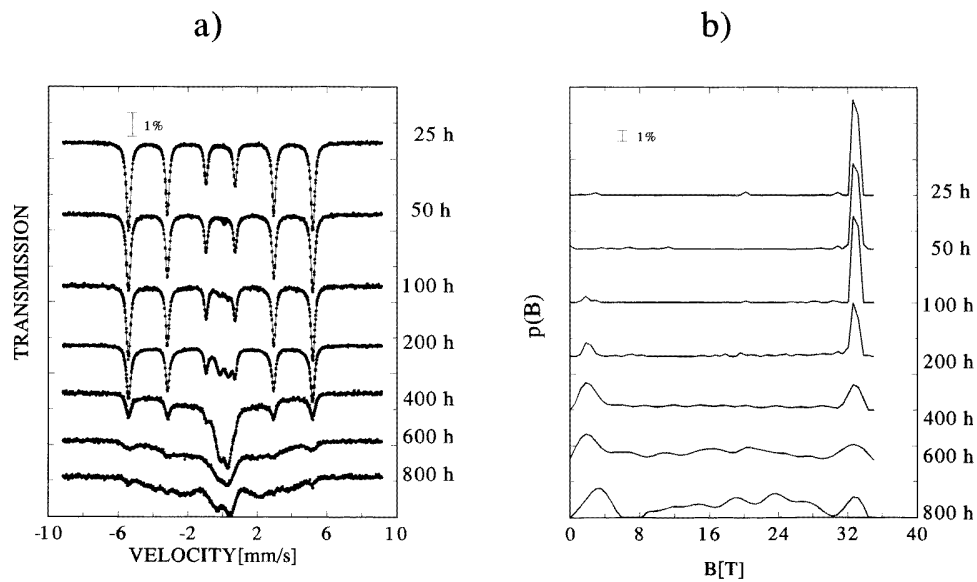


Figure 5. (a) Room-temperature Mössbauer spectra of mechanically alloyed Fe-50 at.% Al for the various milling times and (b) hyperfine magnetic field distributions.

model may be applied. The average magnetic field of about 29 T corresponds to three and fewer Al atoms as the nearest neighbourhood of the ⁵⁷Fe atom. This result is in good agreement with the data reported for the DC sputtered Fe-Al alloys [5]. In the case of the Fe-40 at.% Al and the Fe-50 at.% Al alloys any number of Al neighbours might be present.

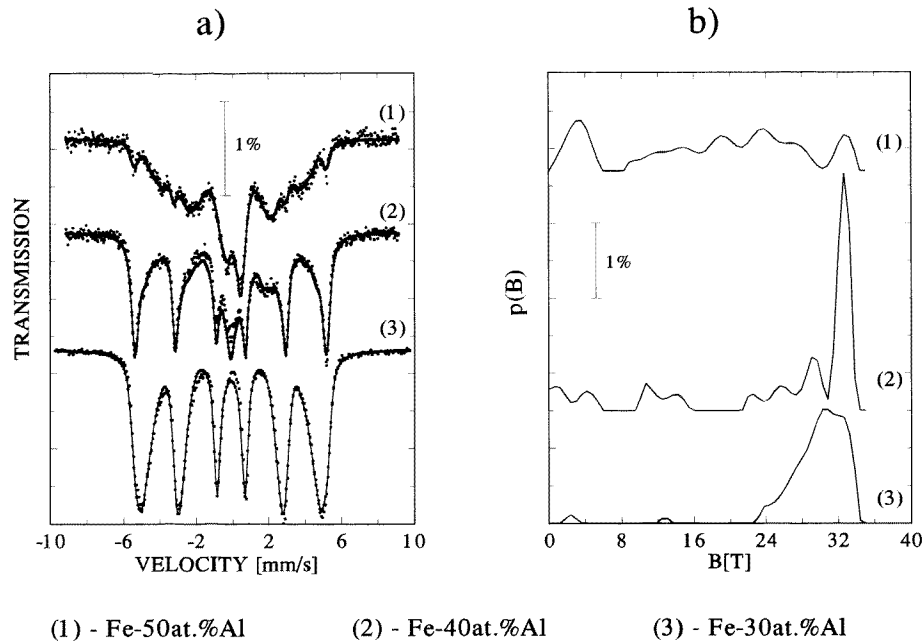


Figure 6. (a) Mössbauer spectra of 800 h milled Fe-50 at.% Al (1), Fe-40 at.% Al (2) and Fe-30 at.% Al (3) alloys and (b) the corresponding hyperfine magnetic field distributions.

4. Discussion and conclusions

The performed studies indicate a strong influence of the mechanical treatment on the magnetic properties of the investigated Fe–Al alloys. The analysis shows that prolonged milling affects the formation of nanocrystalline phase. Powder subjected to ball-milling contains a large amount of strain located probably near the boundary regions of each grain, as suggested by Nasu and Shingu [17].

The alloy Fe-50 at.% Al is of particular interest. In the disordered state of FeAl where the Al and Fe atoms randomly occupy a bcc lattice the Mössbauer spectrum is a doublet due to non-cubic Fe-site symmetry. Some groups found a doublet in the equiatomic Fe–Al alloys. For example in DC magnetron sputtered thin films of Fe–Al alloys the quadrupole splitting $\Delta = 0.35 \text{ mm s}^{-1}$ was obtained by Hsu and Chien [6]. Also Enzo *et al* observed a doublet with $\Delta = 0.48 \text{ mm s}^{-1}$ and the line width $\Gamma_{\text{exp}} = 0.50 \text{ mm s}^{-1}$ in the equiatomic FeAl alloy obtained by high energy ball milling [7]. However, a singlet spectrum was also found in the disordered FeAl alloys quenched in ice water [4]. Curiously, Bohorquez *et al* observed two paramagnetic sites in disordered FeAl alloy, i.e. a singlet and the doublet with $\Delta = 0.137 \text{ mm s}^{-1}$ and $\Gamma_{\text{exp}} = 0.32 \text{ mm s}^{-1}$ [18]. In our case, the fitting of the spectrum of 800 h milled alloy gave the quadrupole splitting $\Delta = 0.32(1) \text{ mm s}^{-1}$ and the line width $\Gamma_{\text{exp}} = 0.33(1) \text{ mm s}^{-1}$ for the doublet. However, apart from the doublet we also observed the hyperfine magnetic field distribution that revealed a relatively strong ferromagnetic interactions in MA nanocrystalline FeAl equiatomic alloy.

Summarizing, the structural investigations proved that in the low energy mechanical alloying process of iron and aluminium the disordered bcc solid solution was formed up to 50 at.% Al. The final products of milling were nanocrystalline alloys with magnetic

properties somewhat different as compared with microcrystalline alloys. The following effects were observed:

(i) the magnetic ordering temperature of the mechanically synthesized nanocrystalline Fe–Al alloys was larger than T_c of the microcrystalline alloys;

(ii) the room temperature magnetization of the nanocrystalline Fe–30 at.% Al and Fe–40 at.% Al alloys was 10% smaller than in the microcrystalline alloys while σ of the Fe–50 at.% Al alloy was about three times larger as compared with the corresponding microcrystalline alloy;

(iii) low energy ball milling allowed us to extend the solid solubility of Al in the Fe lattice up to 50 at.% Al; however the obtained alloys were highly strained;

(iv) the mechanically synthesized Fe–50 at.% Al alloy exhibited not only paramagnetic character, but also strong ferromagnetic interaction revealed both by magnetic and Mössbauer studies.

Since the structure and the lattice constants of the studied Fe–Al alloys are the same as for alloys prepared by other techniques, the observed effects seem to be caused by the influence of the grain boundaries. However, the nature of grains and grain boundaries is still under investigation.

Acknowledgments

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