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Correlations between hyperfine magnetic field and some macroscopic magnetic quantities in mechanosynthesized $Co_xFe_yNi_z$ alloys

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Abstract. In this work correlations between some macroscopic magnetic quantities and hyperfine magnetic field (HMF) were studied in the case of mechanosynthesized $Co_xFe_yNi_z$ alloys. The series of twelve samples was prepared by high energy ball milling. As the products of such process, disordered solid solutions with bcc or fcc crystalline lattice type were obtained. The magnetic measurements proved that in this case soft magnetic alloys with relatively high value of saturation magnetization were obtained. The semi-phenomenological relationship between the HMF value and the mean magnetic moment was also found for the studied samples. Moreover, correlations between some magnetic quantities and mean concentration of the $3d+4s$ electrons were investigated.

Key words: CoFeNi alloys • hyperfine interactions • mechanical alloying • Mössbauer spectroscopy • soft magnetic materials

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Introduction

The most of an industrial applications of CoFeNi alloys is connected with their soft magnetic properties (e.g. write head cores of magnetic memories). Within the space of last years numerous, scientific groups were trying to produce CoFeNi alloys with a low value of coercive field H_c and simultaneously, with a high value of saturation magnetization $\mu_0 M_s$ [1, 7, 9]. They have tried to achieve this by changing concentration of components in the alloy, using different production methods like traditional melting, electrodeposition, vacuum deposition, or applying different conditions of such processes. The ideal material for write head core production should posses: (1) low value of H_c, (2) high value of $\mu_0 M_s$, (3) low magnetostriction and (4) high corrosion resistance [9]. Applying a material with low coercive force causes lower energy consumption. Furthermore, the magnetization of the core may be switched faster, so we are able to write information at greater speed. Next, using the material with a higher value of magnetization causes a higher value of magnetic flux over a bit area and makes it possible to use harder magnetic materials for a storage medium production. Consequently, smaller bits on the surface of magnetic medium may be thermally stable what causes an increase of a disk capacity [1].

The mechanical synthesis is another method which may be used for soft magnetic CoFeNi alloys production [5]. It represents a completely new approach to alloy metals because it relies on interdiffusion of components in a solid state. High level of crystalline lattice defects and internal strains arising during milling stimulates the interdiffusion and makes it possible to overcome relatively low temperature of the process [12].

In our previous works [5, 10, 11], the series of Co-rich $Co_xFe_yNi_z$ alloys prepared by the mechanical alloying method were characterized using several experimental techniques, like X-ray diffraction, Mössbauer spectroscopy, scanning electron microscopy and macroscopic magnetic measurements. As was proved by magnetic studies, the alloys possess soft magnetic properties (coercive field H_c of the order of tens of Oe) simultaneously with relatively high values of saturation of magnetization (1.6–2.2 T). Therefore, we proposed the mechanical alloying method as potential technology for production of soft magnetic powders.

In this work the results of Mössbauer spectroscopy and macroscopic magnetic investigations obtained for mechanosynthesized $Co_xFe_yNi_z$ alloys were analyzed to study correlations between the hyperfine magnetic field (HMF) induction, B_{hf}, and the values of some magnetic quantities, like saturation magnetization, coercive field, macroscopic magnetic moment. Moreover, correlations between some magnetic quantities and mean concentration of the $3d+4s$ electrons were investigated. Such considerations are especially desirable in the context of soft magnetic materials engineering.

Experimental details

A series of twelve $Co_xFe_yNi_z$ alloys was successfully produced by the mechanical alloying (MA) method. The compositions of alloys, presented in Table 1, were chosen on the basis of literature reports which show that the best soft magnetic properties may be achieved for Co-rich samples. The Fritsch P5 high-energy ball mill with hardened steel vial and balls was used in the process of alloying. All MA processes were carried out under an argon atmosphere and lasted up to 100 h. The following experimental methods were used to investigate structural and magnetic properties of as-prepared alloys: X-ray diffraction (XRD), Mössbauer spectroscopy (MS), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), vibrating sample magnetometry (VSM), magnetic measurements with Faraday balance (FB). The description of all experimental details may be found in [10].

Results and discussion

As the products of MA, the powdered $Co_xFe_yNi_z$ alloys with an average particle size of the order of 10–20 μm were obtained. XRD and EDX investigations proved that the particles were of nanocrystalline character, i.e. they consisted of grains with an average size, D, 10–60 nm (see Table 1). After 100 h of MA process, all the samples were disordered solid solutions. The disordered atomic state of the alloys means that Co, Fe and Ni atoms occupy the lattice sites randomly. As was proved by XRD and Mössbauer spectra analysis, all the samples were one-phase systems with bcc or fcc crystalline lattice type. It is worth emphasizing that the most of samples studied in this work cannot be obtained by traditional melting in the one-phase form. It may be stated in this context that in some cases MA allows to produce unique materials which cannot be obtained by traditional methods. Detailed structural data of the $Co_xFe_yNi_z$ mechanosynthesized alloys may be found in [10].

All products of milling were subjected to comprehensive Mössbauer studies. The samples were characterized by six-line magnetic patterns with diversified values of hyperfine interactions parameters. Since the alloys were of disordered atomic character, the Mössbauer spectra were fitted using the quasi-continuous HMF distribution method in accordance with the Hesse-Rübartsch procedure [4]. Linear correlation between HMF and isomer shift (IS) as well as between HMF and quadrupole splitting (QS) was assumed. The obtained Mössbauer spectra and HMF distributions may be found in [10]. It may be noted that the shape of all HMF distributions for mechanosynthesized $Co_xFe_yNi_z$ alloys were close to the Gaussian function. This is the result of different atomic configurations occurrence in

Table 1. Selected structural and magnetic properties of mechanosynthesized $Co_xFe_yNi_z$ alloys; D – average grain size, n – mean number of $3d+4s$ electrons, B_{hf} – average hyperfine magnetic field induction, J_s – saturation magnetization, H_c – coercive field, μ – average magnetic moment per formula unit

Alloy	Lattice	D (nm)	n	B_{hf} (T)	J_s (T)	H_c (A/m)	μ (μ_B)
$Co_{40}Fe_{60}$	bcc	50(40)	8.4	35.45(10)	2.22	5403	2.26(4)
$Co_{40}Fe_{50}Ni_{10}$	bcc	60(30)	8.6	34.36(15)	1.99	3962	2.00(4)
$Co_{50}Fe_{45}Ni_5$	bcc	20(20)	8.6	33.90(10)	2.00	5228	2.02(5)
$Co_{40}Fe_{45}Ni_{15}$	bcc	20(20)	8.7	33.88(12)	1.96	2825	1.96(4)
$Co_{50}Fe_{40}Ni_{10}$	bcc	15(1)	8.7	31.38(20)	1.65	5252	1.67(5)
$Co_{60}Fe_{35}Ni_5$	bcc	40(30)	8.7	33.50(10)	1.96	3143	1.92(4)
$Co_{40}Fe_{40}Ni_{20}$	bcc	36(1)	8.8	33.10(15)	1.83	1885	1.84(3)
$Co_{50}Fe_{35}Ni_{15}$	bcc	60(30)	8.8	33.06(11)	1.82	2228	1.83(3)
$Co_{60}Fe_{30}Ni_{10}$	bcc	60(30)	8.8	32.94(10)	1.87	2657	1.92(3)
$Co_{65}Fe_{23}Ni_{12}$	fcc	10(1)	8.89	30.63(30)	1.62	4249	1.53(4)
$Co_{40}Fe_{35}Ni_{25}$	fcc	20(15)	8.9	32.76(10)	1.71	1344	1.65(3)
$Co_{52}Fe_{26}Ni_{22}$	fcc	24(1)	8.96	32.20(10)	1.68	1122	1.63(4)

the neighborhood of the ^{57}Fe nuclei. The average HMF induction values, B_{hf}, are listed in Table 1. The IS values for studied alloys were ranged from 0.02 mm/s to about 0.04 mm/s. Since the samples were characterized by a regular crystalline structure, the QS values were close to zero.

The macroscopic magnetic investigations allowed to find the values of some magnetic properties, i.e.: saturation magnetization $J_s = \mu_0 M_s$ in [T], coercive field H_c in [A/m] and the average magnetic moment of the alloy per formula unit, μ, in Bohr magnetons. Such values for each of $Co_xFe_yNi_z$ specimen are shown in Table 1. All results presented below are arranged after the quantity n, i.e. the average number of $3d+4s$ electrons per atom. For each of $Co_xFe_yNi_z$ alloy composition, the n parameter was calculated as follows:

$$n = 9x + 8y + 10z \quad (1)$$

where x, y, z denote the relative concentration of Co, Fe and Ni atoms in at.%.

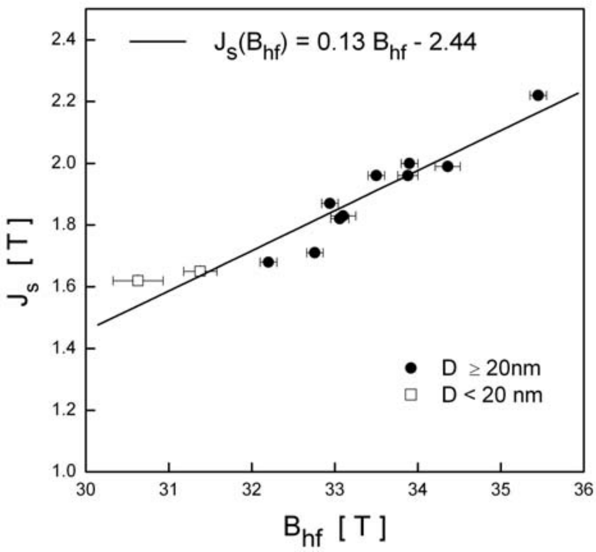

Fig. 2. Saturation magnetization vs. HMF induction for mechanosynthesized $Co_xFe_yNi_z$ alloys. The error bars of J_s do not exceed the area of points plotted on the graph.

Saturation magnetization J_s

The virgin magnetization curves were registered to obtain J_s values. They were characteristic of typical strong ferromagnets. The samples were saturated in an external magnetic field of 12 kOe ($9.5 \cdot 10^5$ A/m). Figure 1 presents the dependence of J_s on n parameter. The linear dependence is clearly visible – an increase of the average electronic concentration causes a decrease of the number of unpaired spins (a decrease of the average atomic magnetic moment). Surprisingly, the change of the type of crystalline lattice had no influence on J_s values. Significant deviation of magnetization from this tendency may be observed for $Co_{50}Fe_{40}Ni_{10}$ and $Co_{65}Fe_{23}Ni_{12}$ alloys. These are the most fine-grained samples with the average grain size of 15 nm and 10 nm, respectively. It may be estimated that for the specimen with 10 nm grains, about 30% of atoms is located at the grain boundary area. The increase of the volume of structurally disordered grain boundaries partially destroy ferromagnetic arrangement of magnetic moments.

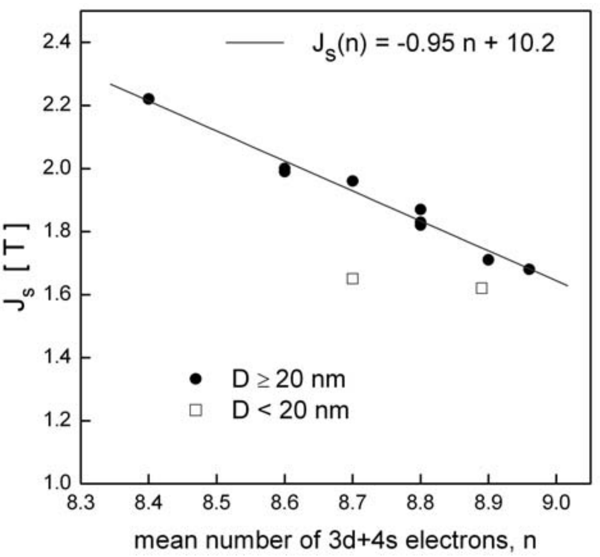

Fig. 1. The dependence of saturation magnetization on the mean number of $3d+4s$ electrons for mechanosynthesized $Co_xFe_yNi_z$ alloys. The error bars of J_s do not exceed the area of points plotted on the graph.

Figure 2 shows the dependence of J_s value on B_{hf}. The visible linear correlation may be described by the following formula:

$$J_s(B_{hf}) = C_1 < B_{hf} > -C_2 \quad (2)$$

where: $C_1 = 0.13$ and $C_2 = 2.44$ T are the constants.

It is worth noting that even the values of J_s for the most fine-grained samples may be approximated correctly by the mentioned expression.

Coercive field H_c

The magnetic hysteresis loops were registered to obtain H_c values for mechanosynthesized $Co_xFe_yNi_z$ alloys. Such values may be found in Table 1. The hysteresis loops were narrow and symmetric for all studied samples. Figure 3 presents the $H_c(n)$ dependence. The linear decrease of the coercive field with an increase of the mean electronic concentration with the rate of 7902 (A/m)/electron (99.3 Oe/electron) may be observed. An increase of the mean number of electrons on $3d$ magnetic shell causes a decrease of atomic magnetic moment. The lower atomic magnetic moment needs less energy to change its direction and lower value of H_c may be observed. In the case of alloys with smallest grains, i.e.: $Co_{50}Fe_{40}Ni_{10}$ (D = 15 nm), $Co_{65}Fe_{23}Ni_{12}$ (D = 10 nm) and $Co_{50}Fe_{45}Ni_5$ (D = 20 nm) the biggest deviation from the linear tendency may be detected. The increase of H_c value for the most fine-grained alloys is a surprising effect in the context of the opposite dependence presented by Herzer in [3]. The reason of such discrepancies may be the relatively high number of defects of the crystalline lattice and high level of internal strains which arise during the MA process.

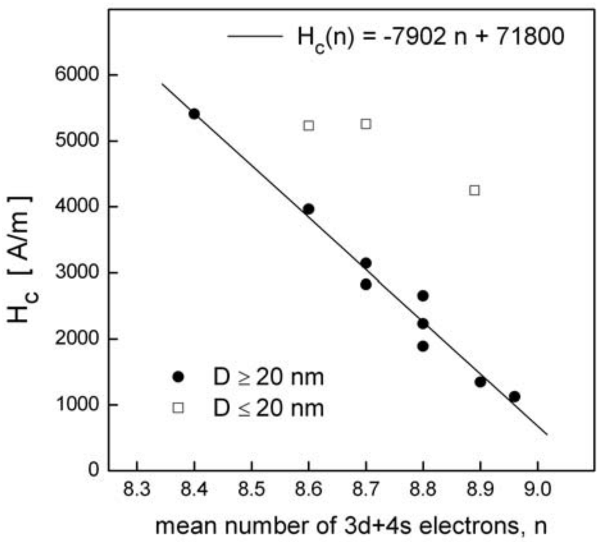

Fig. 3. The dependence of coercive field on the mean number of $3d+4s$ electrons for mechanosynthesized $Co_xFe_yNi_z$ alloys. The error bars of H_c do not exceed the area of points plotted on the graph.

The average magnetic moment per formula unit μ

The magnetization vs. temperature curves were used to obtain the values of magnetic moment per formula unit which are listed in Table 1. Figure 4 presents the values of μ as a function of n parameter given by expression (1). The linear decrease of magnetic moment with an increase of the mean number of $3d+4s$ electrons may be noted. Such a trend may by described quantitatively by the following equation:

$$\mu(n) = C_3 n + C_4 \quad (3)$$

where: $C_3 = -1.09$ μ_B/electron and $C_4 = 11.39$ μ_B are the constants.

It is important to note that the rate of magnetic moment decrease is close to the theoretical value of 1 μ_B per electron. The $\mu(n)$ dependence shown in Fig. 4 is consistent with the course of right branch of Slater-Pauling curve obtained for two-component alloys [8]. The biggest deviation from the linear trend shows again the μ values for the most fine-grained alloys.

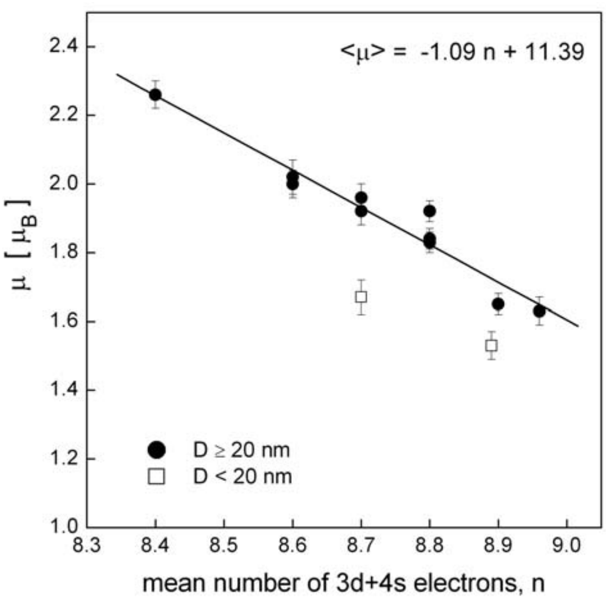

Fig. 4. The dependence of average magnetic moment per formula unit on the mean number of $3d+4s$ electrons for mechanosynthesized $Co_xFe_yNi_z$ alloys.

Mössbauer spectroscopy is the method frequently used to investigate magnetic compounds or alloys. In this case the HMF induction is taken as the main spectral parameter. Numerous authors were studying the relationship between μ and B_{hf}. It is well known that there is no such universal relationship – some iron alloys or compounds are characterized by different $\mu(B_{hf})$ functions with parameters determined experimentally [2]. It was shown in [6] that in some ranges of concentration of components the average magnetic moment of the $Co_xFe_yNi_z$ alloy may be described correctly by a simple additive model given by the expression:

$$\mu = x\mu_{Co} + y\mu_{Fe} + z\mu_{Ni} \quad (4)$$

where μ_{Co}, μ_{Fe}, μ_{Ni} denotes the atomic magnetic moment of the suitable component.

The values of μ calculated from the above formula for mechanosynthesized $Co_xFe_yNi_z$ alloys studied in this article are not consistent with the experimental data (see Fig. 5). To remove such discrepancies the additive model (4) was extended by additional term connected with HMF induction:

$$<\mu> = x\mu_{Co} + y\mu_{Fe} + z\mu_{Ni} + \frac{B_{hf} - A}{B} \quad (5)$$

where: $A = 32$ T and $B = 14$ T/μ_B are the constants determined experimentally.

The values of μ calculated from formula (5) as well as the values obtained experimentally are plotted in Fig. 6 as the functions of B_{hf}. It may be added that expression (5) consists of two parts: (I) the term connected with atomic magnetic moments of the components, and (II) the term related to the mean hyperfine magnetic field value. The first one reproduces the local curvature of experimental $\mu(B_{hf})$ plot while the second allows to follow its global tendency.

By using the extended additive model, a relatively good agreement of theoretical and experimental values

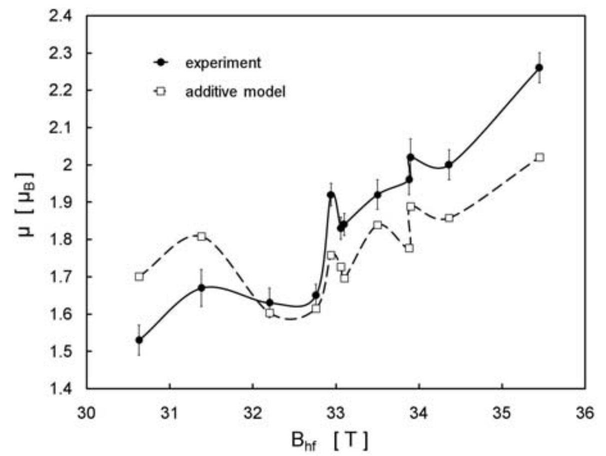

Fig. 5. The average magnetic moment vs. HMF induction for mechanosynthesized $Co_xFe_yNi_z$ alloys – comparison of experimental data and the values obtained from the additive model.

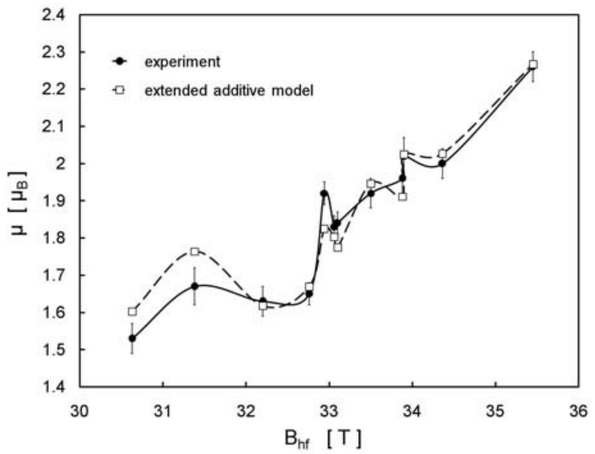

Fig. 6. The average magnetic moment vs. HMF induction for mechanosynthesized $Co_xFe_yNi_z$ alloys – comparison of experimental data and the values obtained from the extended additive model.

of μ was obtained with the exception of $Co_{50}Fe_{40}Ni_{10}$ and $Co_{65}Fe_{23}Ni_{12}$. In the case of such fine-grained samples, the experimental values of μ were less than the theoretical one by 0.09 μ_B and 0.07 μ_B, respectively.

Conclusions

On the basis of the studies performed for mechanosynthesized $Co_xFe_yNi_z$ alloys, the following conclusions can be drawn:

1. The saturation magnetization J_s is linearly correlated with the average HMF induction B_{hf}.
2. The values of coercive field H_c decreases linearly with an increase of the mean number of $3d+4s$ electrons, n.
3. Average magnetic moment μ decreases with the increase of n with the rate close to the theoretical 1 μ_B/electron value.
4. The extended additive model can be successfully used to specify correlation between the HMF induction B_{hf} and the average magnetic moment, μ, of the alloy.

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