

Hyperfine fields and magnetoelastic surface effects in $\text{Fe}_{72}\text{Cu}_{1.5}\text{Nb}_4\text{Si}_{13.5}\text{B}_9$ nanocrystalline alloy

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Abstract In this work hyperfine fields of two-phase nanocrystalline $\text{Fe}_{72}\text{Cu}_{1.5}\text{Nb}_4\text{Si}_{13.5}\text{B}_9$ alloys were studied in order to verify the existence of surface effects. To obtain a series of nanocrystalline samples with small grains of different sizes, a special non-isothermal annealing procedure of an initially amorphous ribbon was applied. In the case of samples with a significant amount of crystallites, a high field (about 27.5 T) component of continuous part of the hyperfine field distribution was found that could be attributed to boundary regions between the grains and rest of the sample. The existence of the surface effects was confirmed in the magnetostrictive experiment.

Key words FINEMET • Mössbauer spectroscopy • nanocrystalline alloys • surface effects • surface magnetostriction

Introduction

A number of specific properties – both magnetic and mechanical – of nanocrystalline alloys based on Fe are a consequence of their complex structure. Among them, so called FINEMET-type and NANOPERM systems distinguish themselves by soft magnetic behavior [3, 6, 7]. Materials constituted of iron-metalloid based alloys (70–80 at.% of Fe) with addition of Cu and Nb – in order to modify grain growth – belong to the former group. Nanocrystalline FINEMET-type alloys are produced by controlled annealing of amorphous ribbons, which results in precipitation of crystalline grains from disordered matrix. Magnetic properties of thus obtained materials strongly depend on the amount of crystalline phase, shape and size of grains, structure and chemical content of both crystalline and amorphous regions, interactions between grains and a coupling between grains and the matrix. Beside of the pure crystalline phase inside grains and the amorphous one, boundaries regions are important that comprise atoms situated on the surface of grains and in its vicinity. Although number of authors point to the role of these regions to magnetic properties of nanocrystalline alloys, it is not easy to evidence the surface effects experimentally, particularly in the case of FINEMET, because of complicated structure of grains in these materials. High initial magnetic permeability and low coercivity are characteristic of nanocrystalline FINEMET ribbons. Excellent soft magnetic properties of these alloys are relevant to the very small value of magnetostriction, which plays an important role on properties of systems with various coexisting phases distributed in regions of nanometers sizes, because of stresses involved by different atomic arrangement and, consequently, different density, thermal expansion and other real physical peculiarities.

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Sample	Annealing conditions			TEM <i>D</i> (nm)	X-ray diffractometry		
					<i>D</i> (nm)	<i>p</i> (%)	<i>x</i> _{Si} (at.%)
1	as quenched			–	–	0	–
2	↑200°C/min	[600°C]	↓200°C/min	~7	5.2 ± 0.4	25.0 ± 0.8	18.6
3	↑200°C/min	[610°C]	↓200°C/min	–	8.4 ± 0.2	38.2 ± 0.2	18.2
4	↑200°C/min	[620°C]	↓200°C/min	–	10.5 ± 0.1	51.7 ± 0.1	18.6
5	↑200°C/min	[630°C]	↓200°C/min	~10	10.0 ± 0.4	54.1 ± 0.1	18.6
6	↑200°C/min	[725°C]	↓200°C/min	~12	12.1 ± 0.1	73.1 ± 0.2	18.5

Table 1. Samples characterization results from X-ray diffractometry and TEM. *D* means an average size of grains, *p* – percentage of crystalline phase, *x*_{Si} – silicon content of grains.

Experimental details and characterization of samples

FINEMET-type family derives from the alloy with the nominal composition of Fe_{73.5}Cu₁Nb₃Si₁₃B₉ [5, 15]. In order to prepare a series of nanocrystalline samples with small grain sizes and a large amount of surface regions, an initially amorphous ribbon of modified content of Fe₇₂Cu_{1.5}Nb₄Si_{13.5}B₉ (with small excess of niobium and copper in relation to classical FINEMET), obtained by the rapid quenching method, was subjected to a non-isothermal annealing process. In the first stage of annealing, the temperature was raised in about 3 min to the maximal value 600–725°C for various samples, and in the second one the temperature was reduced with a similar rate. A small furnace connected with a DSC set (differential scanning calorimetry) made it possible precise control of temperature variations. This complicated procedure enabled effective production of small crystallites of different sizes, depending on the maximum temperature applied.

Samples have been characterized by X-ray diffractometry and electron microscopy. Sizes of crystalline grains have been evaluated from the width of reflections. Independently, these values were derived from electron micrographs. Average diameter values fall in the range 5 nm < *D* < 12 nm; the larger sizes correspond to higher maximum temperature of the heat treatment procedure (Table 1). Moreover, an increase of temperature causes the growth of crystalline phase content found from X-ray diffractograms. Sharp Bragg reflections correspond to the crystallites whereas the smeared ones come from the amorphous matrix. From the relative contributions of these two components it is possible to estimate a crystalline volumetric fraction (the method used e.g. in [4]). However,

the precision of this evaluation is limited by the broadening of peaks because of the small grain sizes and other effects [7]. On the basis of precisely derived unit cell constant, the silicon content of grains *x*_{Si} was evaluated. For all samples *x*_{Si} ≈ 18.5%, that corresponds to disordered DO₃ structure.

In order to examine the local properties of investigated alloys, transmission Mössbauer spectroscopy based on ⁵⁷Fe was employed. Room temperature measurements were performed using a standard spectrometer with a Co(Rh) source, in constant acceleration mode.

Hyperfine fields

The Mössbauer spectrum of the amorphous ribbon that makes a precursor of other samples takes shape of a broadened Zeeman sextet (typical for such materials) with a nearly symmetric single peak of hyperfine field distribution (HFD) and an average hyperfine field of about 19.5 T. In the case of nanocrystalline samples, complex Mössbauer spectra are observed, because of the coexistence of amorphous and crystalline phases (Fig. 1). Additionally, due to comprising of silicon, which enters into the grains, there are several non-equivalent positions of iron atoms in crystalline enclaves represented by a set of sharp sextets in the spectra. In almost all spectra the best fit was achieved using the continuous (histogram-like) HFD for amorphous remainder and five sharp Zeeman sextets (with hyperfine fields values of 31.3–32.0 T, 30.2–31.0 T, 27.2–28.5 T, 24.1–24.2 T, 19.3–20.7 T), attributed to the Fe-Si system with DO₃-type structure and containing about 18–19 at.% of Si [2, 8]. Fitting procedure was performed with the MOSFIT program [14]. A slight evolution of the hyperfine

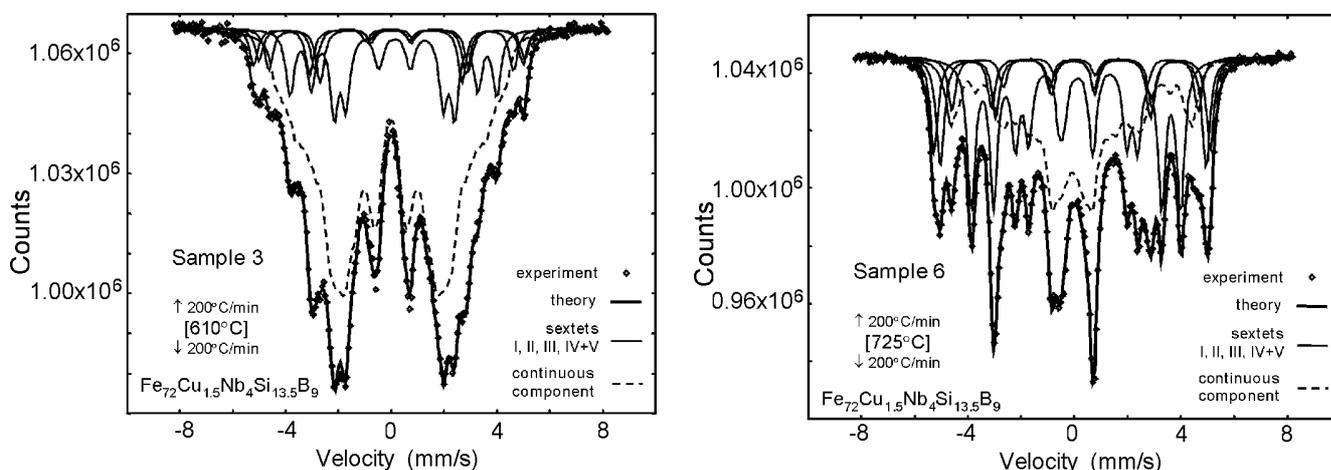


Fig. 1. Room temperature Mössbauer spectra of selected nanocrystalline samples and subspectra obtained by the fitting procedure.

Table 2. Percentage of Mössbauer subspectra (individual Zeeman sextets I–V, sum of sextets z , sum of sextets and interfaces z') and corresponding values of: volumetric fraction of crystallites $p = z x/y$, ($x = 0.72$, $y = 0.815$), volumetric fraction of crystallites + interfaces: $p' = z' x/y$, percentage p_i and width $h_i \approx p_i R/3p$ of interfaces (R – average radius of grains).

Sample	Zeeman sextets contributions (%)					Crystalline fraction (%)				p_i (%)	h_i (nm)
	I	II	III	IV	V	z	p	z'	p'		
1	–	–	–	–	–	0	–	–	–	–	–
2	0.4	3.1	4.3	6.5	4.4	18.7	16.5	–	–	–	–
3	5.0	4.4	5.7	8.6	7.7	31.4	27.7	–	–	–	–
4	9.8	5.7	5.1	11.6	11.7	42.9	37.9	~48	~43	~5	~0.2
5	6.0	10.2	5.6	14.7	14.1	50.6	44.7	~59	~52	~8	~0.3
6	10.3	12.1	5.9	16.2	15.7	60.2	53.2	~74	~66	~14	~0.5

fields was observed, inconsistently with X-ray diffraction results. No distinct magnetic texture was found.

From the spectral area of the sextets, the relative content of iron atoms in individual phases z was evaluated. Depending on the heat treatment conditions, from 19 to 60 at.% of iron atoms belong to crystalline grains. The corresponding values of volumetric fraction of crystallites, $p = z x/y$, ($x = 0.72$, $y = 0.815$ – Fe atoms fraction in initial material and in crystallites, respectively) are several atomic per cent smaller than that derived from X-ray diffractometry (Table 2). The hyperfine field distribution obtained for the amorphous remainder shows a smeared shape. In the case of samples with the larger content of crystalline phase, an additional small maximum at about 27.5 T is visible (Fig. 2) that could be attributed to boundary (surface) regions between grains and the rest of sample. The similar surface contribution was observed in NANOPERM as reported in several papers, for instance [1, 6]. In the case of FINEMET alloys, it is more difficult to distinguish the interfacial component due to the presence of Si in the crystallites and, consequently, the complex structure of Mössbauer spectra. It would be reasonable to consider also other possible sources of the high-field component in HFD – such as Nb- or Cu-rich phases in the amorphous matrix. However, the expected hyperfine field values of them are rather low. The presence of magnetostrictive surface effects (described in the next section) is an additional argument for attributing the observed HFD component to the surface regions.

The sum p' of intensity of the “surface” component p_i and the “crystalline” one ($p' = p + p_i$) is in better agreement with X-ray results. The small discrepancies can be explained by the difficulties in separating of a discrete component from the continuous one in the Mössbauer spectra as well as in diffractograms. Taking into account values of p' , p_i and the average radius of grains R , the width of interfaces $h_i \approx p_i R/3p$ was evaluated (Table 2), which increases with rising R and falls in the range 0.2–0.5 nm. This means that one or two atomic layers at the boundary of grains belong to the mixed phase, the properties of which are different from those of the crystalline grains and the amorphous matrix. The dissimilarities in width of this area can be related to different heat treatment. Higher maximum temperature and larger heating rate are propitious to the faster grain growth; at the same time, because of the different structure and chemical content of crystalline and amorphous phases as well as because of confined diffusion rate, this causes a stronger distinction between the amorphous matrix and broader interfaces.

Magnetostriction

In the case of nanocrystalline systems obtained by controlled annealing of amorphous ribbons, the coexistence of crystalline and amorphous phases plays an important part to the magnetoelastic behavior [5, 9, 10–13]. The model proposed by Herzer for the effective magnetostriction constant λ^{eff} in a two-phase nanocrystalline system [1], based on the balance of the magnetostriction between the grains and the residual amorphous matrix, predicts the linear dependence of λ^{eff} on the volumetric fraction of crystalline phase p . In classical nanocrystalline FINEMET and some NANOPERM alloys (for instance FeZrB(Cu)) contributions originated from both phases have an opposite sign, so for a sufficiently large value of p , the effective magnetostriction constant approaches zero. Significant deviations from this simple model of effective magnetostriction are observed in real systems, which can be explained in context of two different effects: (i) the evolution of magnetostrictive properties of amorphous matrix upon the crystallization process, (ii) the contribution of crystallites surfaces and interfaces to the effective magnetostriction. Both effects are included in the following relation [10–13]:

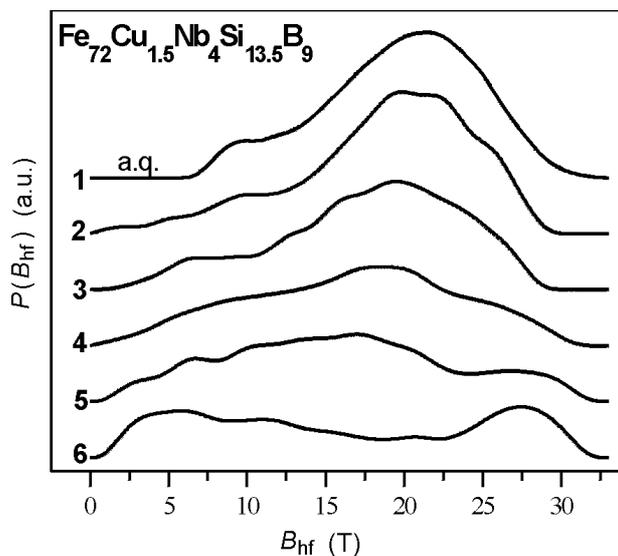


Fig. 2. A continuous part of hyperfine field distribution derived for samples subjected to various kind of the heating procedure (see Table 1).

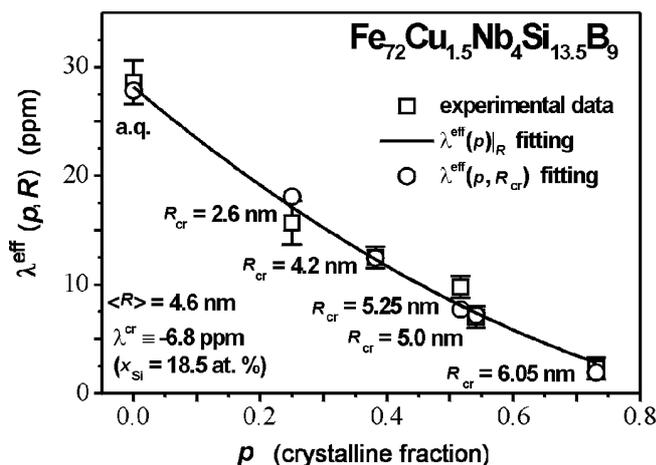


Fig. 3. Effective saturation magnetostriction constant plotted with crystalline fraction obtained by X-ray spectrometry.

$$\lambda^{\text{eff}} = p\lambda^{\text{cr}} + (1-p)(\lambda_0^{\text{am}} + kp) + 3p\lambda^{\text{s}}/R,$$

where λ^{cr} means crystallites magnetostriction constant, λ^{s} – surface constant, λ_0^{am} – amorphous matrix constant, k – parameter of matrix magnetostriction evolution, R – average radius of grains.

Magnetoelastic properties were examined using a SMFMR technique (strain-modulated ferromagnetic resonance). FONER-type magnetometry results showed that resonant field of the order of 0.1 T, used for SMFMR experiment, is sufficient to saturate a magnetization, so saturation magnetostriction constant was measured. On the basis of above dependence, the results were fitted by two means (Fig. 3): (i) the effective saturation magnetostriction constant λ^{eff} was analyzed as a function of crystalline fraction p ; a constant, average radius $R = \langle R \rangle = 4.6$ nm of nanocrystallites was assumed, (ii) $\lambda^{\text{eff}}(p, R)$ was fitted as a function of two variables p, R . In both cases, we used $\lambda^{\text{cr}} = -6.8$ ppm, the value characteristic for polycrystalline $\text{Fe}_{71.5}\text{Si}_{18.5}$ alloys; $\lambda^{\text{s}}, \lambda_0^{\text{am}}$ and k were fitting parameters. The obtained results, collected in Table 3, point to the presence of significant surface effects in the grains – the value of average surface magnetostriction constant $\lambda^{\text{s}} \approx 8.5$ ppm·nm (which is positive, as for the amorphous residue) is about 50% higher than in classical FINEMET [10, 12]. Moreover, some arguments were found, which support the surface magnetostriction constant evolution when changing the annealing conditions and, consequently, the size of nanocrystallites. Besides, the strong decrease of the amorphous matrix magnetostriction in the course of crystallization is confirmed, because of the significant value of $k = -19.4$ ppm.

Table 3. Values of parameters (λ_0^{am}, k and λ^{s} – see text) obtained from fitting of the effective magnetostriction constant for $\text{Fe}_{72}\text{Cu}_{1.5}\text{Nb}_4\text{Si}_{13.5}\text{B}_9$ (see text).

$\text{Fe}_{72}\text{Cu}_{1.5}\text{Nb}_4\text{Si}_{13.5}\text{B}_9$	λ^{cr} (ppm)	λ_0^{am} (ppm)	k (ppm)	λ^{s} (ppm·nm)
Dependence: $\lambda^{\text{eff}}(p) _{R=4.6\text{ nm}}$	-6.8	28.1	-19.4	8.5
Dependence: $\lambda^{\text{eff}}(p, R)$	-6.8	27.8	-19.4	8.9

Conclusions

The non-isothermal annealing procedure and higher – than in classical FINEMET – niobium content enabled the effective production of small crystallites of different sizes on a nanometer scale. The analysis of Mössbauer spectra confirmed the coexistence of both the DO_3 -type crystalline phase and the amorphous one. Besides, an additional maximum in the hyperfine field distribution is attributed to surface and interface regions, which occur at the boundaries of grains. Likewise, surface effects are evidenced on the basis of magnetostriction investigation. The average value of the surface magnetostriction constant is about 50% larger than in classical FINEMET and seems to be dependent on heat treatment conditions. In addition, a strong evolution of magnetostriction constant of amorphous matrix was observed.

References

- Brzózka K, Ślawska-Waniewska A, Nowicki P, Jezuita K (1997) Hyperfine magnetic fields in $\text{FeZrB}(\text{Cu})$ alloys. *Mater Sci Eng A* 226/228:654–658
- Hägström L, Gránäs L, Wäppling R, Devanarayanan S (1973) Mössbauer study of ordering in FeSi alloys. *Phys Scripta* 7:125–131
- Herzer G (1993) Nanocrystalline soft magnetic materials. *Phys Scripta T* 49:307–314
- Kulik T (1998) Annealing temperature dependence of size, morphology and composition of primary crystals created in $\text{Fe}_{76.5}\text{Cu}_1\text{Si}_{13.5}\text{B}_9$ glass. *Mater Sci Forum* 269/272:707–712
- Kulik T, Hernando A (1996) Magnetoelastic properties of $\text{Fe}_{76.5-x}\text{Cu}_x\text{NbSi}_{13.5}\text{B}_9$ alloys nanocrystallized from amorphous state. *J Magn Magn Mater* 160:269–270
- Miglierini M, Grenèche JM (1997) Mössbauer spectrometry of $\text{Fe}(\text{Cu})\text{MB}$ -type nanocrystalline alloys: II. The topography of hyperfine interactions in $\text{Fe}(\text{Cu})\text{ZrB}$ alloys. *J Phys-Condens Mater* 9:2321–2347
- Miglierini M, Grenèche JM (1999) Mössbauer spectrometry applied to iron-based nanocrystalline alloys II. In: Miglierini M, Petridis D (eds) *Mössbauer spectroscopy in materials science*. Kluwer, Netherlands, pp 257–272
- Stearns MB (1963) Internal magnetic fields, isomer shifts and relative abundances of the various Fe sites in FeSi alloys. *Phys Rev* 129:1136–1144
- Szumiata T, Brzózka K, Gawroński M *et al.* (2000) Mössbauer and magnetostriction studies of crystallization process in FeCuSiB alloy. *Molecular Physics Reports* 30:159–166
- Ślawska-Waniewska A, Roig A, Molins E, Grenèche J-M, Żuberek R (1997) Surface effects in Fe-based nanocrystalline alloys. *J Appl Phys* 81:8:4652–4654
- Ślawska-Waniewska A, Żuberek R (1998) Surface magnetostriction in nanocrystalline magnets. *Electron Technology* 31:1:29–32
- Ślawska-Waniewska A, Żuberek R, González J, Szymczak H (1997) On the magnetostriction in Fe-based nanocrystalline alloys – surface and bulk contributions. In: Duhaj P, Mrafko P, Svec P (eds) *Rapidly quenched and metastable materials*. Proceedings. Elsevier, Amsterdam, pp 220–223
- Ślawska-Waniewska A, Żuberek R, Nowicki P (1996) Saturation magnetostriction of $\text{FeZrB}(\text{Cu})$ nanocrystalline alloys. *J Magn Magn Mater* 157/158:147–148
- Teillet J, Varret F (1986) MOSFIT program
- Yoshizawa Y, Oguma S, Yamauchi K (1988) New Fe-based soft magnetic alloys composed of ultrafine grain structure. *J Appl Phys* 64:6044–6046