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Effective magnetostriction in nanocrystalline alloys

A. ŚLAWSKA-WANIEWSKA*

Institute of Physics, Polish Academy of Sciences, al. Lotników 32/46, 02-668 Warszawa, Poland

Magnetostriction is one of the most important properties of magnetic materials considering both basic research and technical applications. In this paper, a review of the experimental results (both of the crystalline fraction and temperature) and theoretical models (two-component and three-component Reuss-type approximations as well as the effective-medium model) of the magnetostriction in soft magnetic nanocrystalline alloys is presented.

Key words: *nanocrystalline materials; magnetostriction; interfaces, soft magnets*

1. Introduction

Nanocrystalline alloys, produced by the controlled devitrification of the amorphous ribbons, are composed of two main magnetic phases – nano-sized crystallites embedded in a residual amorphous matrix. They exhibit exceptionally soft magnetic properties, which arise from a substantially reduced magnetic anisotropy as well as a very small effective saturation magnetostriction [1–3]. The interpretation of the magnetostrictive effects in such heterogeneous magnetic systems is a difficult problem: the properties of respective phases, complex states of the internal stresses and strains as well as magnetoelastic interactions and high density of topological defects arising at the interfaces should be considered.

In the paper, experimental results of the effective magnetostriction in the nanocrystalline alloys as well as the review of the existing phenomenological models, which are usually used to interpret the experimental dependencies, are presented.

2. Phenomenological models of the effective magnetostriction

The simplest model of the effective magnetostriction of alloys at the different stages of crystallization has been proposed by Herzer [2, 3]. It is based on the Reuss-

* E-mail: slaws@ifpan.edu.pl.

type approximation, which assumes that the stress is the same in the whole material, both in the particles and in the matrix. In this model, the effective magnetostriction λ_s^{eff} is interpreted as a volumetrically weighted balance between the positive contribution from the residual amorphous matrix and the negative one from the crystallites according to

$$\lambda_s^{\text{eff}} = p\lambda_s^{cr} + (1-p)\lambda_s^{am} \tag{1}$$

where p is the volume fraction of the crystalline phase and λ_s^{am} and λ_s^{cr} are the saturation magnetostrictions of the amorphous and crystalline phases, respectively. However, the changes in composition of the residual amorphous phase, which occur with the evolution of the crystalline fraction (leading to its enrichment with B and Nb or Zr), indicate that λ_s^{am} is not a constant value, but it is in fact a function of p. Moreover, in the Finemet-type alloys, the composition of Fe–Si crystallites, created under various annealing conditions, can be different and, therefore different λ_s^{cr} values, corresponding to the appropriate Si concentration, should be considered. The $\lambda_s^{am}(p)$ values can be found either from the measurements of the amorphous materials with the composition similar to that estimated for the residual amorphous matrix [4] or from phenomenological models [5, 6]. In the latter case, Eq. (1) can be presented in the form [6]

$$\lambda_s^{\text{eff}} = p\lambda_s^{cr} + (1-p)\left(\lambda_{so}^{am} + kp\right) \tag{2}$$

where λ_{so}^{am} is the saturation magnetostriction of the amorphous precursor and k is the parameter that expresses changes of the magnetostriction in the residual amorphous phase with the evolution of the crystalline phase.

It should be noted that this simple two-component Reuss-type approximation ignores the effects connected with the reduction of size of such systems to the nanoscale and relevant to the matter in hand, an increasing role of the interfaces. As was shown by means of the Mössbauer spectroscopy [7, 8], the properties of atoms at the interfaces differ from those located inside the crystalline and amorphous phases. In the nanocrystalline alloys, the interfacial atoms, having neither short nor long range order, create in fact an additional phase which is characterized by a high density of topological defects. When the size of the crystallites decreases, their surface-to-volume ratio dramatically increases and then the atoms situated at the interfaces play important and sometimes even dominant role in the overall behaviour of the material.

The existence of the interfacial phase in the nanocrystalline alloys, where the magnetoelastic coupling differs from those in the bulk of the two main constituent phases, as confirmed by theoretical modelling [9], led to the modification of the simple model by introducing into Eq. (2) the term that describes the interfacial contribution and depends on the surface-to-volume ratio S/V for individual crystallites [10–12]

$$\lambda_s^{\text{eff}} = p\lambda_s^{cr} + (1-p)\left(\lambda_{so}^{am} + kp\right) + p\lambda_s^s \frac{S}{V} \tag{3}$$

where λ_s^s is the saturation magnetostriction of the interfacial layer.

For spherical grains, with the average radius *R*, Eq. (3) transforms to the form

$$\lambda_s^{\text{eff}} = p\lambda_s^{cr} + (1-p)\left(\lambda_{so}^{am} + kp\right) + 3p\frac{\lambda_s^s}{R} \tag{4}$$

In this approximation, just as in the simplest model, the stresses are assumed to be the same in all phases, which is not exactly fulfilled in the nanostructures considered. Moreover, the interfacial magnetostriction constant λ_s^s used in this model was introduced by analogy to the surface magnetostriction considered for thin films and superlattices and it has the units of length [13]. The question remains whether the thickness of the interfacial layer, which is a parameter well estimated e.g. by means of the Mössbauer spectroscopy, should also be considered in this model.

The most general approach to the analysis of the effective magnetostriction in the nanocrystalline alloys has recently been proposed by Ce-Wen Nan et al. [14] who assumed that additional magnetoelastic stresses are localised at the surface of the crystallites, due to their limited radius. In this model, the interface regions surrounding the crystallites are considered as clusters of atoms having various interatomic distances. The interfacial effects are described using an effective-medium type method based on the Green-function technique [15]. It has been shown that, assuming the equal shear moduli in the whole material, the effective magnetostriction of the nanocrystalline magnetic system can be described as

$$\lambda_s^{\text{eff}} = p\left[1-\left(\frac{3\delta}{R}\right)^2\right]\lambda_s^{cr} + \left[1-\frac{3\delta}{R}\right]\lambda_s^{am} + p\left(1+\frac{3\delta}{R}\right)\frac{3\delta}{R}\lambda_s^i \tag{5}$$

where δ is the thickness of the interfacial layer and λ_s^i is its saturation magnetostriction with $\lambda_s^s = \delta\lambda_s^i$. If the thickness of the interfacial layer is negligibly small in comparison with the particle radius, i.e. $\delta/R \to 0$, this equation reduces to the three-component Reuss-type approximation given by Eq. (4).

3. Experimental results

3.1. Dependence of the effective magnetostriction on the crystalline fraction

The most widely studied nanocrystalline materials are the Finemet-type (Fe–Nb–Cu–Si–B) and Nanoperm-type (Fe–Zr–B–Cu) alloys. The typical room-temperature

experimental data for the effective magnetostriction in these alloys show that in the as-quenched state and after annealing at sufficiently low temperature (after structural relaxation) the saturation magnetostriction is positive and it is around $(20–30)\times10^{-6}$ in Finemet-type alloys [1–3] and $(2–8)\times10^{-6}$ in Nanoperm-type ones [10, 16]. After annealing at higher temperature, with the evolution of the crystalline fraction p, the magnetostriction rapidly decreases and in the fully nano-crystallized state it is close to zero. It has been shown that even the simplest two-component approximation, described by Eq. (1), gives a qualitative explanation of the $\lambda_s^{\mathrm{eff}}(p)$ dependencies and a number of room temperature experiments show that λ_s^{eff} is roughly a linear function of p [4, 17]. In turn, more accurate approximation, given by Eq. (2), used by Twarowski et al., revealed a quadratic $\lambda_s^{\mathrm{eff}}(p)$ dependence in $Fe_{73.5}Cu_1Nb_3Si_{15.5}B_7$ nonocrystalline alloys [6]. However, for $Fe_{76.5-x}Cu_1R_xSi_{15.5}B_7$ (R = V, Mo, W, Ta, Nb) alloys and for Fe–Zr–B–(Cu) materials Müller et al. [4, 5] and Ślawska-Waniewska et al. [10], respectively, have shown that the parabolic dependence for the effective magnetostriction does not fit the experimental results of $\lambda_s^{\mathrm{eff}}(p)$ (see also the dotted curve in Fig. 1(b)), indicating that in many cases the effective magnetostriction of nanocrystalline materials cannot be described as a balance between the crystalline and amorphous contributions.

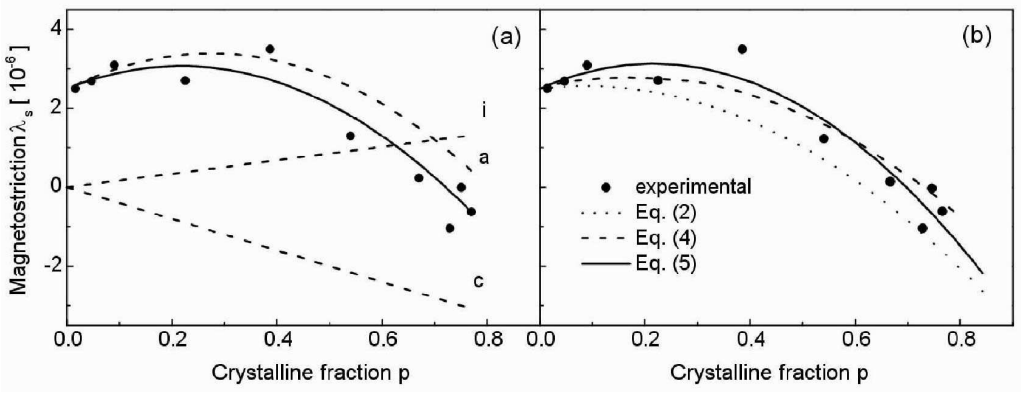

Fig. 1. Effective magnetostriction in $Fe_{85}Zr_7B_6Cu_2$ nanocrystalline alloys vs. crystalline fraction: a) broken lines correspond to crystalline *c*, amorphous *a* and interfacial *i* contributions, solid line calculated from Eq. (4); b) comparison of the experimental data and fitted curves by using two-component Reuss-type approximation (Eq. (2)), three-component Reuss-type approximation (Eq. (4)) and the effective medium model (Eq. (5) [13])

The Reuss-type approximation, which considers the interfacial effects (Eq. (3) or (4)), has been applied to analyse the experimental $\lambda_s^{\mathrm{eff}}(p)$ dependencies measured both in Finemet-type [11, 12] and Nanoperm-type [8,10] alloys. The exemplary results, obtained for $Fe_{85}Zr_7B_6Cu_2$ nanocrystalline samples, are shown in Fig. 1(a). In this figure, the contributions to the effective magnetostriction originating from the individ-

ual phases: crystalline, amorphous and interfacial are shown as broken lines (curve *c*, *a* and *i*, respectively), whereas the solid line represents the fitted $\lambda_s^{\text{eff}}(p)$ curve. In $Fe_{85}Zr_7B_6Cu_2$ nanocrystalline samples, in which the simple α-Fe crystallites are formed, the fitting of the experimental data to Eq. (3) have been performed for $\lambda_s^{cr} = -4\times10^{-6}$ (i.e., the value usually assumed for the polycrystalline iron). The parameters of this fit are as follows: $\lambda_s^s S/V = 1.71\times10^{-6}$, $k = 12.1\times10^{-6}$. The positive value of the *k*-parameter indicates that the magnetostriction of the amorphous phase increases with a decrease of Fe-content, being in an agreement with the experimental results [10]. For spherical crystallites with their radius $R \approx 5$ nm, the magnetostriction constant that describes the interface was estimated to be $\lambda_s^s \approx 2.85\times10^{-6}$ nm.

Interpretation of the $\lambda_s^{\text{eff}}(p)$ dependencies obtained for Finemet-type alloys using the model given by Eq. (4) shows that the value of the magnetostriction constant, which characterizes the crystal-amorphous interface, is in the range of $4.4\times10^{-6} \le \lambda_s^s \le 6.1\times10^{-6}$ nm [11, 12].

The model with the effective medium description of interfacial effects, given by Eq. (5), has been applied to the analysis of $\lambda_s^{\text{eff}}(p)$ dependence in the $Fe_{85}Zr_7B_6Cu_2$ nanocrystalline alloys and the results obtained are shown in Fig. 1b – solid line [14]. In this figure, the comparison of the experimental data and $\lambda_s^{\text{eff}}(p)$ curves, calculated using the three models described above (Eq. (2), Eq. (4) and Eq. (5)) is presented. It is seen that the simple balance of the crystallites and amorphous matrix contributions (Eq. (2)) does not appropriately describe the experimental data. The approximation is definitely improved when the interfacial effects are taken into account. The Reuss-type approximation (Eq. (4)) gives a lower estimate for the interface magnetostriction, $\lambda_s^i = \lambda_s^s/\delta \approx 4.5\times10^{-6}$ (where $\delta = 0.6$ nm, as was shown in [8, 12]) than the effective-medium approach (Eq. (5)) which gives $\lambda_s^i \approx 8\times10^{-6}$ [14]. This difference is mainly caused by the underestimation of the volume fraction of the interface layer by taking $\delta/R \to 0$ in the former model, which is too rough assumption for the nanostructure studied, where $\delta/R = 0.12$. Though both of these models can well approximate the experimental data, it seems that more reliable values for the interface magnetostriction constant can be obtained from the effective-medium approach.

3.2. Thermal evolution of the effective magnetostriction

The characteristic feature of the temperature dependencies of the effective magnetostriction in Finemet-type alloys is the appearance of a compensation temperature, defined as the temperature at which the magnetostriction becomes zero [6, 18, 19]. The experimental data obtained for selected $Fe_{73.5}Cu_1Nb_3Si_{15.5}B_7$ samples are presented in Fig. 2(a). The most surprising results regarding $\lambda_s^{\text{eff}}(T)$ dependence are

obtained at temperatures above the Curie point of the amorphous matrix T_C (*am*). Instead of negative magnetostriction, expected from the balance (Eq. (1)) between the negative contribution of Fe-Si grains and vanishing contribution from the residual amorphous matrix, Nielsen et al. [20] revealed that at $T > T_C$ (*am*) the experimentally observed λ_s^{eff} values were either close to zero or positive. This indicated again that the effective magnetostriction of the nanocrystalline materials is more complex than that described by the simple two-component Reuss-type model given by Eq. (1).

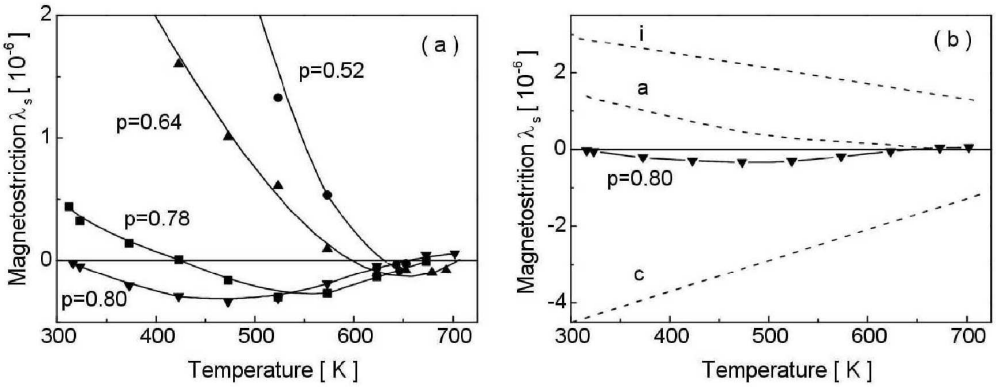

Fig. 2. Temperature dependencies of the effective magnetostriction in $Fe_{73.5}Cu_1Nb_3Si_{15.5}B_7$ nanocrystalline alloys: a) with different crystallite content; b) for $p = 0.80$; broken lines correspond to crystalline *c*, amorphous *a* and interfacial *i* contributions calculated by using the three-component Reuss-type approximation (Eq. (4))

The most detailed studies of the thermal evolution of the effective magnetostriction in the Finemet-type alloys were conducted by Grössinger et al. [18, 19] who have also measured the temperature dependencies of the saturation magnetostriction in the micro-crystalline Fe-Si alloys and used these results as reference data to model the behaviour of the crystalline phase in nanocrystalline alloys. The interpretation of the effective magnetostriction was made within the framework of the model described by Eq. (1), whereas the thermal dependencies for the individual components were described by the critical exponent method. The exemplary experimental data, obtained for $Fe_{73.5}Cu_1Nb_3Si_{16.5}B_6$ nanocrystalline alloy, containing about 78% of $Fe_{80}Si_{20}$ crystalline phase, as well as those for the micro-crystalline $Fe_{80}Si_{20}$ are shown in Fig. 3a. The apparent magnetostriction of the residual amorphous phase λ_s^{am}, presented in this figure, was calculated from Eq. (1) using for λ_s^{cr} the values obtained for the micro-crystalline counterpart. In this sample, as well as in many other Finemet-type alloys of $Fe_{96-z}Cu_1Nb_3Si_yB_w$ compositions (y = 14.5, 15.5, 16.5, 17.5, 18.5 and w = 5, 7) with $p(Fe_{80}Si_{20}) \approx 70\%$, Grössinger et al. [18, 19] have found remarkable and positive λ_s^{am} values (Fig. 3b) – at temperatures above the usually determined Curie temperature of

the amorphous phase (T_c^{am} ~575 K). The observed $\lambda_s^{am}(T)$ behaviour was ascribed to an enhancement of the Curie temperature of the remaining amorphous phase after annealing due to an exchange, driven polarization of the matrix by ferromagnetic grains, postulated by Hernando [21]. A simple linear regression of the $\lambda_s^{am}(T)$ dependencies presented in Fig. 3b indicates that λ_s^{am} does not vanish up to the Curie temperature of the crystalline phase (~870 K) (see the dotted line in Fig. 3a); therefore, the increase of the Curie point of the amorphous phase should exceed 250 K. It ought to be noticed that such an enhancement of T_c^{am}, estimated from the magnetostriction measurements [18, 19], is neither supported by the magnetization nor by Mössbauer spectroscopy measurements and has never been observed in the nanocrystalline alloys.

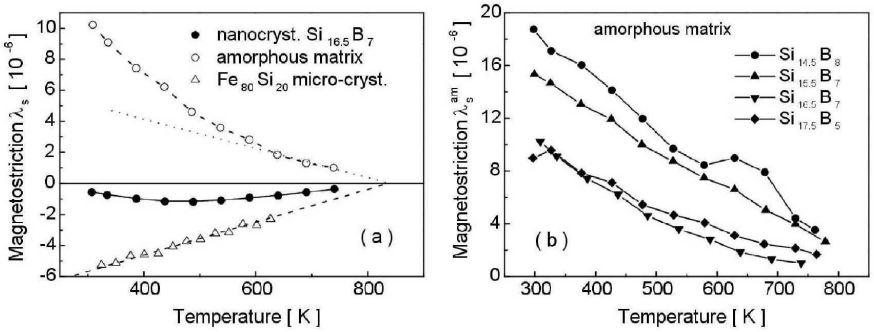

Fig. 3. Temperature dependencies of the saturation magnetostriction:
a) measured in $Fe_{72.5}Cu_1Nb_3Si_{16.5}B_7$ nanocrystalline alloy with $p = 0.74$ (closed circles) [18], $Fe_{80}Si_{20}$ microcrystalline alloy (open triangles) [19] and λ_s^{am} calculated from Eq. (1) (open circles); the dotted line represent the possible interfacial magnetostriction; b) of the residual amorphous matrix calculated from Eq. (1) for $Fe_{96-z}Cu_1Nb_3Si_yB_w$ alloys annealed at 813 K for 1 h (after [18])

The interpretation of the $\lambda_s^{\text{eff}}(T)$ dependencies becomes clearer when considering the additional positive contribution from the interfacial phase. Since the interfaces exhibit a magnetic ordering at elevated temperatures (far above the Curie point of the amorphous alloy), as was shown by the Mössbauer spectroscopy investigations [7, 12], this interfacial contribution can account for the observed $\lambda_s^{\text{eff}}(T)$ dependencies. The three-component Reuss-type approximation given by Eq. (4) was applied to analyse the experimental data presented in Fig. 2a, and the exemplary results obtained for the sample with $p = 0.8$ are presented in Fig. 2b. The crystalline, amorphous and interfacial contributions are shown as broken lines (curve *c*, *a* and *i*, respectively). The contribution from the crystalline phase was estimated based on the temperature dependence of the saturation magnetostriction reported by Grössinger et al. [18, 19] in $Fe_{80}Si_{20}$ microcrystalline ribbon (see also open triangles in Fig. 3a). The contribution from the inter-

faces was calculated assuming that at a room temperature λ_s^s has a value obtained from $\lambda_s^{\text{eff}}(p)$ fitting in the Finemet-type alloys ($\lambda_s^s \approx 6\times10^{-6}$ nm) and decreases with increasing temperature. The contribution from the residual amorphous matrix obtained from the three-component model given by Eq. (4) is small and, moreover, vanishes at $T \approx T_c^{am}$ which seems to have more physical meaning than the $\lambda_s^{am}(T)$ results shown in Fig. 3b and found from the two-component model (Eq. (1)). Considering the above, the apparent large, positive magnetostriction of the amorphous phase $\lambda_s^{am}(T)$, found even at the highest temperatures applied ($T >> T_c^{am}$) [18, 19] (Fig. 3b), should be interpreted as originating, in fact, from two terms: a contribution from the residual amorphous matrix (much reduced in comparison with the results presented in this figure) and a contribution from the interfacial phase which becomes dominant with increasing temperature and is responsible for the positive values of the effective magnetostriction observed at high temperatures (the dotted line in Fig 3a).

4. Conclusions

Three phenomenological models of the effective magnetostriction in nanoncrystalline alloys are presented: one considers only the crystalline and amorphous matrix contributions and two others take additionally into account a contribution from the interfaces formed at crystallite–matrix boundaries, i.e. the Reuss-type approximation and the effective medium model. Application of these models to the analysis of the experimental dependencies of the effective magnetostriction on the crystalline fraction as well as on the temperature show that the simple two-component model is not sufficient to describe the experimental data and only the models which take into account the interfacial effects can well approximate the dependencies $\lambda_s^{\text{eff}}(p)$ and $\lambda_s^{\text{eff}}(T)$. The most important outcome of the analysis carried out within these models is that the interfacial magnetostriction has positive values, while the saturation magnetostrictions of the corresponding bulk crystals are negative. Although both of these models give satisfactory fitting of the experimental curves, it seems that a more complex model based on the effective medium description, in which local magnetoelastic effects (characteristic of individual phases) as well as the thickness of the interfacial layer are considered, gives more reliable values of the saturation magnetostriction.

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