

Magnetostrictive behaviour of $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_{3-x}\text{Mo}_x\text{Cu}_1$ alloys

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ABSTRACT

Magnetostriction, dilatation and calorimetric measurements were performed on FINEMET type as-quenched and heat treated ribbons. Nb was gradually replaced by Mo in order to study the influence of the refractory elements exchange on several magnetostriction parameters. The results could be correlated with magnetic and structural transformations throughout thermal treatments and assured that the whole series is suitable for technical applications.

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1. Introduction

Magnetostriction is the deformation of a material due to a change in its magnetization. This physical property is important from the technological point of view since it significantly influences the performance of ferromagnetic materials. Its value depends on external conditions (temperature, applied field, stress, etc.) and on the intrinsic properties of the material (chemical and topological short range order CRSO and TSRO, respectively, homogeneity, density, internal stresses and shape) [1–3].

The spontaneous volume magnetostriction of a solid is defined as a relative volume reduction between the magnetically ordered ground state and a paramagnetic state. Therefore, it can be obtained from the following equation [4]:

$$\omega_{\text{spont}} = 3 \int_0^{T_C} (\alpha_f - \alpha_p) dT \quad (1)$$

where α_f and α_p are the ferromagnetic and paramagnetic thermal expansion coefficients, respectively.

Eq. (1) leads to

$$\omega_{\text{spont}} = 3[(\Delta l/l)_f - (\Delta l/l)_p] \quad (2)$$

where $(\Delta l/l)_p$ and $(\Delta l/l)_f$ are the thermal expansion terms in the hypothetical paramagnetic and in ferromagnetic state, respectively. Then, ω_{spont} below T_C can be graphically calculated from thermal expansion curves by subtracting $(\Delta l/l)_p$ from $(\Delta l/l)_f$. The evaluation

of $(\Delta l/l)_p$ is quite difficult to carry out because of the absence of theoretical background and, in the case of amorphous materials, flow and crystallization during heating are additional difficulties. Different approaches were performed by several authors in order to choose the appropriate $(\Delta l/l)_p$ for amorphous alloys [4,5]. This choice depends on the values of the Curie, crystallization and glass temperatures. As the material flows when heated above its glass temperature (T_g) and in the studied alloys (FINEMETs) T_g is very close to T_C , it is not possible to extrapolate the dilatation curve above T_C to obtain ω_{spont} . Accordingly, following the procedure introduced by Vlasák and Švec [6] we used the curve corresponding to the crystalline paramagnetic phase for each alloy in order to calculate ω_{spont} (Fig. 2).

The Invar effect is characterized by a very small or even negative thermal expansion coefficient below T_C which is caused by a negative contribution to the thermal expansion coefficient product of the magnetic properties of the alloy. This behaviour has been observed in different systems whether ferromagnetic or antiferromagnetic, composed by two, three or even more elements. The Invar effect is not influenced by the lattice parameter and is present in systems with diverse crystalline structures, e.g. fcc, bcc, hexagonal, etc., as well as in amorphous samples. In order to have Invar effect it is crucial for the alloy to be rich in at least one 3d transition element [7]. Another characteristic of the Invar effect is the large spontaneous volume magnetostriction that these alloys present [8].

Over the last years, soft magnetic nanocrystalline alloys have led to an increasing interest for both scientific and technological purposes due to their two-phase structure and excellent magnetic properties. The first system was developed by Yoshizawa et al. [9] and was called FINEMET ($\text{Fe}_{73.5}\text{Si}_{13.5}\text{Nb}_3\text{B}_9\text{Cu}_1$). The nanocrystallization of

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Fe–Si phase is obtained after a controlled annealing of amorphous samples: Cu increases the nucleation rate of Fe–Si crystallites and favours homogeneous nanocrystallization process, whereas Nb hinders the growth of the grains [10]. Herzer [11] explained that by keeping the grain dimensions below the ferromagnetic exchange length, random anisotropy distribution of homogeneously distributed nanocrystals leads to low magnetocrystalline anisotropy. In addition, this composite structure leads to the compensation of the magnetostriction between the amorphous (positive contribution) and crystalline (negative contribution) phases, thus decreasing the magnetoelastic energy.

Some Chinese and Russian works [12–15] have reported a great increase in the permeability of this material when Nb was partially replaced by Mo. In order to understand this interesting and unexpected behaviour, which was not explained by the authors, we have begun to characterize several physical properties of this system. X-ray diffraction, Mössbauer spectroscopy and coercivity were studied in Refs. [16,17]. The present paper discusses experimental results of spontaneous volume magnetostriction, magnetostriction, volume magnetostriction and forced volume magnetostriction obtained for $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_{3-x}\text{Mo}_x\text{Cu}_1$ alloys. The aim of this work is to verify if there is any significant influence on these last properties with the Nb by Mo replacement and at the same time to have the materials well characterized for future applications.

2. Experimental

FINEMET ribbons (10 mm wide and 20 μm thick) in which Nb was gradually replaced by Mo ($\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_{3-x}\text{Mo}_x\text{Cu}_1$; $x=0, 1, 1.5, 2$ and 3 , named Mo0, Mo1, Mo1.5, Mo2 and Mo3, respectively) were prepared by planar flow casting technique in air. Their chemical composition was checked by inductively coupled plasma spectroscopy. The samples were heat treated at 813 K for 1 h under vacuum to induce the crystallization of FeSi nanograins with DO3 structure. X-ray diffraction (XRD) analysis was done on as-quenched and annealed ribbons checking both, amorphous state on the as-quenched ribbons and FeSi precipitation after annealing. XRD was performed using a HZG 4 with graphite monochromator $\text{Cu K}\alpha_1$ radiation. The field dependence of the parallel ($\lambda_{\parallel}(H)$) and perpendicular ($\lambda_{\perp}(H)$) magnetostriction in the sample plane was measured at room temperature on the as-quenched as well as on the heat treated samples. A magnetic field was applied in the sample plane along the ribbon axis and in the perpendicular direction. A special device for direct measurement of magnetostriction designed and constructed at the Institute of Physics SAS [18] was used. The dilatometer described in [6] was employed for measuring the length dependence with temperature for the samples under the following two different conditions: (1) continuous heating run (5 K/min) of the as-quenched sample from room temperature up to 900 K and a subsequent cooling from 900 K to room temperature and (2) same heat treatment but with the sample previously relaxed as follows: continuous heating run (5 K/min) from room temperature up to 623 K and a subsequent cooling down to room temperature at the same velocity. Since in dilatation experiments we have measured only one dimension (length) we will use Eq. (2) divided by 3 and the results will be the ω_{spont} in the longitudinal direction. The Curie temperature of the amorphous samples was obtained by differential scanning calorimetry (DSC).

3. Results and discussion

The phenomenological description of magnetoelastic coupling in isotropic magnetic materials for linear magnetostriction is

described by

$$\lambda(H) = \frac{\Delta l}{l} = \frac{1}{3} \omega(H) + \frac{3}{2} \lambda_S(H) \left(\cos(2\theta) - \frac{1}{3} \right) + \lambda_F \quad (3)$$

where H the applied magnetic field, $\omega(H) = \Delta V/V = \lambda_{\parallel}(H) + 2\lambda_{\perp}(H)$ the volume magnetostriction, $\lambda_S = (2/3) (\lambda_{\parallel} - \lambda_{\perp})$ the saturation magnetostriction, θ the angle between H and the direction of the deformation measurement and λ_F the bipolar magnetostriction (form effect). The latter is nearly zero for a thin film or ribbon magnetized in a direction parallel to its plane and will be maximal if it is magnetized perpendicular to its plane. For the calculation of λ_S , the values of λ_{\parallel} and λ_{\perp} obtained as the intersection of the tangent of the corresponding measured curve with ordinate at $H=0$ were used. $\partial\omega(H)/\partial H$, called isotropic forced volume magnetostriction, is a magnitude used for technological applications which is constant for a certain region of $\omega(H)$.

Curie temperatures for the as-quenched and for the relaxed up to 623 K (5 K/min) amorphous samples obtained from DSC and saturation magnetostrictions for the as-quenched and annealed materials at 813 K are shown in Table 1.

Montgomery et al. [19] demonstrated that T_C strongly depends on the exchange interaction (J_0) and at the same time, this one depends on the distance between the Fe atoms based on the Bethe–Slater curve. As previously observed [20], amorphous T_C increased when the material was relaxed as a result of the structural order induced by the thermal treatment in the amorphous material. On the other hand, the replacement of Nb for Mo resulted in a decrease of T_C . This behaviour can be explained based on the different atom sizes between Nb and Mo: as Mo atom is smaller than Nb, Fe atoms in the amorphous state are closer to each other and this leads to a decrease of T_C .

The values of λ_S , $\omega(H)$ and $\partial\omega/\partial H$ were obtained from the $\lambda_{\parallel}(H)$ and $\lambda_{\perp}(H)$ measured curves for all as-quenched and annealed samples. These results are shown in Fig. 1.

Previous results on the study of these alloys showed that the replacement of Nb for Mo increased both the crystalline fraction and the amount of Si in the nanograins when the heat treatment was kept at 813 K for 1 h [16]. Based on these two facts, we would have expected a decrease of the λ_S for these treated alloys with Mo addition, since λ_S sensitively depends on the crystal fraction and on $\lambda_{S,Cr}$ (λ_S of the crystalline phase), which varies with Si content in the grains [11]. However, λ_S also depends on $\lambda_{S,Am}$ (λ_S of the amorphous phase) which in turn varies with the composition of the amorphous remaining matrix and its change with Nb/Mo rate has been reported [16]. Measured λ_S values showed no trend with the exchange of refractory elements neither for the as-quenched (~ 19 ppm) nor for the annealed samples (~ 2 ppm). On the other hand, λ_S decreased one order of magnitude when the alloys were heat treated at 813 K for 1 h as a result of the formation of the non-stoichiometric Fe_3Si nanograins with negative magnetostriction that compensates the positive one of the amorphous phase [11].

In Fig. 1 λ_{\parallel} and $2\lambda_{\perp}$ as function of Mo content, volume magnetostriction as function of the applied field ($\omega(H)$) and forced volume magnetostriction for the as-quenched and annealed alloys are shown.

The relation $|\lambda_{\parallel}| \neq 2|\lambda_{\perp}|$ indicates that the sample in the demagnetized state is anisotropic. $|\lambda_{\parallel}| < 2|\lambda_{\perp}|$ shows an anisotropy in the direction of the sample axis. They are the product of stresses frozen during the rapid quenching. This behaviour was observed for all the as-quenched and heat treated alloys, except for annealed Mo1 and Mo1.5 where $|\lambda_{\parallel}| \cong 2|\lambda_{\perp}|$ suggesting that the sample is isotropic.

The obtained values of $\partial\omega(H)/\partial H$ differs from zero, which indicates that all the samples, even after the nanocrystallization process, present internal stresses.

Table 1
Curie temperatures (T_C) of amorphous alloys before and after the relaxation treatment obtained from DSC, FeSi crystallization temperature (T_{cryst}) before and after the relaxation treatment obtained from dilatation curves, saturation magnetostriction (λ_S) for as-quenched and heat treated alloys (813 K, 1 h).

Alloy	T_C (K)	$T_{C, relax}$ (K)	T_{cryst}^{dilat} (K)	$T_{cryst,relax}^{dilat}$ (K)	λ_S as-q (ppm)	λ_S 813 K 1 h (ppm)
Nb3Mo0	594	600	792	790	18.7	2.2
Nb2Mo1	596	604	783	782	19.4	2.3
Nb1.5Mo1.5	592	600	778	779	19.5	2.6
Nb1Mo2	590	598	773	772	20.4	2.7
Nb0Mo3	587	596	767	768	19.5	2.7

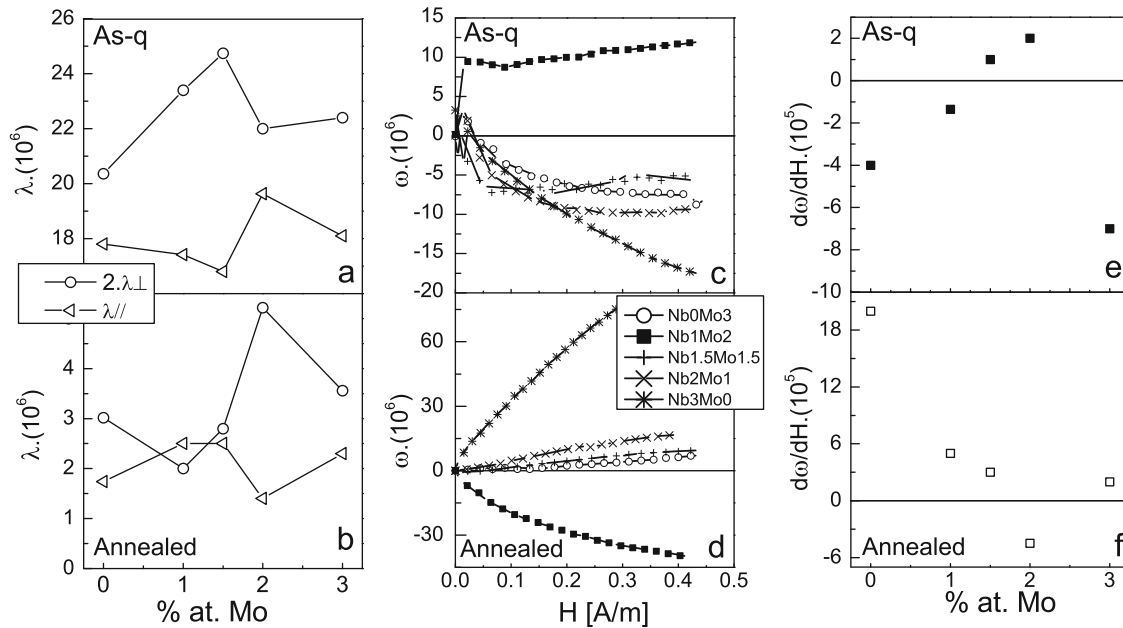


Fig. 1. (a) and (b) $\lambda_{||}$ and $2\lambda_{\perp}$ as function of Mo content for as-quenched and annealed alloys (813 K, 1 h); (c) and (d) volume magnetostriction ($\omega(H)$) for the as-quenched and annealed alloys (813 K, 1 h); (e) and (f) forced volume magnetostriction ($d\omega(H)/dH$) for the as-quenched and annealed alloys (813 K, 1 h).

Different transformation processes of metallic glasses such as structural relaxation, crystallization, ferro/para magnetic transformation, can be studied by dilatation measurements. Temperature dependence of dilatation of the $Fe_{73.5}Si_{13.5}B_9Mo_3Cu_1$ sample is shown in Fig. 2 as an example. Structural and magnetic relaxation of the ferromagnetic amorphous samples take place up to T_C , where the amorphous samples become paramagnetic and relaxation process finishes. The Curie temperature coincides with T_C values measured by DSC (Table 1). Around 750 K, FeSi crystals start to precipitate leading to a structural contraction transformation. By the end of the curve, the second crystallization has begun, i.e. borides phases, causing a structural contraction. As many effects are occurring at this last stage, the small effect of FeSi ferro/para magnetic transformation cannot be observed by means of dilatation measurements and should be studied, for instance, by magnetization vs. temperature measurements ($T_{C,FeSi}=856$ K [21]). Finally, the cooling run is governed by thermal contraction.

Relaxation processes are accompanied by changes in volume; there is usually a contraction of the material because the density of the relaxed material is higher than the density of the material without relaxation. For that reason, in order to distinguish whether the small dilatation coefficient (α) observed in our samples next to the Curie temperature corresponds to the Invar effect it is necessary to previously eliminate the possibility of relaxation. Thus, the material was heated from room temperature (T_{room}) up to 623 K and cooled down to T_{room} at the same velocity before the heating run up to 900 K. The relaxation treatment did not influence

the Fe_3Si crystallization temperature (T_{cryst}) as it can be seen in Table 1. Moreover, dilatation curves showed that the replacement of Nb for Mo diminished the T_{cryst} in agreement with previous results obtained by other calorimetric measurements [21].

The Invar effect was found distinctly for all the studied alloys. Following the procedure described before, ω_{spont} was calculated and the results are shown in Figs. 3 and 4.

The values of ω_{spont} reflect the electronic structure of the elements in the alloy, but the physics that governs the behaviour of this magnitude is not still completely understood.

The values of ω_{spont} decreased with decreasing temperature, being zero at T_C . $\omega_{spont, 300K}$ did not change significantly with composition for the alloys without relaxation, while it seemed to rise with increasing Mo content for the relaxed samples.

4. Conclusions

Magnetostrictive properties reflected the transformations that took place in FINEMET type samples when subjected to thermal treatments. Thermal stability and T_C of the amorphous samples slightly decreased after replacing Nb by Mo. However, this small variation does not seem to imply a decrease in the material performance.

Chinese and Russian researchers [12–15] have reported an improvement in the magnetic permeability of the annealed samples containing both Nb and Mo. In this work, it was shown that neither

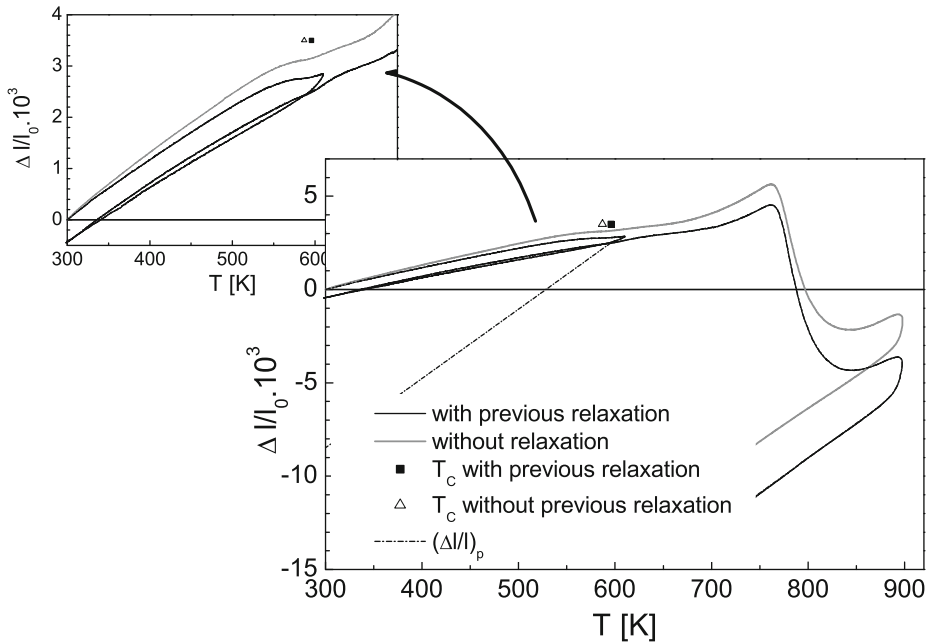


Fig. 2. Dilatation curves corresponding to the $Fe_{73.5}Si_{13.5}B_9Mo_3Cu_1$ alloy with and without previous relaxation.

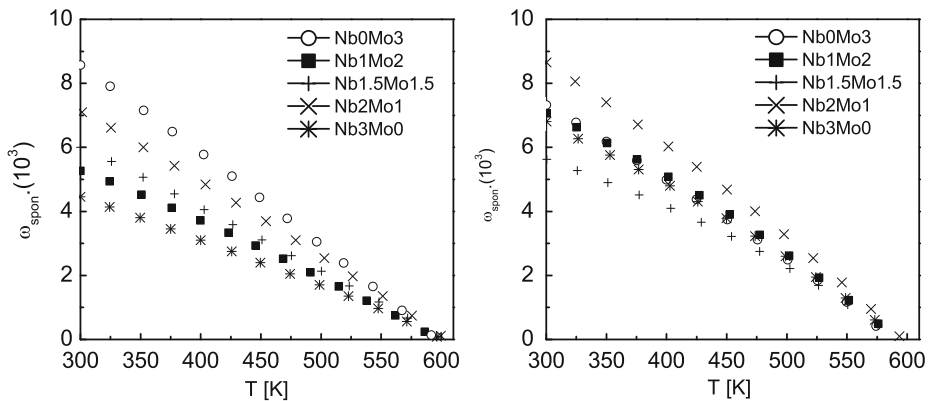


Fig. 3. Spontaneous volume magnetostriction as function of temperature of the amorphous samples: (a) without previous relaxation and (b) with previous relaxation.

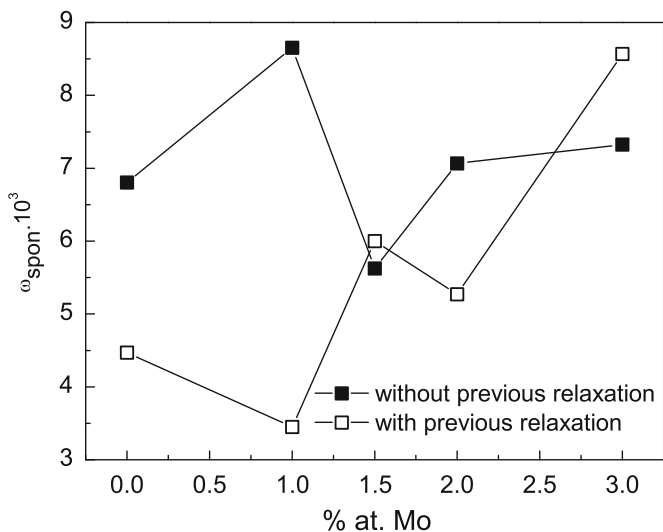


Fig. 4. Spontaneous volume magnetostriction at 300 K as function of Mo content obtained from Fig. 3.

deterioration nor improvement in magnetostriction values occurred with the refractory element exchange; it remained around 2 ppm after the corresponding annealing in all the alloys. Therefore, with our magnetostriction results we were not able to explain the better coercivity and permeability, observed by Chinese and Russian researchers, after a partial replacement of Nb with Mo. Nevertheless, this study reinforces the fact that the series is suitable for technical applications, for which a precise characterization of the magnetostrictive parameters is now known.

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