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Correlation between thermal and magnetic properties of glass coated microwires

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ABSTRACT

We studied magnetic and thermal properties of Fe and Co based glass coated microwires. We evaluated the magnetostriction constant of all prepared samples using the small angle magnetization rotation method. We observed the correlation between the change of heat capacity in T_C, ΔCp, and the magnetostriction constant. We observed considerable change of Curie temperature and improvement of the GMI effect after annealing of Fe-rich Finemet-type microwires. Nanocrystallization of Fe-rich Finemet-type microwires results in magnetic softening.

1. Introduction

Ferromagnetic metallic glass coated microwires with metallic nucleus diameters typically ranging between 10 and 20 μm in diameter (although recently fabrication and characterization of samples with metallic nucleus diameter below 1 μm is reported) attracted considerable attention owing to a number of outstanding magnetic properties such as magnetic bistabilty and Giant magnetoimpedance, GMI effect [1–3]. Recent papers reported on considerable progress in achievement of excellent soft magnetic properties and GMI effect of glass coated microwires [4,5]. The other important advantage of magnetically soft microwires is their reduced diameter (below 10 μm) that is quite important for micro-miniaturized sensor application [1,2].

As reported elsewhere, the overall shape of hysteresis loops and most attractive magnetic properties such as the GMI effect and the features of the magnetic bistability, as the velocity and the field of the magnetization switching are determined by the composition of the metallic nucleus as well as on the composition and thickness of the glass coating [1,6]. Amorphous microwires with nearly-zero magnetostriction exhibit the best soft magnetic properties. But even for the microwires with nearly-zero magnetostrictive compositions of metallic nucleus the magnetic softness and GMI effect are affected by the glass coating thickness [2,6].

Magnetoelastic energy is proportional to saturation magnetostriction as well as to the value of internal stress. The magnetostriction constant depends mostly on the chemical composition and takes nearly-zero values in amorphous Fe–Co based alloys with Co/Fe 70/5 [7,8]. On the other hand the strength of the internal stresses inside the ferromagnetic nucleus induced during simultaneous fast solidification of the composite microwire depends on ρ-ratio defined as the $\rho = d/D$ (d is the metallic nucleus diameter and D-total microwire diameter) [9–11].

Among the experimental evidences of existence of such stresses the dependence of hysteresis loops and particularly magnetic properties (coercivity, remanent magnetization) on ρ-ratio, effect of glass removal on hysteresis loops and stress dependence of the switching field must be underlined [12,13].

Accordingly, studies of the magnetostriction constant and internal stresses of glass-coated microwires are essentially important for optimization of their magnetic properties.

Nevertheless, only a few papers reported experimental studies of the saturation magnetostriction constant in glass-coated microwires [7,14–17].

It is assumed that the most convenient methods for studying of the magnetostriction constant, λ_s, in amorphous materials are indirect methods, such as the small angle magnetization rotation (SAMR) or the stress dependence of initial permeability [18,19]. Usually it is assumed, that the SAMR method is suitable for the materials where the magnetization process is determined by the magnetization rotation. Consequently for the case of

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glass-coated microwires this method must be limited by Co-rich compositions.

On the other hand it was demonstrated that at certain conditions the SAMR method can be extended to the materials with rectangular hysteresis loops, i.e. for Fe-rich microwires [20]. In this case only magnetization rotation in the outer domain shell must be considered. But it is commonly assumed that the main volume of Fe-rich microwires is remagnetizing by the domain wall propagation [1,2]. Therefore the magnetic permeability corresponding to the magnetization rotation is rather low. Consequently realization of this method for microwires and especially in the case of Fe-rich microwires is related with the experimental difficulties to manipulate with such glass-coated microwires considering their thin dimensions and requires improvement of the resolution.

Additionally, the stress dependence of the GMI effect has been also employed to evaluate the magnetostriction constant of wire shaped samples [7].

Moreover few reports on utilization of differential scanning calorimetry, DSC, method for the studies of the properties of amorphous alloys in vicinity of Curie temperature have been published [21,22]. This method allows determination of T_C and activation energy of relaxation and crystallization processes. Besides, DSC method allows to measure the change of heat capacity in vicinity of T_C, ΔCp. As it was shown in [23], the Curie temperature and the value of ΔCp in vicinity of magnetic transition depend on the degree of structural relaxation achieved by annealing. Since it is known that structural relaxation connected with the internal stresses and the magnetostriction constant, it has been suggested that the change of heat capacity in vicinity of T_C may be correlated with the magnetostriction constant. Present paper is devoted to the verification of this assumption.

Consequently the objectives of this paper are to measure the magnetostriction constant of different Fe- and Co-rich amorphous microwire by the SAMR method and to study the correlation between the measured magnetostriction values and the experimental results obtained by the DCS method

2. Experimental details

We prepared various Co and Fe rich amorphous microwires by Taylor–Ulitovski method (see Table 1) [1,2]. Hysteresis loops have been measured by a conventional induction method as described elsewhere [2,6].

Microwires with 10 cm length were used for the measurements of the saturation magnetostriction constant, λ_s, using the SAMR method described elsewhere [8]. In this method the sample is saturated by an axial magnetic field, H_z, while applying simultaneously a small *ac* transverse field, H_y, created by an *ac* electric current flowing along the sample. The *dc* axial magnetic field, H_z, is elected in order to achieve roughly saturated state in all as-prepared and annealed samples. The combination of these fields leads to a reversible rotation of the magnetization within a small angle, θ, out of the axial direction. The induction voltage, $V(2\omega)$, due to the magnetization rotation is detected by a coil wound around the microwire. The magnetostriction constant is determined from the measurement of the dependence of axial magnetic field, H_z, versus applied stress σ at fixed value of induction voltage $V(2\omega)$ in according to the expression:

$$\lambda_s = -(\mu_o M_s/3)[\Delta H_z/\Delta\sigma]_{V(2\omega)=\text{constant}} \qquad (1)$$

Table 1
Compositions and geometric parameters of studied microwires.

No.	Composition	d, µm	D, µm	ρ
1	$Fe_{70.8}Cu_1Nb_{3.1}Si_{14.5}B_{10.6}$	13.2	17.6	0.75
2	$Fe_{70.8}Cu_1Nb_{3.1}Si_{14.5}B_{10.6}$	15.6	21.8	0.72
3	$Fe_{70.8}Cu_1Nb_{3.1}Si_{14.5}B_{10.6}$	8.2	16.6	0.49
4	$Fe_{58.9}Co_{14.7}B_{16.2}Si_{10.2}$	20	25	0.8
5	$Fe_{47.42}Ni_{26.6}Si_{11}B_{12.99}C_{1.99}$	29	32.2	0.9
6	$Fe_{6.1}Co_{57}Ni_{10}B_{15.9}Si_{11}$	20.4	24	0.85
7	$Fe_{3.83}Co_{66.94}Ni_{1.44}B_{11.51}Si_{14.59}Mo_{1.69}$	19.4	22	0.88

where $\mu_o M_s$ is the saturation magnetization and σ – the applied tensile stress. The $\mu_o M_s$ values of the investigated microwires obtained from at room temperature from measurements of magnetization curves at high magnetic field are given in the Table 2.

As mentioned above application of the SAMR method for microwires and especially in the case of Fe rich microwires is related with the experimental difficulties to manipulate low signals from glass-coated microwires with thin dimensions.

For this purpose we designed and realized a novel set-up for SAMR measurements of the magnetostriction of low dimensional materials. In this set-up we applied to a microwire an *ac* electric current higher frequency ($f = 9$ kHz, $\omega \sim 56$ kHz) and amplitude ($I_0 > 15$ mA). Also a low noise preamplifier ($V_n < 2nV/H_z^{1/2}$, gain 10^4) and lock-in amplifier were used to measure the weak induction voltage $V(2\omega)$.

We measured magnetic field dependences of impedance, Z, and GMI ratio, $\Delta Z/Z$, for as-prepared samples and after heat treatments as described elsewhere [2]. The samples have been annealed in conventional furnace at different annealing temperature. As a rule we used 1 h annealing time (in this case we do not indicate it below).

Structure and phase composition have been checked using a BRUKER (D8 Advance) X-ray diffractometer with Cu Kα ($\lambda = 1.54$ Å) radiation.

DSC measurements were performed using DSC 204 F1 Netzsch calorimeter in Ar atmosphere at a heating rate of 10 K/min. The Curie temperature and the peak area were estimated from DSC curves using standard IT application. The specific heat was determined by the standard ratio method with sapphire as reference.

3. Results and discussion

As expected from previous knowledge on amorphous microwires [1,2], Fe-rich compositions show rectangular hysteresis loops and Co-rich compositions show inclined hysteresis loops (see Fig. 1). The annealing of Finemet-type $Fe_{70.8}Cu_1Nb_{3.1}Si_{14.5}B_{10.6}$ microwires leads to decreasing of the switching field, H_s. When the annealing temperature, T_{ann}, is above 550 °C, the hysteresis loops loose rectangular shape and considerable magnetic softening related with the devitrification process is observed (Fig. 2).

As deduced from Fig. 3 (for the sample with ρ – ratio 0,72) a main crystalline peak appears in the range between 42° and 45° which is correspond to the precipitation of α-Fe (Si) BCC crystallites [21,24], as well as the other two weak peaks appears in the range between 65° and 85°. Using the Deybe–Sherrer equation and the width of the crystalline peak we have been able to estimate the average grain size (D). After annealing at $T_{ann} \approx 550$ °C the $D \approx 12$ nm growing with increasing of the T_{ann} up to $D \approx 27$ nm at $T_{ann} \approx 650$ °C.

We also observed the Curie temperature increasing after different regimes of annealing. As seen from Fig. 4 the T_C is going up with increase the annealing temperature and its duration. At the same time with a shift of Curie temperature the value of the heat capacity jump in vicinity of Tc changes and reduces to zero (Fig. 5).

According to the Egami's model the topological and chemical short-range ordering are responsible for the Curie temperature changes induced by the annealing [25,26]. Change of average distances between the Fe atoms related with the release of the "free volume" during the topological ordering must be associated to some increase of the Curie temperature for the Fe-based amorphous alloys.

The GMI ratio, $\Delta Z/Z$ in as-prepared Fe rich microwires is rather small. After annealing we observed increasing of the GMI effect. Enhancement of the $\Delta Z/Z$ ratio is related with magnetic softening of studied microwires after annealing and internal stress relaxation. Indeed applied and internal stresses considerably affect GMI effect [12,16].

GMI results for as-prepared and annealed at 400 °C $Fe_{70.8}Cu_1Nb_{3.1}Si_{14.5}B_{10.6}$ microwires ($d = 8$ µm, $\rho = 0.49$) with amorphous structure are shown in Fig. 6.

As-prepared $Fe_{70.8}Cu_1Nb_{3.1}Si_{14.5}B_{10.6}$ amorphous sample exhibit much lower maximum $\Delta Z/Z$ values, $\Delta Z/Z_{max}$ (5% at 200 MHz, see Fig. 6a). After annealing at 400 °C during 30 min we observed some improvement of $\Delta Z/Z_{max}$ (about 10% at 200 MHz) probably related with some magnetic softening due to the internal stresses

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