Invited Paper

Soft magnetic behaviour of nanocrystalline Fe-based glass-coated microwires

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Microstructural and magnetic behaviours of two thin Fe-rich glass-coated microwires ($Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ and $Fe_{79}Hf_7B_{12}Si_2$) with a nanocrystalline structure of such materials are presented. The nanocrystalline state is obtained by heating (300 - 700 ºC, 1 hour) the precursor amorphous microwires. Structural characteristics of the as-cast and annealed samples were determined, at room temperature, by X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques. Such techniques allow to obtain the evolution of the grain size and relative fraction volume (5 - 65%) of the nanograins. Thermal dependencies of H_c are qualitatively similar in both compositions and results to be also qualitatively similar to that reported for the classical *Finemet* ribbon. In fact, H_c decreases from the as-cast (relaxation process) showing a maximum around 450 ºC (pre-nucleation of nanograins) decreasing significantly between 500-600 ºC (exchange coupling of the nanograins). It is remarkable to note that the H_c values are larger in these glass-coated microwires as comparing with the nanocrystalline *Finemet* ribbon of similar composition. Such effect should be ascribed to the presence of the glass insulating sheath inducing strong and complex internal stresses on the metallic nucleus which affects dramatically the soft magnetic character.

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1. Introduction

Fe-based nanocrystalline alloys with very fine microstructure (with trademark *Finemet*), firstly investigated by Yoshizawa et al. [1] can be considered as one of the best representative soft nanocrystalline material. In fact, it combines high-saturation magnetization with very small coercive force and very low effective saturation magnetostriction and are, therefore, especially interesting from the standpoint of their use as soft magnetic materials [2]. These materials are characterized by a microstructure consisting basically of two phases, i.e., crystalline grains (with sizes of the order of the tens of nm and random orientation of their easy axes) embedded in a residual amorphous matrix [3]. Such a microstructure is usually produced by partial crystallization of an amorphous precursor. Such as has been evidenced by different studies, the basic mechanism leading to the achievement of such a good soft magnetic behaviour is that the magneto-crystalline anisotropy of the randomly oriented nanocrystalline grains is averaged out by the exchange interactions [4]. Thus, the resulting magnetic behaviour can be well described in the framework of the random anisotropy model [5]. According to this model, the very low values of coercivity in the nanocrystalline state are ascribed to the small effective magnetic anisotropy (K_{eff} around 10 J/m^3). Consequently, the excellent soft magnetic properties of these nanocrystalline biphase materials should be related to the strong coupling between the crystalline grains, which could be linked to a significant enhancement of the microstructure-magnetization interactions. These interactions originating in large units of coupled magnetic moments suggest a relevant role of the magnetostatic interactions as well as in the formation of these coupled units [6,7].

On the other hand, glass-covered microwires produced by a modified Taylor-Ulitovski method [8] have, recently, emerged as a new family of very promising magnetic materials. This method allows to produce, in a continuous way, a wide range of microwires varying the composition of the metallic nucleus (to be of amorphous or nanocrystalline or nanogranular character) as well as the geometrical parameters (diameter of the metallic nucleus and the glass insulating thickness) [9]. It must be noted that a number of outstanding magnetic properties, such as magnetic bistability, enhanced magnetic softness and giant magnetoimpedance effect (up to 600 %) have been found recently in such microwires [10-12]. These properties are correlated with the shape and magnetoelastic anisotropies depending on the dimensions, microstructure, composition and strong internal stresses originating from the difference of the thermal expansion coefficients of the metallic nucleus and the glass sheath.

Concerning soft nanocrystalline microwires there is a significant research work in the so-called *finemet* composition ($Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$) [13-15], where the nanocrystal grains are α–Fe(Si) with an uncertainty to determine the Si content inside such grains. This aspect has motivated the research on the FeZrBCu ribbons, since these alloys can be easily nanocrystallized by thermal treatment (550 ºC, 1 hour) with the segregation of α-Fe (with absence of Si) and the residual amorphous matrix exhibiting extremely low values of coercivity. Consequently, we have made many attempts to fabricate Fe-based glass-coated microwires (without Si content) which can be nanocrystallized by a post thermal treatment. Unfortunately, we have not been able to produce such a kind of microwires. Nevertheless, following the idea of reducing the Si content, we have recently fabricated Fe-rich ($Fe_{79}Hf_7B_{12}Si_2$) glass-coated microwire which is susceptible to nanocrystallize in similar way to those already mentioned by the segregation of α-Fe(Si) nanograins with low Si content.

Consequently, the aim of this paper is to review the more interesting aspects of the soft magnetic character of *Finemet*-type microwires as well as in a new composition (FeHfBSi) in order to analyse the effect of the composition.

2. Microstructural analysis

2.1. Finemet microwires

X-ray diffraction of the FeCuNbSiB (Finemet-type) microwire does not detect the presence of crystalline phases in as-prepared state in these samples with different geometry. On the other hand, transmission electron microscopy (TEM) diagrams of the sample annealed at 550 ºC permits to detect a small amount of fine grains of α-Fe, γ-Fe and α-Fe(Si) [16]. The TEM image presented in Fig. 1 shows that the average grain size of such crystallites results to be around 20-70 nm in annealed sample at 550 ºC.

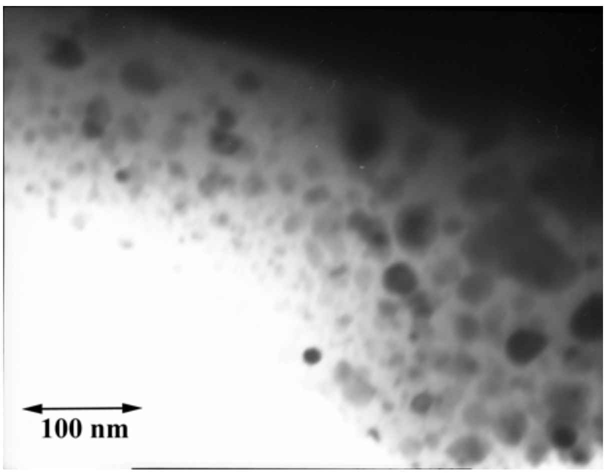

Fig. 1. TEM diagram of $Fe_{72.5}Cu_1Nb_3Si_{14.5}B_9$ glass coated microwire annealed at 550 ºC during 1 hour.

As has been mentioned, strong internal stresses due to the glass coating can result in a change of structure of the precipitating fine grains. As a consequence, strong internal stresses (about 10^3 MPa or even more) are mainly induced by the difference in the thermal expansion coefficients of the glass and the metallic nucleus. It is well known that internal strains of different nature can be the origin of martensite-type transformations in alloys of Fe. Probably, the strong internal stresses induce a precipitation of the γ-Fe fine grains instead or apart from α-Fe(Si) grains during the first stage of the crystallization process. Particularly, the presence of γ-Fe crystallites could be the reason for the observed magnetic hardening [16]. Consequently, the origin of such strong magnetic hardening at low annealing temperatures without deterioration of mechanical properties could be ascribed to some peculiarities of the first crystallization process under the effect of strong internal stresses induced by glass coating and differences in the alloy composition.

2.2. FeHfBSi microwire

Fig. 2 shows the first peak of the X-ray diffractograms of as-prepared and annealed sample. As can be seen, the position and width of such peaks change significantly with the annealing. It is worth mentioning that even as-prepared sample exhibit slightly crystalline structure. The average grain size estimated from the peak width using Debay-Sherrer equation gives values about 17 nm.

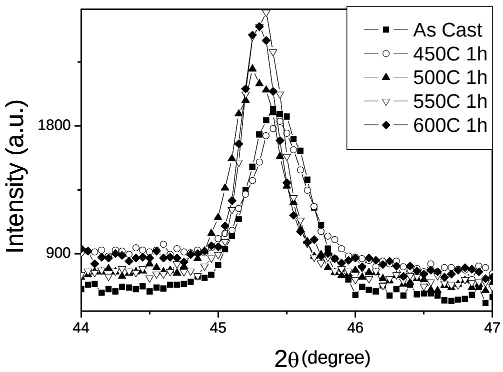

Fig. 2. XRD patterns (first peaks) of $Fe_{79}Hf_7B_{12}Si_2$ glass coated microwire as-cast and annealed.

The evolution of the average grain size of nanocrystals with annealing temperature is presented in the Fig. 3. The grain size of the nanocrystals increases from about 17 nm up to 35 nm after annealing at 600 ºC. In fact such increase of the grain size does not correlate the random anisotropy model proposed by Herzer for the nanocrystalline material [17,18]. In according to such model an enhanced magnetic softness correlates with the grain size and the best magnetic softness is achieved under conditions that the average grain size, typically of 10-15 nm, is much below the exchange correlation length, being around 35-40 nm [7] (An estimation of error margins was around 5%). These differences could be ascribed to the strength and complexity of the internal stresses acting on the metallic nucleus due to the glass coating. In this way the magnetoelastic anisotropy associated with the internal stresses probably plays more important role than the grain size. Such internal stresses can affect the nanocrystallization process such as has been previously observed in glass coated *Finemet*-type microwires [13,14].

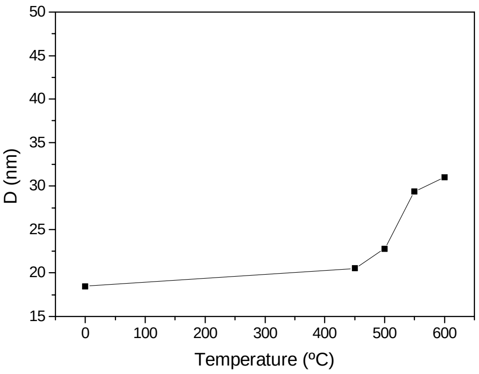

Fig. 3. Annealing temperature dependence of the grain size of $Fe_{79}Hf_7B_{12}Si_2$ glass coated microwire.

3. Soft magnetic behaviour

3.1 Finemet compositions

3.1.1. Coercivity of soft nanocrystalline microwires

The properties of the as-prepared *Finemet*-type $Fe_{73.5}Cu_1Nb_3Si_xB_{22.5-x}$ (x = 11.5, 13.5 and 15.5 of composition) depend significantly on their geometry [13,19] Hysteresis loop, of typically rectangular shape, has been observed in the as-prepared state. The coercivity, H_c, of $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ sample strongly increases as the ρ=d/D ratio (d = metallic nucleus diameter and D = total diameter of the microwire) decreases. These results of H_c versus ρ could be understood taking into account that the strength of internal stresses acting inside the metallic nucleus increases with ρ [19-21].

The typical dependence of the coercive field, H_c, of $Fe_{72}Cu_1Nb_3Si_{15}B_9$ alloy with the annealing temperature, Tann, with ρ as parameter is shown in the Fig. 4. Generally, a decrease of H_c with T_{ann} has been observed below 400 ºC. A weak local minimum of H_c has been observed at about 400-450 ºC with the temperature of that minimum depending of both alloy composition and geometry. Such a decrease of H_c could be associated to the structural relaxation of the material remaining the amorphous character such as has been widely reported in metallic glass alloys. A small relative magnetic hardening can be observed after annealing around 450-500 ºC, which could be ascribed to the very beginning of the first stage of devitrification [13,22]. It is interesting to note that the geometry of the sample affects the value and position of the local extremes on the $H_c(T_{ann})$ dependence as can be seen in Fig. 4, where the dependencies of the coercivity with the annealing temperature for the $Fe_{73.5}Cu_1Nb_3Si_{15.5}B_9$ glas coated microwire with the ρ parameter are plotted. A deeper softening (optimum softness) with a rather low value of H_c is obtained in samples annealed at 500-600 ºC. Such magnetic softening is related to the nanocrystallization associated to the precipitation of fine grains (10-15 nm) of α-Fe(Si) phase within the amorphous matrix.

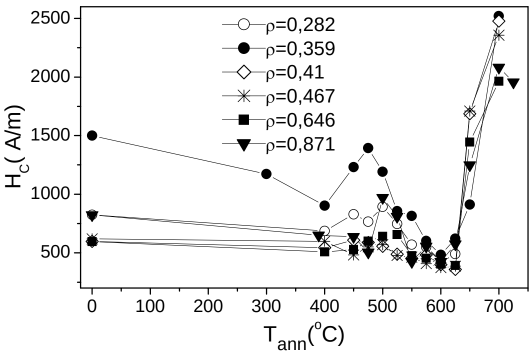

Fig. 4. Dependence of coercivity on the annealing temperature of $Fe_{73.5}Cu_1Nb_3Si_{15.5}B_9$ glass coated microwires with different ρ = d/D ration ranging from 0.282 to 0.871.

3.2.1. Semihard magnetic nanocrystalline microwires

As can be seen from Fig. 4, an abrupt of H_c is observed in $Fe_{73.5}Cu_1Nb_3Si_{15.5}B_9$ glass coated microwires with different ρ = d/D ratio treated above 600 ºC, indicating the beginning of the precipitation of the second crystalline-iron borides (with grain size larger than 50 nm). Such beginning of the increase of H_c depends, mainly, of the sample composition as well as of the geometry. It must be noted that for the glass coating, the increase of H_c appears at lower temperature, which could be related to the fact that the internal stresses induce some ordering to hinder the crystallization. It is important that the hysteresis loop in certain microwires remains roughly the rectangular in the whole range of annealing temperatures (Fig. 5). Such temperature dependence of the hysteresis loops permits one to tailor the coercivity with rectangular hysteresis loop in a wide range of coercivities.

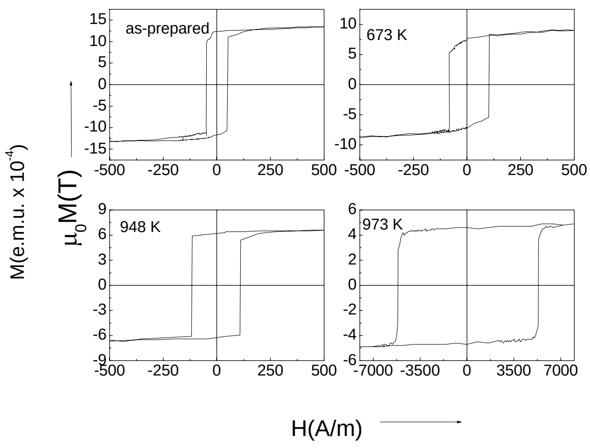

Fig. 5. Hysteresis loops of $Fe_{72}Cu_1Nb_3Si_{15}B_9$ microwire in as-cast and annealed at different temperatures.

The effect of annealing temperature on the coercivity, H_c of the $Fe_{72.5}Cu_1Nb_3Si_{14.5}B_9$ alloy, with the ratio ρ as parameter, is shown in the Fig. 6 A sharp magnetic hardening (increase of coercivity) can be observed after annealing around 500-650 ºC. It should be indicated that such maximum takes place at the same range of annealing temperature as the first small increase of H_c. The annealing temperature deperndence of the coercivity, H_c of the $Fe_{73.5}Cu_1Nb_3Si_xB_{22.5-x}$ alloy (x = 11.5 and 13.5) allows to detect the first crystallization process (compare with Fig. 4).

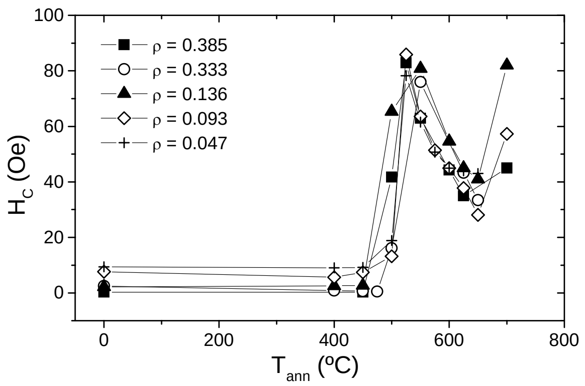

Fig. 6. Coercivity dependence with the annealing temperature of $Fe_{72.5}Cu_1Nb_3Si_{14.5}B_9$ glass coated microwire.

The strong magnetic hardening is followed by new magnetic softening with an increase of T_{ann} above 550 ºC and consequent magnetic hardening at T_{ann} > 650 ºC which is accompanied by deterioration of mechanical properties.

3.2. FeHfBSi microwires

Fig. 7 shows the changes of the coercive field, H_c, with the annealing temperature. In the range 500-600 ºC a significant improvement of the soft magnetic character takes place, which results to coincide with the increase of the grain size, D (see Fig. 3). Nevertheless, the values of $H_c \approx 600$ A/m and $D \approx 30$ nm for these annealed samples (500-600 ºC) are quite larger than those reported in the classical *Finemet* Fe-rich nanocrystalline ribbon shaped ($H_c \approx 1$ A/m and $D \approx 10$ nm). These differences could be associated, as has been mentioned, to the strength and complexity of the internal stresses acting on the metallic nucleus due to the glass coating. Such internal stresses arise some ordering to hinder the nanocrystallization process as it has been previously observed in glass-coated *Finemet*-type microwires [13].

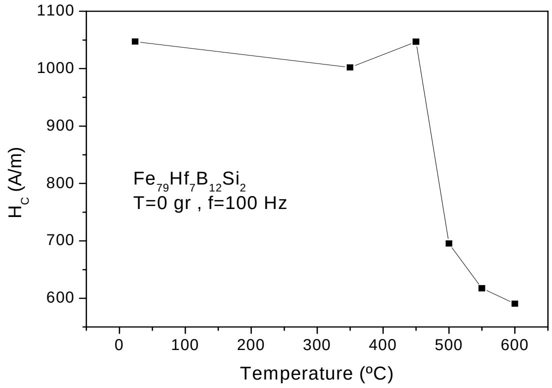

Fig. 7. Coercivity dependence with the annealing temperature of $Fe_{79}Hf_7B_{12}Si_2$ glass coated microwire.

Observed structural features permit to correlate observed magnetic hardening with precipitation of fine nanocrystallites. Such a difference in magnetic behaviour with conventional *Finemet* alloy ribbon can be attributed to different composition as well as to high internal stresses present in the case of microwires. It is well known that the best magnetic softness is achieved when the nanocrystalline structure consists of small fine grains and amorphous matrix being very low the effective magnetostriction constant. It is possible that even a small change of the alloy composition does not permit to achieve such a vanishing magnetostriction constant.

4. Conclusions

The correlations between structural and soft magnetic properties and the geometry (ratio ρ) in two families of Fe-based glass coated microwires (Finemet-type and FeHfBSi) have been studied. The microstructural properties are strongly dependent on the geometry, that is, the relation rate of the metallic core diameter to the total diameter of the microwire. This effect should be attributed to the internal stresses within the metallic core arising from the different thermal expansion coefficients of the glass coating and the core.

With respect to the novel nanocrystalline $Fe_{79}Hf_7B_{12}Si_2$ thin glass coated microwire under annealing, an improvement of the magnetic softness is observed and analysed. It has been found from comparison of X-ray technique and magnetic properties that the nanocrystalline samples cannot develop the extremely soft magnetic behaviour as in nanocrystalline Fe-rich ribbons and thin wires. Such difference can be attributed to the internal stresses arising from the glass covered sheath. Nevertheless, the control of the nanostructure from careful thermal treatments lead to significant improvement of the coercivity. A deeper understanding of the mechanisms involve in this soft magnetic behaviour requires however further studies which are actually in progress.

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