Description of the Nanocrystallization Process in $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ Through the Study of the Anelastic and Magnetoelastic Behavior

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Abstract: A description of the nanocrystallization process of the amorphous $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ alloy as deduced by a study of the anelastic and magnetoelastic behavior is reported. ΔE effect measurements were performed on the as-prepared alloy and on samples previously submitted to heating treatments in furnace at selected temperatures. The results were coupled to internal friction and dynamic Young's modulus vs. temperature measurements performed both in saturating magnetic field and in zero field. Different stages of the structural evolution towards the final crystalline state have been distinguished and their strict relationship with the observed changes in the magnetoelastic response has been pointed out. In particular a strong ΔE effect was observed in samples annealed at temperatures very close to the one at which the crystallization process starts.

1. INTRODUCTION AND EXPERIMENTAL

It's well known that the nanocrystalline $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ alloy shows excellent soft magnetic properties combined with a high saturation magnetization [1]. The nanocrystalline state is obtained by devitrification of an amorphous precursor, produced by ultrarapid quenching technique, and is achieved thanks to Cu and Nb, supposed to enhance the nucleation of the nanograins and to hinder their growth, respectively [2]. The optimal soft magnetic behavior is obtained when the microstructure is composed of α -FeSi crystallites (typical grain size ~ 10 nm), constituting the 50-70 % of the volume of the material, embedded in a residual amorphous phase. In fact, due to the reduced dimensions and to the random distribution of the magnetically coupled grains the magnetocrystalline anisotropy averages out [1]. Moreover the nanocrystalline alloy has an almost vanishing saturation magnetostriction which finally determines its superior soft magnetic properties [1].

In this work, the mechanical spectroscopy technique has been employed to analyze the structural evolution of the amorphous $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ alloy towards the nanocrystalline state.

In particular, the study of the ΔE effect has provided useful information on the structural relaxation of the amorphous phase preceding the nanocrystallization and on the relationship between structural and magnetic properties.

The $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ amorphous ribbons were produced by planar flow casting technique (peripheral wheel velocity = 25 m/s). Internal friction (Q^{-1}) and dynamic Young's modulus (E) measurements were carried on through a vibrating reed apparatus operating in the 10 - 10000 Hz range as a function of temperature (heating rate = 4 K/min) and of an applied magnetic field H . The samples, cut from the amorphous ribbon, had dimensions (2×0.03) mm² in cross section and 6-8 mm in length. The magnetic field was applied parallel to the sample's main axes.

The measurements were performed on the as-cast alloy and on samples previously annealed, in furnace, at different temperatures (heating rate = 4 K/min) at which they were kept for one minute. Both the thermal treatments and the anelastic measurement were performed in a vacuum of 10^{-3} mb.

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2. RESULTS

In figure 1, the dynamic Young's modulus and internal friction vs. temperature trends for the as-cast $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ ribbon are shown (E_0 is the modulus at 300 K). The modulus increases starting from about 450 K whereas at 770 K a strong softening stage is visible. As regards the internal friction, at 300 K it presents a typical value of $6-8 \times 10^{-3}$ and decreases up to about 600 K. Then, it increases again and gives rise to a maximum in correspondence to the modulus minimum. Modulus defects and internal friction peaks affect the anelastic parameters behavior, their presence and features strongly varying from sample to sample and depending from the heating rates.

Figure. 1 Dynamic Young's modulus E (circles) and internal friction (Q^{-1}) (triangles) vs. temperature for the as-cast $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$. E_0 is the room temperature modulus value. Vibration frequency at 300 K = 1000 Hz

Figure 2 shows the modulus and Q^{-1} vs. H for the as-cast alloy. The result relative to E has been plotted as $(E_s - E)/E$, E_s being the dynamic modulus value at saturation magnetization. Defining the ΔE effect as $\Delta E/E = (E_s - E_{\min})/E_{\min}$ (where $E_{\min}$ is the lowest modulus value measured at a certain H), a ΔE effect in the 0.05-0.08 range is usually observed in the as-cast ribbon. Noteworthy is the background damping of the order of $(3.5 \pm 4) \times 10^{-3}$.

Figure 2 Magnetic field dependence of the modulus (circles) and of the internal friction (triangles) for the as-cast $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ alloy. E_s is the modulus value in a saturating field.

Figure 3 Magnetic field dependence of the modulus for three $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ samples previously annealed at (a) 695 K, (b) 745 K, (c) 830 K. E_s identified as in figure 2.

By annealing the amorphous ribbons, a progressive enhancement of the ΔE effect, at 300 K, has been detected (figure 3); in particular $\Delta E/E = 0.26$ after a thermal treatment up to 695 K (fig. 3,a), and $\Delta E/E = 1.21$ after annealing at 745 K (fig. 3,b). On the contrary, the samples heated at 830 K don't show a significant ΔE effect (fig. 3,c). The modulus vs. temperature for a sample previously annealed at 745 K is shown in figure 4,a together with a measurement performed in magnetic field ($H=120$ Oe) up to 600 K (fig. 4,b). A strong increase of E/E_0 measured in zero field is observable at the lower temperatures whereas the measurement in magnetic field shows just the usual decreasing trend due to anharmonicity. Noteworthy is the presence of the strong softening stage at 770 K. The associated internal friction measurements are depicted in figure 5. The Q^{-1} in zero field (curve a) presents initially a very high value (11×10^{-3}) and decreases strongly with approaching 600 K. On the contrary, up to this temperature, the Q^{-1} measured in applied field keeps very low (2×10^{-3}) and almost constant. At higher temperature, Q^{-1} increases following a similar trend as for the as-cast alloy. The presence of the errating damping peaks is removed.

Figure 4 Modulus vs. temperature respectively (a) in zero field and (b) in saturating magnetic field of a $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ sample previously annealed at 745 K. E_0 identified as in fig. 1

Figure 5 Internal friction vs. temperature (a) in zero field and (b) in saturating magnetic field for the sample in figure 4.

3. DISCUSSION

In order to provide an explanation for the irregular modulus and Q^{-1} vs. temperature trends (fig. 1) of the as prepared $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ alloy, several effects must be considered. In general, the anelastic behavior of the magnetostrictive amorphous alloys up to the Curie temperature is affected by magnetoelastic coupling phenomena [3]. For the present composition, a value of the saturation magnetostriction $\lambda_s \sim 20 \times 10^{-6}$ and of the Curie temperature $T_c = 605$ K have been reported [1,4].

Taking into account the low value of the ΔE effect in the as-cast alloy and the magnetoelastic contribution of about $(2 \div 4) \times 10^{-3}$ to the internal friction (fig. 2), it can be concluded that two competing processes determine the anelastic behavior with temperature of the as-cast samples: an irreversible increase of the modulus, accompanied by a decrease of Q^{-1} , connected to the structural relaxation of the amorphous phase, and a decrease of E and corresponding increase of Q^{-1} , due to an enhancement of the atomic mobility [5]. As regards the first effect, although the irreversible decrease of the background damping is not clearly observable in fig. 1 due to the presence of several superimposed peaks, it can be clearly deduced by the Q^{-1} vs. T measurement in applied field relative to the sample previously annealed at 745 K (fig. 5,b) which reports a room temperature value of about 1.7×10^{-3} , significantly lower than the as-cast one measured at 300 K at the magnetic saturation (fig. 2). The softening stage characterizing the as-cast spectra (fig. 1) in the 770-830 K range has been related to the occurring of the nanocrystallization process [6]. As regards the modulus field dependence, the following general relation holds [7]:

$$(E_s - E) / E \propto \lambda_s^2 \cdot E_s / K$$

where E is the modulus at a definite field value and K the anisotropy constant. In the present case, the dependence of the ΔE effect on the magnetic domains configuration of the samples is neglected since they are all supposed to present a random domain structure apart from their thermal history. In the amorphous alloy as well as in the nanocrystalline one, the only contribution to the anisotropy is provided by the magnetoelastic one [1]. Therefore, the small ΔE effect in the as-cast ribbon has been attributed to the presence of high quenched-in internal stresses making K large. By annealing the amorphous ribbons at temperatures lower than the crystallization one, it is possible to induce a relaxation of the internal stresses leading to an increase of the ΔE effect. Actually, a significant enhancement of $\Delta E/E$ is measured in the sample annealed at 695 K, but the same explanation seems insufficient to account for the highest value $\Delta E/E = 1.21$ occurring in the sample heated at 745 K. In fact, even considering a typical increase of 20-30 % of E_s following the heating treatment, a drastic reduction of the internal stresses between 695 and 745 K should occur, in open contrast with reported data on amorphous alloys showing that the internal stresses decrease linearly with rising the annealing temperature [3]. The spectra in figs. 4, 5 relative to the sample heated at 745, indicate that, due to the thermal treatment, the structural relaxation of the amorphous phase must have been accomplished to a great extent. In fact, the modulus and Q^{-1} measured in magnetic field show a regular behavior typical of a stable structure and demonstrate that the increase of E/E_0 in the zero field spectrum and the associated high damping are totally determined by magnetoelastic coupling effects. On the other hand, the presence of the softening stage at high temperature indicates that the sample is still amorphous. According to a recent model for the structural evolution of the $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloy, the formation of cooper clusters should occur just before the onset of the nanocrystallization causing the formation, within the amorphous matrix, of regions with enhanced Fe concentration [8]. Following this description, the proposed explanation for the strong ΔE effect observed in the sample annealed at 745 K is that the structural relaxation involves an atomic rearrangement process, preceding the crystallization, as observed also in other amorphous alloys of different composition. This, in turn, induces a compositional fluctuation in the amorphous phase which could lead to an increase of the saturation magnetostriction. This last statement is in contrast with the result obtained by Herzer [1] demonstrating that λ_s doesn't change up to the onset of the crystallization, but is in excellent agreement with reported data by Vázquez et al [9]. Finally, the lack of ΔE effect in the sample heated at 830 K indicates that a developed nanophase formed leading, as well known, to a reduction of the saturation magnetostriction towards a near-zero value due to the balance between the negative contribution of the crystalline phase and the positive one of the residual amorphous phase [1].

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