IF Studies of Amorphous Fe₈₁B_{13.5}Si_{3.5}C₂ Alloy: Thermal and Magnetic Structural Behaviours

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Abstract : Ferromagnetic Fe₈₁B_{13.5}Si_{3.5}C₂ amorphous alloy exhibit also a structural relaxation domain like iron-based amorphous alloys which involve both thermal and magnetic relaxation. The features of this relaxation domain depend on annealing and cold-working treatments. Upon longitudinal magnetic field, the alloy exhibits discrete saturated states related to Fe clusters which are linked to the thermal and the mechanical history of the amorphous structure. In a "field annealing" and an as-cast conditions some of these discrete saturated states appear respectively at 0.4, 50 and 200Oe.

1. INTRODUCTION

Iron-based amorphous alloys undergo structural relaxation in a wide range of temperatures from -15 to 100-400°C well-described by internal friction spectra[1, 2, 3, 4]. This structural reorganisation stage of amorphous alloys reflects both magnetic and thermal structure evolution while the magnetic transition appears without any ambiguity. In our comparative studies on the structural evolution of ferromagnetic amorphous alloys under heating, we conducted IF experiments on the amorphous Fe₈₁B_{13.5}Si_{3.5}C₂ alloy. Pre-annealed and cold-worked IF spectra versus temperature are drawn. The experimental details are described elsewhere[4]. In order to have access to the magnetic contribution to the spectra and mainly to the structural relaxation maxima, IF experiments have been conducted under longitudinal magnetic field from 0 to 1kOe. The aim of these last studies is to determine the value H_s of the saturation magnetic field. From the literature, different values for the iron-based amorphous alloys were found. Berry and Pritchard[1] used a field of 100Oe for their Fe-based alloys including Fe₈₀B₂₀ while for the same alloy, Moser and Kronmüller[5] applied a field of 750Oe. Since the data in the literature have no consistency, we decided to conduct experiments on this alloy and also because the saturation state could reveal the pure anelastic phenomena. In this paper, the IF data fluctuations are about $\pm 3 \cdot 10^{-4}$ at room temperature.

2. RESULTS AND DISCUSSION

2.1 IF structural evolution of as-cast specimen

The IF spectrum of as-cast samples in figure 1 exhibits the same trends observed for other amorphous alloys[4]. The structural evolution spectra is divided into four steps which are respectively, the incubation or stress relaxation domain, the structural relaxation domain, the Curie temperature and amorphous-crystalline transition domain and crystallisation domain. For this alloy, the first domain 20-140°C, presents a maximum related to some structural events. The structural relaxation domain 140-430°C exhibits a broad maximum which holds some slight ones. The third domain 430-490°C contains two maxima which are characteristic of this alloy. The last domain 490-550°C is related to the crystallisation of the amorphous structure which is confirmed by DSC measurements.

2.2 IF structural evolution of the pre-cold-working specimen

Figure 1 shows also the IF spectrum dependence on pre-cold-working treatment. The whole spectrum is above the as-cast one with high Q⁻¹ values in the temperature range 23-300°C which covers the structural

relaxation maximum. The more shear-stressed structure is mainly relaxed in the first stage than in the second one. This result supports the free volume and voids redistribution which allow species diffusion or a reorganisation of stress fields. Although the last domain seems to be affected by the treatment on the IF spectrum, electron microscope micrographs of crystallised specimen did not show clear difference in crystallites shape and size. However, the f^2 evolution (f =frequency) shows a slight shift of the end of structural relaxation. The overall IF spectra have IF contributions from magnetic phenomena which we would like to characterise. For this purpose, we have conducted IF experiments under longitudinal field to detect the magnetic saturation of the alloy.

Figure 1.a : IF spectra of as-cast and cold-worked Fe₈₁B_{13.5}Si_{3.5}C₂

Figure 1.b : f^2 evolution of as-cast and cold-worked Fe₈₁B_{13.5}Si_{3.5}C₂

2.3 IF evolution of the annealed specimens under temperature

Like other iron-based amorphous alloys, the structural state of Fe₈₁B_{13.5}Si_{3.5}C₂ is sensitive to preliminary annealing and to heating rates. These effects are observed in different domains of the IF spectra [4][6]. The annealing temperature is chosen from the as-cast IF spectrum shown in Figure 1. It corresponds to the peak (around 300°C) of the structural relaxation phenomenon maximum.

Figures 2.a&b show respectively IF and f^2 evolution spectra of short time pre-annealed specimens at 300°C. In the first domain, the results show the particular effect of each annealing conditions. The spectrum of the specimen annealed for 30 minutes lies under the as-cast one which in turn is located under those annealed for 3H and 1H. In regard to these last spectra, the annealing would contribute to the high Q^{-1} level in the same way as the cold-working treatment. Furthermore the importance of the first domain affect the structural relaxation domain where only the high temperature part of the maximum appears with a high recovery for all the specimens as shown also in f^2 curves. The last part of the spectra contains the anomalies already observed for the as-cast specimen with more definition in spite of the scattering of the data.

Figure 2.a : IF spectra versus temperature after pre-isothermal annealing of Fe₈₁B_{13.5}Si_{3.5}C₂ amorphous alloy

Figure 2.b : f^2 evolution versus temperature after pre-isothermal annealing of Fe₈₁B_{13.5}Si_{3.5}C₂ amorphous alloy

These features of the IF spectra suggest an atomic reorganisation rather connected with free volume redistribution than only free volume reduction[6] starting strongly in the first domain through the structural relaxation stage to the onset of the crystallisation. These observations contrast with those observed for the Fe₈₁B₁₃Si₉ alloy[6]. Another characteristic of this alloy is expressed by the small maximum occurring around 50°C which though reduced remains with the increasing annealing time. This maximum could be considered as due to first stage thermal instability of the alloy structure but it was not seen on the spectra of the other alloys investigated [4, 6]. It may be attributed to a particular

manifestation of one solvent component of the alloy. Some authors have found a relaxation maximum in this range of temperature [3, 5]. In the case of this study, we think that this maximum could be linked to carbon atom relaxation similar to the so-called Snoek effect.

2.4 IF evolution of as-cast and annealed specimens against magnetic field.

Figure 3 shows the IF spectra versus longitudinal magnetic field of the Fe81B13.5Si3.5C2 alloy. The spectra of specimen pre-annealed and pre-cold-worked are also reported. In this figure, the as-cast specimen spectrum on increasing field exhibits a slight maximum around 550Oe and a plateau starting at 200Oe which could characterise the saturation state of the magnetic structure. On decreasing field the plateau state are well-fitted but the maximum disappears suggesting some reversible and irreversible phenomena. However, the little maximum could either be attributed to structure defects reorganisation within the magnetic domain or to α -domains orientation with α from 0 to 90° in the field direction which is also the amorphous ribbons casting direction.

Pre-treatments on the specimen modify the as-cast magnetic structure as is seen in the figure.

Following the annealing treatment the IF spectra present with increasing field a wide maximum (for relaxed structure) and a plateau after an increase for partially crystallised specimen (350°C-24H a & b).

We think that this last specimen may contain some Fe-Fe clusters or α -Fe nanocrystals since the annealing time is located in the stage where chemical ordering occurs in the amorphous structure. The features of the spectra in the as-cast and partially crystallised (350°C-24H) states are similar and suggest that the magnetic effect are mainly due to the Fe-Fe clusters. The small maximum found at 550Oe which we attributed to defects pinning of domains walls or domains reorientation is vanished by the collective effect of stress and magnetic field in the as-cast condition and by annealing. The two effects are similar on the amorphous structure. The spectra for the decreasing field present a slight hysteresis related to the spectra anomalies.

Figure 3 : IF spectra of amorphous Fe81B13.5Si3.5C2 alloy versus longitudinal magnetic field
H=0-1KOe, a/increasing H ; b/decreasing H

Figure 4.a : IF spectra of as-cast and "field annealed" Fe81B13.5Si3.5C2 alloy versus longitudinal magnetic field

For the pre-cold-worked specimen, a high maximum is observed around 600Oe after some small maxima. Also for this specimen a hysteresis is observed for the decreasing field and the final part of the spectrum lies below the first spectrum. The results suggest a strong magnetic evolution under the longitudinal field for the treated specimens mainly above 200Oe. These observations confirm the strong anisotropy of the Fe-Fe clusters favoured by the short annealing time treatments between room temperature and 350°C and cold-working treatment which show that the saturated state at 200Oe is a discrete state.

On figure 4, we have reported the IF spectra of as-cast specimens and those heated at indicated temperatures (the heating rate to reach these annealing temperatures was 125°C/H) during the IF experiments (about 2H) versus the longitudinal magnetic field up to 200Oe. Around 0Oe, a sharp decrease of the IF evolution spectra followed by two maxima for the room temperature and the low

temperature annealed specimens are observed. The first maximum appears at about 120Oe and the second about 1200Oe. The as-cast spectrum seems to be similar to the as-cast one in figure 3 except for the IF backgrounds subjected to annealing. A "thermal and magnetic annealing" effect explains the difference between results in figures 3 and 4. Since the field incrementation is shorter than for the results on figure 3, we have replotted the spectra for three low field ranges. It is interesting to note that what we can consider in the whole field spectra as an overall decrease contains some IF maxima. One of these maxima which appears at around 0.15Oe is particular because it seems to depend on the annealing temperature. We have suggested [7] that this maximum may involve the C atoms in a phenomenon like the so-called Snoek-effect. The IF spectra show also a sort of transition between the low and high temperature state of the alloy illustrated by the IF backgrounds which climb from 150 to 300°C annealed specimens. Concerning the magnetic evolution, some discrete magnetic saturation states are reached at 0.4 and 500Oe under the conjugated heating, magnetic field and sinusoidal stresses effect. This behaviour may be compared with the results of Escobar et al.[8] who optimised the magnetic properties of FeSiB alloys by a very short annealing at 430°C. But it seems that the magnetic saturation of this alloy occurs at higher field in accordance of the work of Pankhurst et al.[9] who by Mossbauer studies did not reach the saturation state for the same composition with applied field up to 5T. The magnetic saturation would depend on the internal stresses states resulting from the as-cast conditions and further treatments of the alloy. Escobar et al. have reported also like Kronmüller quoted by Luborsky [10] the coercive field dependence in temperature. Wolfarth[11], Kronmüller [12] again pointed out that the defects concentration and fluctuations affect the magnetic properties of amorphous alloys. Our study, in conclusion, show : i) the annealing and cold-working treatments effects on the thermo-magnetic structural evolution of the Fe₈₁B_{13.5}Si_{3.5}C₂ amorphous alloy, ii) the discrete magnetic saturations at 0.4, 50, 2000Oe settled under magnetic field in relation with particular Fe clusters. However, further investigations are needed to determine the Fe-clusters type involved in the others IF maxima as well as in the whole magnetic stability of this alloy.

Figure 4.b : Spectra for H=0-100Oe

Figure 4.c : Spectra for H=0-50Oe

Figure 4.d : Spectra for H=0-2Oe

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