Thermal stability and magnetic properties of FeSiB amorphous alloy

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It is well known that magnetic amorphous materials, in particular the commercial metallic glass ribbons, have good soft magnetic properties, such as: low coercivity, high magnetic saturation field, and high magnetic permeability. However, these properties change significantly when these materials undergo thermal treatments. For these reasons, the study and controlling of thermal stability of such alloys are key questions for sensor applications. In this work we have investigated the thermal and magnetic properties of the $Fe_{78}B_{13}Si_9$ metallic glass.

All experiments were carried out on pieces of approximately 20 mm^2 of the $Fe_{78}B_{13}Si_9$ metallic glass (supplied by Honeywell International Inc.) prepared by melt spinning technique. Differential scanning calorimetry (DSC) analyses were performed with a Shimadzu DSC-50 equipment between room temperature and 998 K, under an argon flux of 30 ml/min. The signals were always recorded in the heating ramps, with heating-rates (β) of 10, 15 and 20 K/min. Kinetic analysis was carried out according to the Ozawa method [1]. Structural changes in as-received and isothermally annealed samples were explored by X-ray diffraction (XRD) with Cu-K_α radiation. ^{57}Fe transmission Mössbauer spectra (MS) were recorded at room temperature (RT), with a 25mCi ^{57}Co radioactive source in Pd matrix. The γ-rays propagation direction was perpendicular to the ribbon surface. Heat treatments were performed in air with temperature accuracy of $\pm$2 K. The Mössbauer spectra were fitted by a hyperfine field distribution using a histogram method described by Brand and Le Caer [2]. To reproduce the small asymmetry of the spectra, a linear correlation between hyperfine magnetic field (B_{hf}) and isomer shift (IS) was assumed.

Fig. 1 shows the DSC curves recorded with three different heating rates. The occurrence of two exothermic peaks is clearly recognized and associated with distinct crystallization processes occurring upon heating. These peaks are attributed to the crystallization of the Fe_2B (at lower temperature) and Fe_3Si (at higher temperature) phases. The activation energies of these two processes, obtained from the DSC curves (inset), were found to be 370 kJ/mol and 351 kJ/mol, respectively. These values are in agreement with previous results in other amorphous alloys [3, 4].

The XRD patterns of the as-received and annealed samples are displayed in Fig. 2 (right side). For annealing times shorter than 8 min, no Bragg peaks associated with crystalline phases are clearly detected, within our experimental resolution. For longer times (8 and 24 min), it is observed the presence of the Fe_3Si and Fe_2B crystalline peaks superimposed on the residual amorphous phase (broad maximum). Finally, the XRD pattern of the sample annealed for 63 hr exhibits only the presence of the above mentioned crystalline phases. Fig. 2 (left side) also displays the MS of the as-received and annealed samples. The broad MS absorption resonance lines of the as-received samples are due to a topological and chemical disorder on the ^{57}Fe atoms neighborhood. For annealing time of 8 min and above, it is observed a change in the 2 and 5 line intensities (counting from left to right). This result is explained considering that the orientation of the Fe magnetic moments relative to the ribbons plane determined directly from the relative line intensities. These intensities have a 3:x:1:1:x:3 ratio, where x is a function of the angle between the γ-rays propagation direction and magnetic moments orientation in the ribbons plane. For in-plane magnetization, x assumes value of 4, and zero for out-of-plane, considering the γ-rays propagation direction perpendicular to the ribbon plane. It was calculated that, for as-received sample, x has a value close to 3.2, which indicates an average magnetization near the ribbon plane.

The hyperfine magnetic field distributions obtained from the MS of the samples annealed up to 24 min remain nearly unchanged (Fig. 2, inset), indicating that the samples are chemically and structurally similar, in contrast to the clear magnetic reorientation observed for the same samples.

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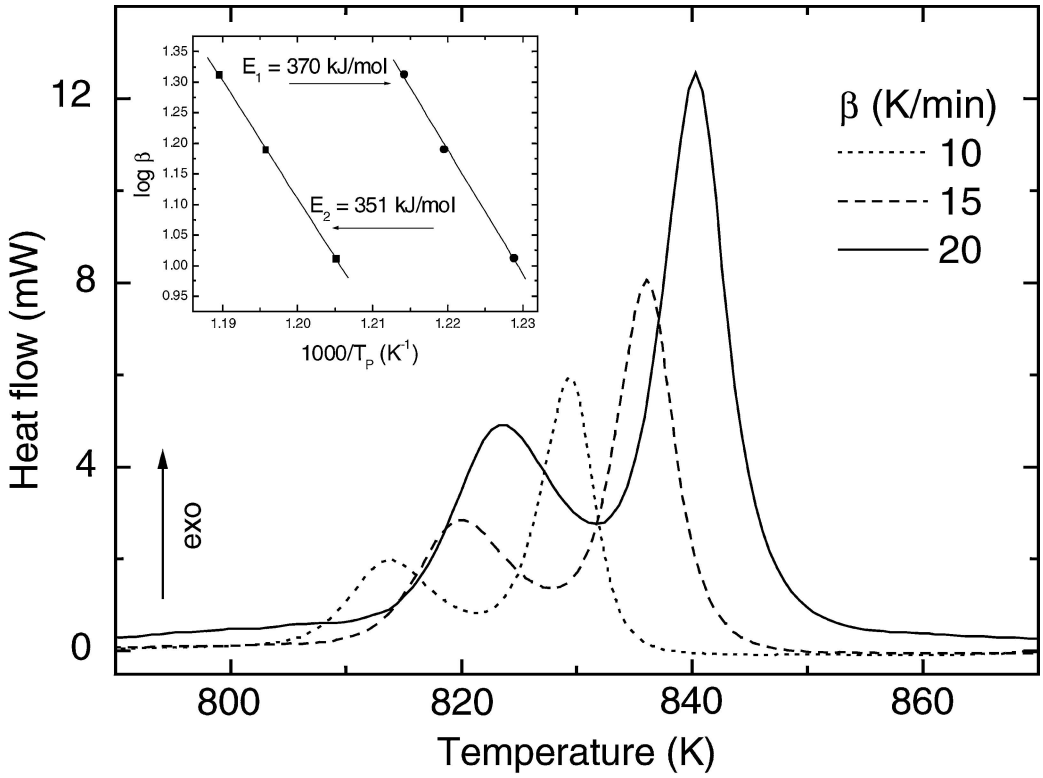

Figure 1 DSC curve for $Fe_{78}B_{13}Si_9$ recorded with three values of heating-rates (β). Inset: Ozawa plot [1].

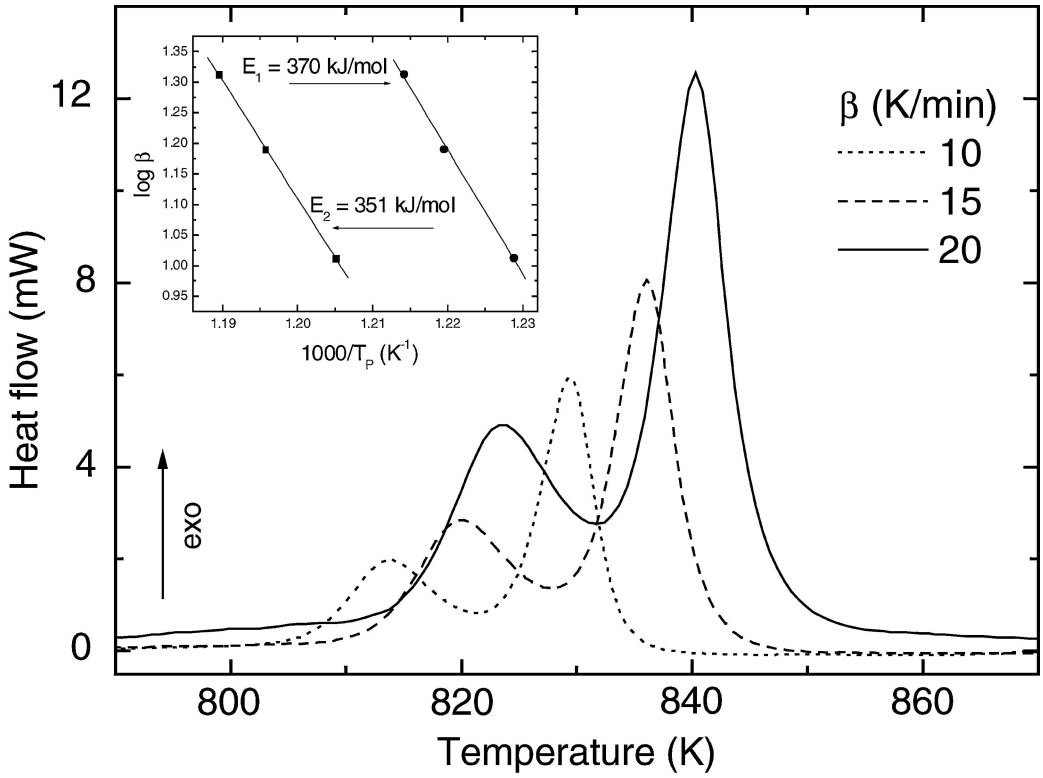

Figure 2 Mössbauer spectra (left) and X-ray diffractograms (right) of as-received and annealed at 773 K samples. (x) Fe_2B and (*) Fe_3Si.

In order to get total crystallization in the material, a sample was annealed for 63 hr at 773 K. Based on XRD results and on magnetic hyperfine parameters found in the literature, the spectrum for this sample was fully fitted with a convolution of five magnetic subspectra, two from the Fe_2B ordered phase [5] and three from the DO_3 phase of Fe_3Si [6].

Looking at the results obtained for annealing times up to 24 min, it is apparent that crystallized fractions observed by the two techniques are quite different. For instance, while there is a considerable crystalline contribution to the diffractogram for the sample annealed during 24 min, the corresponding Mössbauer spectrum shows no crystalline phase formation.

The crystallization begins with the formation of very small crystals and/or atomic clusters with crystalline-like short-range order (embryos), embedded in the amorphous matrix. Mössbauer spectroscopy is more sensitive to the presence of these small associations of atoms with a particular short-range order than X-ray diffractometry. Therefore, the above stated difference between the two techniques results indicates that it may originate from their different sampling ability. The gamma rays emitted by the ^{57}Co source have sufficient energy (14.4 keV) to explore sample bulk as well as the surface regions, whereas the less energetic X-rays can effectively search only few microns deep the ribbons surface. Then, transmission Mössbauer results reflect mostly the state of the sample bulk while XRD seems to be more sensitive to the ribbon regions close to the surface. It may be concluded that the crystalline phases detected by XRD exist essentially at the ribbon surfaces. This conclusion is supported by the well known results which show that small crystalline regions are present at the so called wheel-side of the melt-spun ribbons, even for as-prepared samples.

Now the question to be answered is how the two processes, spin reorientation and crystallization onset, are correlated.

During the annealing at 773 K frozen-in stresses are gradually removed from the ribbons [7]. These stresses are of tensile type in the as-prepared sample and favor the in-plane magnetization state due to the positive magnetostriction of the amorphous alloy. Therefore in-plane domains are large and dominate the magnetization state of the sample as shown by the Mössbauer spectrum of the as-prepared ribbon. As annealing progresses, magnetic domains with different magnetization orientations grow at the expenses of in-plane ones, leading to a more isotropic state, in order to minimize the magnetostatic energy of the material. The fact that for long annealing times (i.e. 24 min) out-of-plane magnetization begins to dominate might be associated with magnetic anisotropy effects at the interfaces amorphous/air or amorphous/crystal. From XRD peak intensities, it seems that the Fe_3Si phase grows with preferential orientation, a fact that would support the previous interpretation. Recently, a structure-magnetization reorientation was also found in FeCuNbSiB films [8].

The frozen-in stress also induces a preferential texture for crystalline phase formation at the ribbons surface during fabrication and annealing processes. This preferential texture would in turn provide a definite magnetic anisotropy at the grain boundaries, with the amorphous phase favoring an out of plane spin distribution after 24 min annealing. A similar behavior, but using temperature instead of time as annealing parameter, was described by Ok and Morrish and also by Herzer and Hilzinger [9, 10]. As shown in Fig. 1, the annealing treatments shown are carried out at temperature well below the first crystallization peak. Furthermore, the present results may also indicate that the thermally activated process had provided a simple way to prepare amorphous ribbons with defined magnetic orientations.

In summary, a clear re-orientation spin effect has been observed in Metglas $Fe_{78}B_{13}Si_9$ amorphous ribbon, from in-plane to out-of-plane, which may be correlated with the beginning of the crystallization process at the surface. We also found that the two processes are related to the existence of a frozen-in stress in the melt-spun alloy. This stress induces an in-plane preferential orientation of the magnetization and its gradual release with annealing may favor an out-of-plane magnetization.

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