Magnetic hardening of FeSiBCuNb ribbons and wires during the first stage of crystallization to a nanophase structure

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The structural and magnetic properties of $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$ alloy wire and ribbon have been studied after thermal treatments up to temperatures at which partial (75%) devitrification to a nanocrystalline structure occurs. Nanocrystals are detected by x-ray diffraction only after treatments around 500 °C, while differential scanning calorimetry studies suggest that substantial structural change is inititiated at a much lower temperature (about 400°). A clear magnetic hardening is observed in samples heated within the temperature range 400–480 °C. This phenomenon is also accompanied by an increase of the linear magnetostriction. These effects are discussed in terms of the local structural rearrangements produced during the first stages of the crystallization process. The study is also extended partly to FeSiB, FeSiBCu, and FeSiBNb alloys.

As observed by Yoshizawa *et al.*[1] for the first time, the addition of small amounts of Cu and Nb to conventional FeSiB amorphous alloy gives rise to an improvement in its soft magnetic behavior after heat treatments above the crystallization temperature. A number of works have been published focusing on this outstanding and unexpected phenomenon, which has been ascribed to the stable and homogeneous nucleation of α-FeSi grains, having a typical mean diameter of around 10 nm, when the sample is heated within the range of temperatures between 530 and 580 °C. Herzer[2] has proposed that the aforementioned softening is a consequence of the averaging out of the effective magnetocrystalline anisotropy of the nanocrystals owing to their having diameters significantly smaller than the exchange correlation length (around 40–50 nm). The magnetoelastic contribution to the magnetization process is also decreased, due to the reduced value of the magnetostriction after devitrification to α-FeSi nanocrystallites. Some recent investigations have also been concerned with the decisive role played by Cu and Nb atoms in promoting such a structure.[3]

On the other hand, it is commonly assumed that annealing at lower temperatures (below 500 °C) relaxes the structure, maintaining its amorphous character and resulting in moderate magnetic softening due to the relaxation of intrinsic cast-in stresses. Previous studies mainly deal with the magnetic softening observed in nanocrystalline samples but little attention is paid to reordering of the glassy structure and to the early stages of the crystallization process. The aim of this letter is to report new results concerning the magnetic behavior of such alloys when thermally treated at temperatures below those for which a substantial degree of crystallization occurs.

Amorphous alloys with nominal compositions $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$, $Fe_{73.5}Si_{13.5}B_{13}$, $Fe_{73.5}Si_{13.5}B_{12}Cu_1$, and $Fe_{73.5}Si_{13.5}B_{10}Nb_3$ were cast at the University of Sheffield by *melt* spinning techniques in the shapes of ribbon (1 mm×20 μm cross section) and wire (120 μm diameter).[4] The length of samples used for magnetic measurements was 100 mm. Thermal treatments were performed in an inert atmosphere in a conventional furnace for 1 h. at different temperatures. Alternatively, wire-shaped alloys were also thermally treated by a current annealing technique for 1 min, using different current densities flowing along the wires.[5]

The structure of as-cast and annealed samples was monitored by x-ray diffraction. For the $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$ alloy, the first diffraction peaks indicating the appearance of α-FeSi nanocrystals were only noticeable after annealing at 520 °C. Treatments below this temperature did not result in a significant change in the structure as indicated by x-ray diffraction. Nevertheless, from the magnetic point of view, significant modifications were detected. The hysteresis loops and their typical parameters (coercivity, susceptibility, etc...) for this composition were obtained by a conventional 15 Hz induction technique, for as-cast wire and after treatments at particular temperatures. In the as-cast state, magnetic bistability is observed.[6] Figure 1(a) shows the dependence of initial susceptibility on the annealing temperature for ribbon- and wire-shaped alloys. It first increases after annealing at around 420 °C which must be ascribed to a reduction of internal stresses during the heat treatment. Then, it decreases to a minimum at around 460 °C and finally increases rapidly again up to the highest measured value at 550 °C corresponding to an optimum degree of crystallization. It should be mentioned that values given for the wire in its as-cast state and after annealing up to about 380 °C correspond to the susceptibility around the remanent state, since its bistable magnetic behavior precluded attainment of the demagnetized state.[6] In order to obtain more information about the hardening observed prior to crystallization, samples of wire having the same quinternary composition were submitted to current-annealing treatments. In this case, the magnitude of the current flowing through the wire determines the temperature.[5] As shown in Fig. 1(b), where susceptibility, χ, is plotted against the current density, j, very similar behavior to that of the furnace treated samples is found (values of χ for j less

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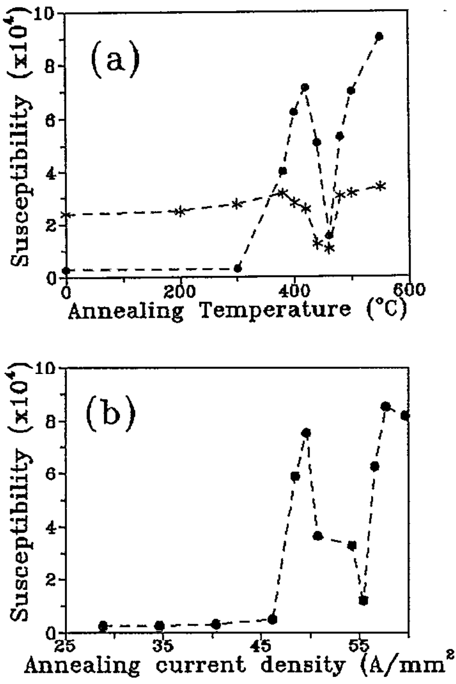

FIG. 1. Initial susceptibility for ribbon (*) and wire-shaped (●) $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$ alloy samples as a function of annealing temperature (a) and current density (b) during the treatment.

than about 45 A/mm^{-2}, correspond to susceptibilities at remanence).

On the other hand, the magnetostriction is known to decrease drastically upon crystallization as a consequence of the competition between the negative contribution of α-FeSi grains and the positive value associated with the residual matrix.[2] Figure 2 shows the modifications of the linear magnetostriction, λ, evaluated by the small angle magnetization rotation method. A clear increase of λ is found beginning at about 400 °C and before the crystallization process is initiated. It achieves a maximum at about 460 °C, evidently when devitrification proper begins, after which it decreases by about one order of magnitude as the nanocrystals grow. It should be added that the maximum value of λ is very close to that for ternary alloys of similar composition, but with no addition of Cu and Nb.[7]

The influence of prior thermal treatments has also been studied by differential scanning calorimetry (Perkin–Elmer DSC-7) at a heating rate of 40 °C/min. Table I gives the data for the exotherm corresponding to the crystallization process as well as the energy of the process (area under the peak). From the decrease of that energy after one hour isochronal treatments at various temperatures below 500 °C it can be deduced that substantial structural rearrangements (occurring after conventional relaxation of the glassy phase) begin beyond about 400 °C, well before crystallization is detected by x-ray diffraction.

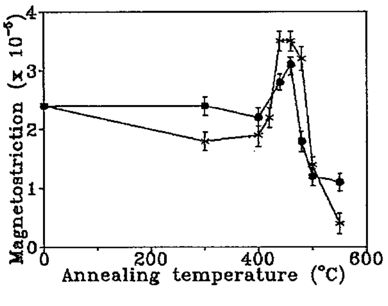

FIG. 2. Evolution of the linear magnetostriction with annealing temperature for ribbon (*) and wire (●) samples of $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$.

TABLE I. Parameters for the exothermic peaks obtained by DSC, corresponding to the crystallization process for wire samples of $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$, previously submitted to 1 h heating at the indicated temperatures.

Annealing temperature (°C)	Crystallization peak data		
	T_{onset} (°C)	T_{maximum} (°C)	energy (*J/g*)
as-cast	550	569	−50
300	547	567	−54
400	551	567	−51
440	551	568	−47
460	549	568	−39
480	546	570	−28

From the susceptibility measurements reported here for the $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$ ribbon and wire samples, it is clear that the alloy becomes magnetically harder after annealing in the temperature range between 400 and 480 °C compared with either its relaxed amorphous state or the nanostructured state after crystallization. A structural change is also manifested over this range by the magnetostriction data. It is interesting to speculate on the origin of the hardening. From the x-ray diffraction patterns, we can deduce only that, if structural rearrangements occur when annealing below 520 °C, they are not sufficiently significant to be detected by this technique. Nevertheless, based on the calorimetric data, we propose that structural reordering, eventually leading to crystallization, begins at annealing temperatures of around 400 °C.

In order to obtain further information about the relationship between the structure and magnetic properties, the studies have been extended to $Fe_{73.5}Si_{13.5}B_{13}$, $Fe_{73.5}Si_{13.5}B_{12}Cu_1$, and $Fe_{73.5}Si_{13.5}B_{10}Nb_3$ alloys (wire and ribbon shaped). Figure 3 shows the evolution of coercivity as a function of the annealing temperature for wire-shaped sample of all four compositions. As observed in this figure, the coercivity of the FeSiB ternary alloy first relaxes and then rapidly increases after annealing beyond about 460 °C when crystallization begins. The addition of Cu to that sample destabilizes the FeSiB glass so that crystallization begins at a lower temperature.[8] On the other hand, the addition of Nb alone delays the final crystallization process for the FeSiB alloy to higher temperature.

Accordingly, the change in magnetic behavior with annealing temperature for the wire sample containing both Cu and Nb can be interpreted as follows: the initial magnetic softening is produced by the relaxation of internal stresses (magnetoelastic anisotropy) within the amorphous state. The latter magnetic hardening (after annealing between 440 and

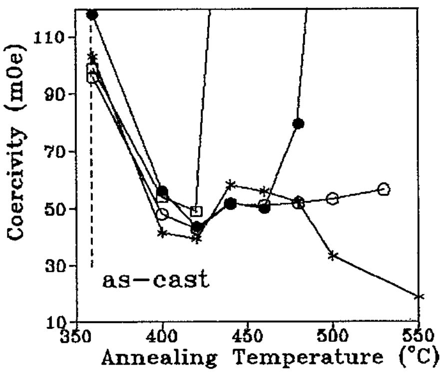

FIG. 3. Dependence of coercivity on annealing temperature for wire samples with compositions $Fe_{73.5}Si_{13.5}B_{13}$ (●), $Fe_{73.5}Si_{13.5}B_{12}Cu_1$ (□), $Fe_{73.5}Si_{13.5}B_{10}Nb_3$ (○), and $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$ (*).

480 °C) seems to be a consequence of the appearance of Cu-enriched clusters of diameter around 5 nm which form even before the onset of crystallization. Simultaneously with this Cu-atom segregation, α-FeSi grains start to nucleate, still representing quite a small volume fraction of the sample (not detected by x-ray diffraction). Both the Cu-enriched clusters and the α-FeSi nanocrystals would act as pinning centers for the domain wall displacements, thus increasing the coercivity. The final magnetic softening is a consequence of the increase in the number and the volume fraction of nanocrystallites (the latter up to about 75%, corresponding to optimal magnetic softness),[2] but with exchange coupling of crystallites operating because of the effect of Nb in preventing classical grain coarsening. Similarly, the observed increase of the magnetostriction, shown in Fig. 3, can also be related to the formation of Cu-rich clusters (also containing Nb) during annealing within the range 400–480 °C. With these initial structural changes, the amorphous matrix would change its local composition closer to ternary FeSiB, resulting in an increase of the effective magnetostriction. This latter increase would also contribute to the observed magnetic hardening.

In conclusion, the reported magnetic hardening for the $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$ during the first stages of the nanocrystallization process seems to be related to the initial atomic rearrangements mainly involving Cu atoms. A more complete experimental study of these effects is currently in progress.

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[1] Y. Yoshizawa, S. Oguma, and K. Yamauchi, J. Appl. Phys. **64**, 6044 (1988).

[2] G. Herzer, IEEE Trans. Magn. **25**, 3327 (1989).

[3] K. Hono, A. Inoue, and T. Sakurai, Appl. Phys. Lett. **58**, 2180 (1991).

[4] A. O. Olofinjana and H. A. Davies, Scripta Metall. Mater. **27**, 161 (1992).

[5] M. Vázquez, J. González, and A. Hernando, J. Magn. Magn. Mater. **53**, 23 (1986).

[6] C. Gómez-Polo, A. O. Olofinjana, P. Marín, M. Vázquez, and H. A. Davies, IEEE Trans. Magn. **29**, 2673 (1993).

[7] M. Müller, N. Mattern, and L. Illgen. J. Magn. Magn. Mater. **112**, 263 (1992).

[8] I. W. Donald and H. A. Davies, Philos. Mag. A **42**, 277 (1980).