Time and temperature dependence of nanocrystalline structure formation in a Finemet-type amorphous alloy

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Abstract

The magnetic softness and nanocrystalline structure formation of Fe_{73.5}Cu_{3}Nb_{3}Si_{13.5}B_{9} Finemet alloy as a function of annealing temperature (500–600°C) and annealing time (5 s–3 h) were investigated by means of magnetic measurements, DSC and X-ray diffractometry. Annealed at 550°C the grain size, the solute silicon content of α-Fe grains and the improvement in magnetic softness saturates as a function of time. The deterioration of the magnetic softness after annealing at 575°C is attributed to the Fe_{3}Si compound which segregates from the α-Fe solid solution, giving a third intermediate peak on the well-known double-peaked DSC diagram. The crystallization products appearing after annealing at 600°C destroy the intergranular magnetic coupling and give rise to a magnetic hardening.

1. Introduction

The partially crystallizing heat treatment of Fe_{73.5}Cu_{3}Nb_{3}Si_{13.5}B_{9} amorphous alloy [1] leads to a magnetic softening compared with the amorphous state. In other words, the initial permeability increases and the coercivity decreases by about one or two orders of magnitude. This peculiar soft magnetic behaviour is connected with the nanocrystalline structure characterized by the size (and size distribution), composition, and interfaces of the constituent phases. When engineering such a material as Finemet, it is necessary to understand the interplay among these three features with the conditions for good soft magnetic properties, i.e. (i) vanishing magnetic anisotropy (⟨K⟩ ≈ 0); (ii) vanishing magnetostriction (⟨λ⟩ ≈ 0); and (iii) strong intergranular magnetic coupling. According to the random anisotropy model [2], ⟨K⟩ ≈ 0 is a consequence of nanometer grain size (∼ 10 nm, smaller than the exchange length (∼ 35 nm) of the α-Fe(Si)). The magnetostriction is reduced towards zero by the balance between the α-Fe(Si) crystallites with negative λ and the amorphous matrix with positive λ [2]. This balance is rather sensitive to the α-Fe(Si) phase composition and to the degree of crystallinity that increases with annealing time [3]. The intergranular magnetic coupling is weakened when secondary crystallization phases precipitate in the interface region.

The aim of this paper is to study the time-temperature evolution of grain size and composition by X-ray diffraction analysis (linewidth and lineshift), in parallel with the soft magnetic properties: initial permeability and power loss.

2. Experimental

Amorphous alloy ribbons, obtained by melt spinning, with nominal composition Fe_{73.5}Cu_{3}Nb_{3}Si_{13.5}B_{9} (10 mm wide, 30 μm thick) were used as amorphous precursors. Thermal treatments (between 10 min and 3 h) were performed in a conventional field-free furnace in an Ar atmosphere for toroidal samples. The toroidal sample was placed in a toroidal ceramic sample holder.
before heat treatment and it was investigated without touching the brittle crystallized core. Short-term heat treatments (between 5 s and 10 min) and also longer ones for comparison were carried out in a tin bath on sheet samples 6 cm long.

The crystallization products were investigated on powdered samples by X-ray diffraction (Cr Kα radiation) at room temperature using a Guinier camera and a quartz monochromator. The apparent average grain size \( D_{\text{av}} \) was determined from the broadening of the (110) line of bcc α-Fe, using Sherrer's formula [4], the Si content of α-Fe nanocrystals was obtained from the shift in the α-Fe (110) peak position, in accordance with Pearson [5]. The bcc line could be easily separated from the amorphous background but the determination of the line broadening was disturbed by the background so the calculated average grain size is more an estimated value. The nanocrystalline phase consists essentially of Fe and Si, since B, Cu and Nb in α-Fe are not soluble below 600°C according to the binary phase diagrams.

The initial permeability was measured with a Hewlett-Packard 4274 A Multi Frequency LCR Meter at 1 kHz. The power loss was determined with a home-built, highly automated measuring system [6] based on the numerical integration of the hysteresis loop at a given frequency and exciting field.

Crystallization of the as-received and partially crystallized material was investigated by a Perkin-Elmer DSC-2 differential scanning calorimeter.

3. Results and discussion

The evolution of the grain size and grain composition as a function of annealing time, at different annealing temperatures can be followed in Fig. 1. Both structural parameters show saturation with the annealing time at about 10 nm and 20 at% Si content, respectively. This means that the partially crystallized structure is quasi-stable as long as the annealing temperature remains around the first DSC peak (Fig. 2). This stability of Finemet alloy is achieved by the combined effect of Cu and Nb additions [7].

Similar to the structural evolution, an improvement in saturation of the soft magnetic properties as a function of annealing time has been obtained for 550°C (Fig. 3). The power loss decreases rapidly with increasing Si content in the nanocrystalline phase. The initial permeability on the contrary is sensitive not only to the Si content but also to the increase in crystallinity, as that is also needed to decrease the average magnetostriction near to zero.

A small deterioration of the magnetization properties was observed after annealing at 575°C/h. For this sample, X-ray analysis shows the appearance of Fe₃Si precipitates as well as the α-Fe grains. The difference between the samples annealed at 550 and 575°C can be seen on the DSC diagram as well (Fig. 2). For the as-received sample the diagram consists of two peaks: the first corresponds to the α-Fe precipitation, and the second to the crystallization of the remaining amorphous matrix. In reality, however, the shoulder of the first peak covers a third, intermediate peak which we attribute to the formation of ordered Fe₃Si from Fe(Si) solid solution. This small intermediate peak is still present after annealing at 550°C/h, showing that such a heat treatment preserves the Fe(Si) solution. After annealing at 575°C/h, however, the intermediate peak disappeared, indicating the partial decomposition of Fe(Si) solid solution into ordered Fe₃Si. As a consequence, we attribute the small deterioration in the magnetic softness to the decrease in the solute silicon content. The existence of the third peak in the DSC curve was found also by Zhu et al. [8], who attributed it to the disorder-to-order transformation of α-FeSi. They found this third peak after the beginning of Fe₂B.
Fig. 2. DSC diagram of the as-received and some annealed samples taken with 20°C/min.

Form. This discrepancy may be due to the different amorphous structures of the precursor amorphous alloys.

After annealing at 600°C/2 h all the improvements connected with the nanocrystalline structure compared with the amorphous one are lost. The X-ray pattern shows the precipitation of Fe3B from the amorphous matrix, without a significant increase in the α-Fe grains. The magnetic hardening is probably due to the presence of Fe3B precipitates in the interface regions; these Fe3B precipitates reduce the local exchange length and, accordingly, produce a weakening in the intergranular magnetic coupling [9].

4. Summary

We have investigated the conditions for magnetic softening upon partially crystallizing heat treatment of a Finemet alloy. If this is annealed at a temperature corresponding to the first DSC crystallization peak, 550°C, as a function of time, a quasi-stable nanostructure forms with increasing crystallinity and saturating grain size and Si content of the α-Fe grains at about 10 nm and 20 at%, respectively. A corresponding improvement in magnetization properties was observed as a function of annealing time. If the annealing temperature is increased, this leads to a deterioration in the magnetic softness. Precipitation of the ordered Fe3Si at 575°C produces minor damage, but the precipitation of Fe3B at 600°C causes a magnetic hardening, probably because of the weakening of intergranular magnetic coupling.

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References