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Nanocrystalline FeSiBNbCu alloys: Differences between mechanical and thermal crystallization process in amorphous precursors

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Abstract

Nanocrystalline magnetic particles obtained by high energy ball milling of FeSiBNbCu alloy were prepared from rapidly quenched ribbons as a starting material. Structural characterization was made by using X-ray diffraction (XRD), differential scanning calorimetry (DSC), atomic force microscopy (AFM) and Mössbauer spectroscopy. The structural changes observed in this amorphous material suggest that nanocrystallization process takes place in a different way from the one induced by thermal treatments. Our different studies reveals that after short grinding times (up to 40 h) the material is composed by a two phase system of very fine nanocrystals embedded in a residual amorphous phase, while for largest periods of milling (from 140 h) the sample consists of a very fine nanocrystalline phase with a large fraction of grain boundary.

Keywords: Ball milling; Mechanical nanocrystallization; Nanoparticles; Grain boundary

1. Introduction

Thermal crystallization is known to be the most common way of nanocrystallizing amorphous metallic alloys. In FeSiBNbCu material the evolution of the crystallization process in an amorphous sample submitted to a wide range of temperatures is correlated with that of the magnetic properties in ribbons and wire shaped samples [1]. The role of Cu in this system is to destabilize the FeSiB alloy by forming clusters of about 5 nm at relatively low temperatures (450–480 °C), and inducing nucleation and growth of α-Fe(Si) grains at higher temperatures (550 °C) [2]. Beside this, Nb inhibits their growth because of the rejection of Nb into the amorphous matrix. Thus, the progression to a large volume fraction (75%) of fine crystallites of about 10–15 nm promotes the magnetic softening of this material. Heat treatments at higher temperatures (620 °C) give rise to complete crystallization signaled by the appearance of a boride phase with greater crystals which deteriorates the soft magnetic properties.

Another route of crystallization is that consisting of mechanical milling of amorphous precursor [3]. This type of mechanical deformation allows the obtention of different microstructures in terms of crystalline grain size, composition and percentage of amorphous phase, as well as a wide distribution of particle size, even in the range of nanometer scale.

The aim of our work is to give evidence of this nanometer size and to understand the mechanisms responsible for the structural change occurring during ball milling. We investigate the mechanical crystallization process of amorphous Fe–Si–B–Nb–Cu alloy, of which thermal crystallization is known, by means of transmission Mössbauer spectroscopy.

2. Experimental

Rapidly quenched ribbons of nominal composition $Fe_{73.5}Si_{16.5}B_6Nb_3Cu_1$ were prepared by melt spinning. The amorphous nature of the as-quenched ribbons was confirmed by X-ray diffraction. After cutting them into small pieces, they were sealed in the milling vial under a protective atmosphere, and submitted to ball milling using a Retsch PM 400 planetary ball mill for different times between 20 and 200 h. Hardened steel vials and balls were used, the ball to powder weight ratio being 7:1. The mill operated at 200 rpm in the regime 40 min work–10 min stop in order to avoid some overheating. Samples structure was monitored by X-ray diffraction using Cu Kα radiation, and crystallization dynamics was followed by differential scanning calorimetry (Perkin-Elmer Pyris 7). The evolution of hyperfine structure at room temperature was followed by Mössbauer spectroscopy using ^{57}Co source embedded in a Rh matrix in standard transmission configuration. Information about particle size was obtained for the sample submitted to 140 h of milling by means of atomic force microscopy in non-contact tapping mode. For this purpose the powder was ultrasonically dispersed in acetone and this suspension was sprayed onto a mica substrate.

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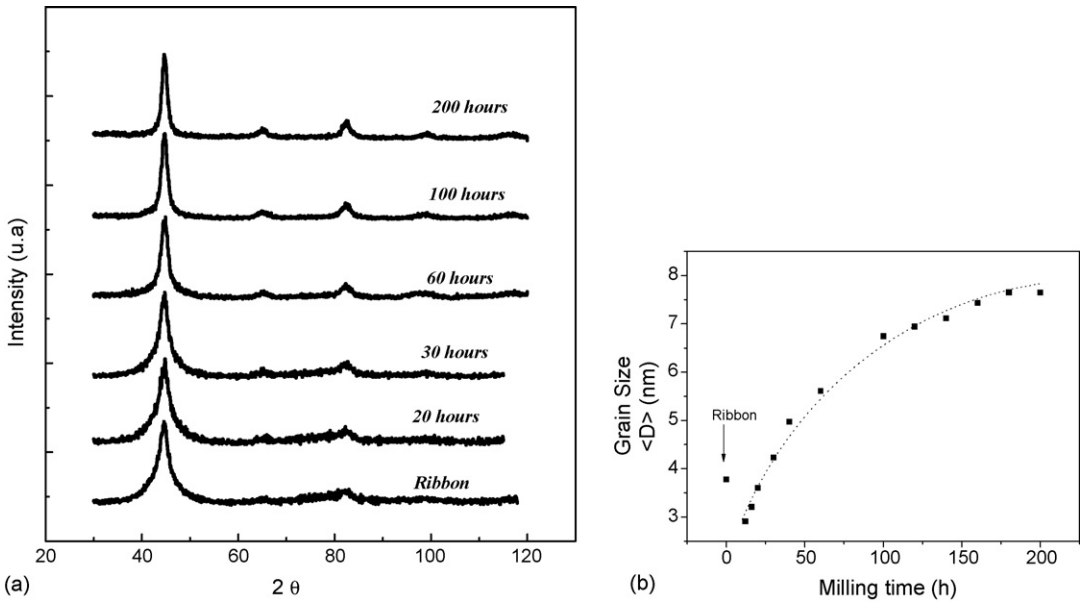

Fig. 1. X-ray diffraction patterns of samples submitted to different milling times (a) and evolution of grain size with grinding time (b).

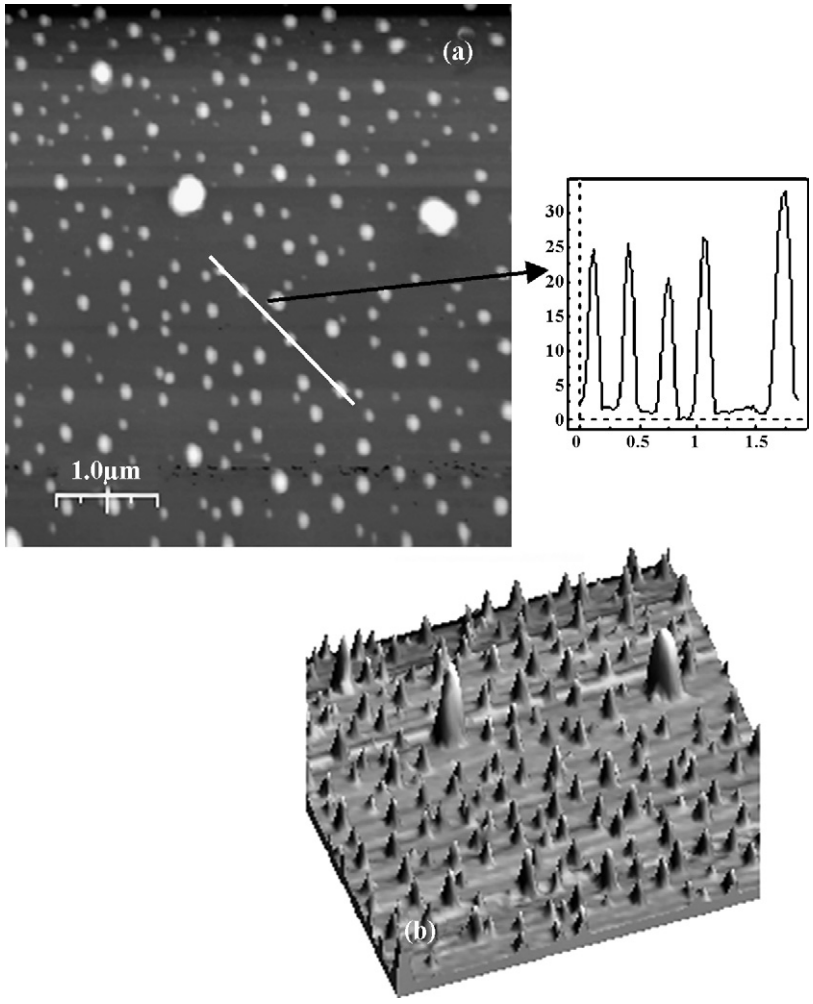

Fig. 2. AFM image (in non-contact tapping mode) of the sample submitted to 140 h of milling (a) and the corresponding topography profile (b).

3. Results and discussion

Diffractograms obtained for the amorphous ribbon and for the samples taken after different milling times up to 200 h show a progressive crystallization of α-Fe(Si). No traces of boride phases are observed during the progression of grinding (Fig. 1a). Average grain size, $\langle D \rangle$, calculated by using Debye–Scherrer equation in the (1 1 0) reflexion reflects an increase of $\langle D \rangle$ with milling time, although it tends to stabilize well below 8 nm (Fig. 1b). Previous studies involving calorimetric results in these samples showed the existence of two stages in the mechanical crystallization process [4]. A first one, including short milling times up to 40 h, is characterized by small nanocrystals induced mechanically and embedded in an amorphous matrix, while the other stage, with more extended grinding times (from 140 h), is described by a completely nanocrystallized and refined structure. These results show how the final microstructure of the as-milled samples differs from the one resulting from conventional thermal annealing (550 °C for 1 h) of amorphous ribbons of the same composition, where the average grain size is higher (10–15 nm).

Since mechanical deformation is a low temperature process, the growth of crystalline phase takes place at a slower rate. Additionally, as the crystals are forming they fracture into smaller pieces due to presence of high density of dislocations and the accumulation of internal stresses, explaining the crystals refinement. These continuous fractures give rise to a further decrease of the micrometer size of the particles. By atomic force microscopy it was possible to image these particles individually, as is shown in Fig. 2a. The particle size can also be measured from the images (Fig. 2b), considering the particle height, while the width is largely distorted by the tip geometry. In this way it was possible to verify the presence of nanoparticles with a wide size distribution (100 to below 10 nm)

The Mössbauer spectrum of the as quenched Fe–Si–B–Nb–Cu alloy is given in Fig. 3a and was fitted considering a distribution of hyperfine magnetic fields (HFF), representative of an amorphous like structure. The average value of the hyperfine magnetic field is around 20 T. When the ribbon is subjected to mechanical grinding, crystallites progressively precipitate within the amorphous matrix, which is reflected by the appearance of different subspectra in the fitting. Thus, after 12 h

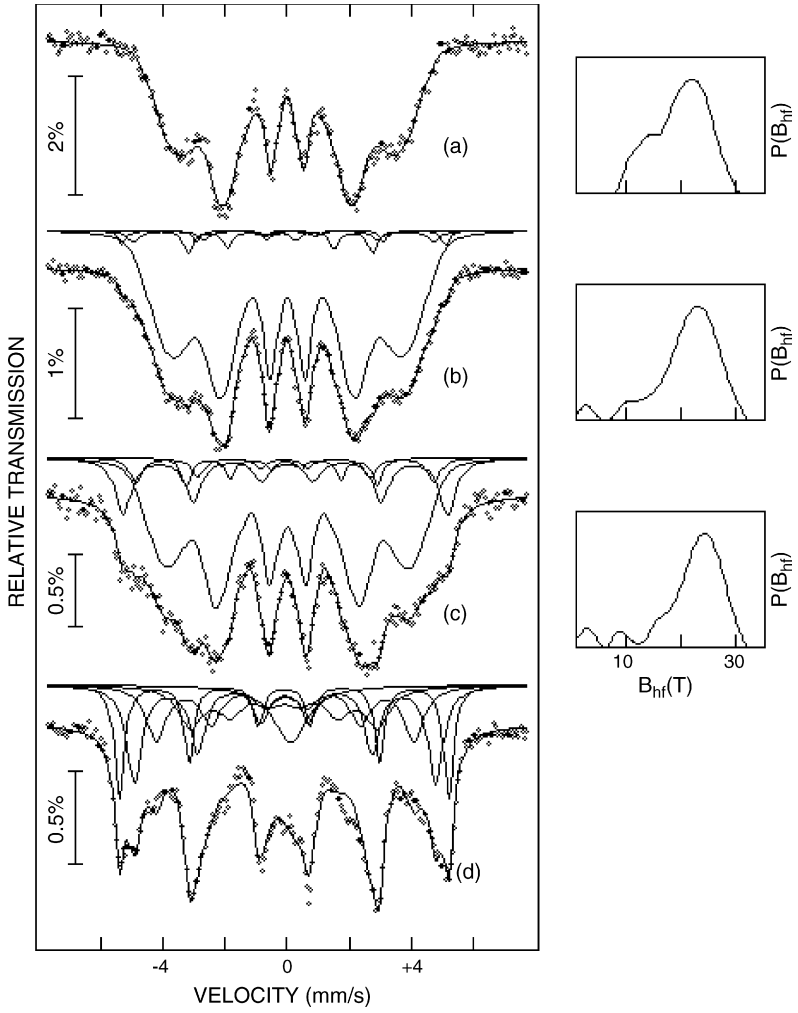

Fig. 3. Room temperature Mössbauer spectra for as-cast ribbon (a), 12 h (b), 20 h (c) and 140 h milled sample (d).

Table 1
Mössbaur parameters of $Fe_{73.5}Si_{16.5}B_6Nb_3Cu_1$ powders after different milling times

Milling time	Amorphous phase		Crystalline phases		Γ (mm/s)
	%	B_{hf} (T)	%	B_{hf} (T)	
Ribbon	100	19.9	–	–	
12 h	90.8	21.1	9.2	32.4, 30.1, 18.5	0.29, 0.47, 0.36
30 h	72.1	21.6	27.9	32.5, 29.9, 19.1	0.63, 0.49, 0.38
140 h	–	–	100	33.0, 30.2, 25.8, 18.7	0.38, 0.59, 0.75, 0.94

of ball milling the spectra are fitted by the combination of a distribution of HFF and three crystalline subspectra including different Fe-environments associated to α-Fe(Si) phase with hyperfine field values 32.5 and 30.1 T. The third contribution, with the lowest value of the hyperfine field (B_{hf} = 18.5 T) indicates an increasing number of nonmagnetic atoms around the iron atoms. Beside this, the larger line-width of these subspectra suggests a more disordered structure, which can be related to the presence of grain boundaries. This agrees with the very small size of the crystals. Further progression of grinding leads to an increment of the relative area of the crystalline subspectra, which is proportional to the crystalline fraction, at the expense of the amorphous phase. After 30 h of milling the mechanically induced crystalline fraction is near 30%.

Prolonged milling times of 140 h produce complete nanocrystallization of the sample. The hyperfine parameters of the sextets, listed in Table 1 indicate how, as the grinding follows, the different Fe-containing environments progress to pure bcc α-Fe (B_{hf} = 33) as well as the α-Fe(Si). An additional Fe-environment is included (B_{hf} = 25.8) which, as XRD confirms, is not related with a boride phase. Finally the sextet with B_{hf} = 18.5 T, associated with the interface is also present.

4. Conclusions

In summary we can conclude that mechanical grinding of amorphous ribbons induces a nanocrystallization process which differs from the one for conventional thermal annealing of Fe–Si–B–Nb–Cu ribbons. It is characterized by a refined microstructure with crystal size well below 10 nm, and consequently a large fraction of grain boundaries as can be associated to Mössbauer subspectra. Finally, evidence of nanoparticle formation during milling was given by AFM images.

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