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NMR studies of ^{93}Nb in FeNbB nanocrystalline alloy

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Abstract

Amorphous and nanocrystalline $Fe_{80.5}Nb_7B_{12.5}$ ribbons were investigated using nuclear magnetic resonance (NMR). A direct observation of the Nb environments was performed. The local anisotropy of the Nb-containing grains or phases is almost the same for the as-cast and the sample heat treated at 510°C for 1 h. After a 610°C/1 h annealing, the presence of pure α-Fe is observed and the anisotropy of the Nb phase decreases. © 2002 Elsevier Science B.V. All rights reserved.

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Nanocrystalline materials can be obtained by partial crystallization of an amorphous precursor, developing excellent soft magnetic properties, a fact that makes them potential candidates for practical applications [1]. The softness in their magnetic behavior has been explained in terms of a reduction in the magnetocrystalline anisotropy due to ferromagnetic coupling between randomly oriented nanocrystals mediated by the remaining amorphous matrix [2]. Fe-based nanocrystalline alloys from the ternary system FeMB (M = Zr, Ti, Ta, Mo and Nb) are of particular interest due to their superior magnetic properties, presenting higher saturation magnetization than the more conventional FINEMET alloy [3]. Among the ternary systems, the FeNbB alloy presents some differences in the crystallization process and exhibits the smallest grain size nanostructure [4]. In the present work, we study the evolution of the structural and magnetic properties of $Fe_{80.5}Nb_7B_{12.5}$ ribbons upon annealing using nuclear magnetic resonance (NMR) measurements. This technique allows us to investigate the niobium sites by means of the ^{93}Nb resonance. The RF power dependence of the spectrum gives unique evidence about the local magnetic stiffness of the various phases in the as-cast and annealed samples.

The samples were prepared by melt spinning process from a $Fe_{80.5}Nb_7B_{12.5}$ master alloy resulting in an amorphous ribbon with an average crosssection of $10 \times 28\,\mu m$. The nanocrystalline material was obtained by furnace annealing pieces of the as-cast ribbons at 510°C and 610°C during 1 h under high vacuum. Structural characterization by X-ray diffraction and transmission electron microscopy reveals that the nanocrystalline samples have a microstructure containing 26% of BCC-Fe crystalline phase after annealing at 510°C and 62% of crystalline phase after annealing at 610°C [5,6]. The NMR spectra were obtained using a home-made zero-field spin echo spectrometer in the frequency range between 20 and 200 MHz [7]. A sequence of two pulses with the following characteristics was used to excite the samples: $\tau_a = 2\,\mu s$, $\tau_b = 4\,\mu s$, pulse separation of 40 μs, and repetition rate of 0.2 kHz. The RF power was controlled by a variable power attenuator at the output of the RF power amplifier, a broadband ENI model 3100LA, of 100 W. The value of B_1/B_1^{max} corresponds to 0 dB of attenuation and $B_1^{max} \approx 10$ G. The RF power dependence of the spin-echo amplitude was taken at the central frequency of each resonance line of the spectra, with the excitation conditions described previously. The measurements were all made at 4.2 K, with the sample immersed in liquid helium.

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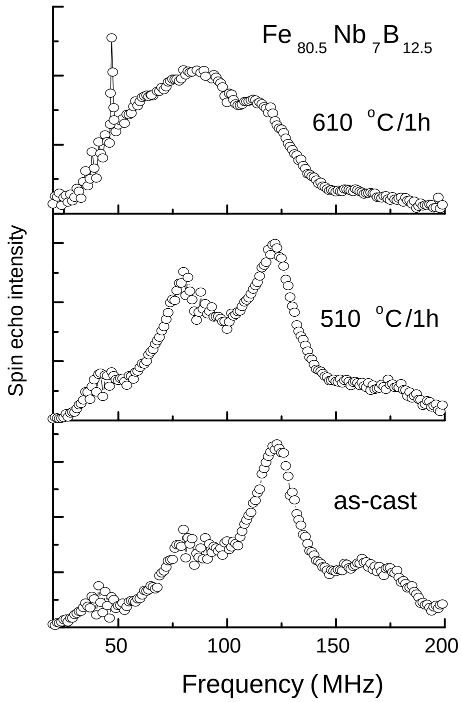

Fig. 1. Evolution of the NMR spectrum of a melt-spun $Fe_{80.5}Nb_7B_{12.5}$ ribbon upon annealing. The peaks at about 80, 120 and 160 MHz correspond to ^{93}Nb resonance with increasing number of Fe nearest neighbors, respectively.

Fig. 1 shows the NMR spectra obtained for the as-cast amorphous and nanocrystalline samples. The measurements reveal spectra composed of very narrow lines at low frequencies (<60 MHz), and three main broad lines at higher frequencies. According to a previous work on an FeB amorphous sample [8], the lower frequency side of the spectra can be related to the resonance of ^{57}Fe and ^{11}B atoms with different neighborhood; it is not the aim of this paper to investigate this region. We shall only notice that in the sample treated at 610°C, there is a well-defined narrow line at 46.8 MHz, the resonance frequency of BCC-Fe, pointing out to the presence of a large amount of pure alpha iron precipitates. Now we focus our attention on the three broad lines at 80, 120 and 160 MHz that correspond to Nb atoms with different atomic surroundings. To our knowledge, this is the first time a direct observation of the Nb environments is performed in soft nanocrystalline materials. As Nb is a non-magnetic atom, the higher the resonance frequency, the higher is the number of Fe atoms in the neighborhood. Comparing the Nb resonance lines in the amorphous and nanocrystalline samples, one can notice that their relative intensities change after heat treatment. More precisely, it is observed that with increasing annealing temperature, the intensity of the highest frequency line (160 MHz) decreases continuously whereas that of the lowest frequency line increases continuously. This observation demonstrates that during the annealing, the Nb atoms move from Fe-rich regions towards Fe-poor regions. Eventually, after the annealing at the highest temperature, Nb is nearly totally expelled from the α-Fe clusters. In addition, it is also clearly seen in Fig. 1 that the Nb NMR lines broaden more and more with the annealing treatment, which shows that the Nb-rich regions of the sample are more and more disordered. Eventually the Nb spectrum shows essentially a broad hump indicating that most of the niobium is now contained in an amorphous phase.

With these structural observations at hand, we have further investigated the correlated behavior of the magnetic softness of the samples by examining the NMR signal response as the excitation RF field strength was varied. In such an experiment, the NMR signal arising from harder and harder regions of the sample is favored as the RF power is increased.

Fig. 2 shows the behavior of the echo intensity for as-cast amorphous and nanocrystalline $Fe_{80.5}Nb_7B_{12.5}$ ribbons by varying the RF field strength. A maximum signal can be observed for some RF field strength that is proportional to the magnetic stiffness, i.e. the reciprocal of the initial permeability. Here it is observed that the

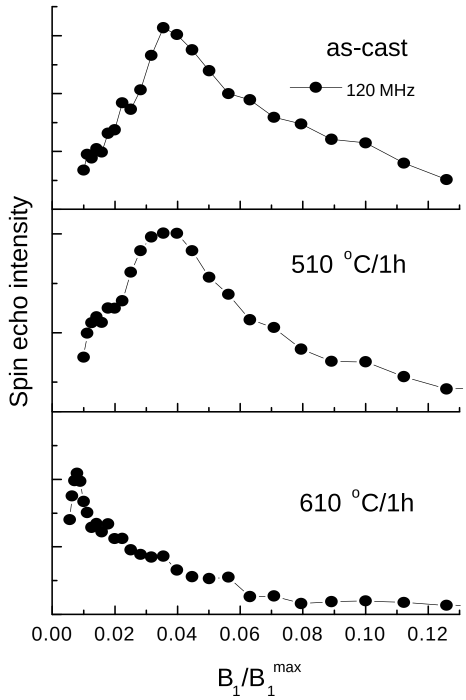

Fig. 2. ^{93}Nb spin-echo amplitude measured in melt-spun $Fe_{80.5}Nb_7B_{12.5}$ ribbons annealed at different temperatures, as a function of the RF relative power level B_1/B_1^{max}, with $B_1^{max} =$ 10 G.

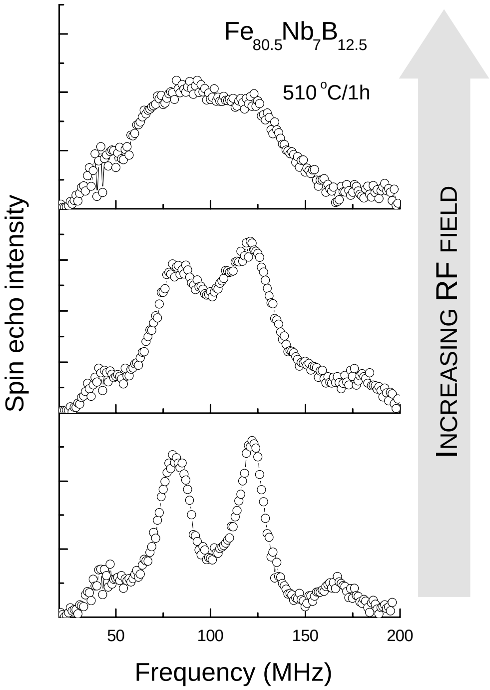

Fig. 3. NMR spectra of nanocrystalline $Fe_{80.5}Nb_7B_{12.5}$ ribbon measured with different RF power conditions, at 4.2 K and zero applied magnetic field. The excitation RF field increases from bottom to top.

maximum signal moves to lower RF power as the sample is heat-treated at higher temperatures, which shows the large softening of the material after annealing, particularly for the highest temperature (610°C).

As to the sample annealed at the intermediate temperature (510°C), the curve (Fig. 2b) shows a main maximum at about the same RF field strength as the as-cast sample. Measurements of the temperature dependence of the coercivity performed in the sample annealed at 510°C reveal an unusual increase of H_c below 50 K [9]. Besides this macroscopic behavior, the NMR results at 4.2 K shows that this sample presents almost the same average magnetic stiffness as the as-cast one. However, a closer look at Fig. 2b shows the existence of a shoulder on the low power side of the main maximum, which could suggest the presence of two Nb-containing phases with different local magnetic stiffness. Actually, the existence of two Nb-containing phases is definitely ascertained in all three samples by the comparison of the spectra observed for the lowest and the highest RF power, respectively. Indeed, Fig. 3 shows clearly that at low RF power, the spectra show rather well-resolved Nb lines corresponding to a well-crystallized softer phase whereas, for high power, the lines are much broader as arising from an amorphous and harder phase. However, both the Nb content in each phase and the average magnetic stiffness evolve with the annealing treatment and, as mentioned above, the quantitative analysis shows that most of the Nb is contained in the disordered phase after the annealing at 610°C, and this phase gets softer than in the other samples.

In summary, our study points out to the presence, in FeNbB alloys, of two Nb-containing phases: a soft Fe-rich phase, more or less crystallized, and a harder one, amorphous like. After annealing treatment, Nb atoms move from the crystalline phase towards the amorphous one. Eventually, after 1 h annealing at 610°C, Nb is essentially present in the amorphous phase and only a very small amount may still be present as diluted impurities in the α-Fe nanocrystals.

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