Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Magnetism and Magnetic Materials 290–291 (2005) 612–614
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

NMR, magnetic and structural study of Fe–Si-X (X = Nb, Ta) alloys

C.F. Barbatti[a,b,*], R. Sato Turtelli[a], M. Schönhart[a], H. Sassik[a], J.P. Sinnecker[c], E.H.C.P. Sinnecker[b], R.S. Sarthour[b], A.P. Guimarães[b], R. Grössinger[a]

[a]*Inst. für Festkörperphysik, TU Wien, Wiedner Hauptstrasse 8, A-1040, Vienna, Austria*
[b]*Centro Brasileiro de Pesquisas Físicas, R. Dr. Xavier Sigaud 150,22290-180, RJ, Brazil*
[c]*Instituto de Física, UFRJ, CP 68528, 21945-970 Rio de Janeiro, Brazil*

Available online 14 December 2004

Abstract

We investigated the structural and magnetic properties of the as-cast $Fe_{100-(x+y)}Si_xNb_y$ (with $9.5 \leqslant x \leqslant 20$ and $0.5 \leqslant y \leqslant 12$) and $Fe_{78.5}Si_{20}Ta_{1.5}$ alloys by means of coercivity measurements and zero-field nuclear magnetic resonance (NMR) technique. The NMR spectra of these alloys present broad resonance lines at around 80 and 130 MHz. An increase in the local magnetic stiffness with increasing Nb content was found. These results are discussed based on previously reported results about the microstructure of the same specimen and coercivity measurements.

PACS: 75.50.Bb; 76.60-Lz; 75.60.Ej

Keywords: NMR; Spin echo; Hyperfine fields–magnetic; Coercivity; Local environment effects

In nanocrystalline soft magnetic materials, a well-suited sample composition is of special importance, which is chosen for supporting the crystallization into nanosized crystallites. A typical example is the nanocrystalline Finemet, which is based on an amorphous Fe–Cu–M-Si–B (M = Nb, Ta) ribbon and transforms after a heat treatment at 550 °C (1 h) into nanocrystalline α-Fe(Si) embedded in the amorphous matrix [1,2]. A small addition of Cu is used to enhance the nucleation of the DO_3 Fe–Si grains, while Nb or Ta hinders their growth. However, the role of Nb in the development of the final structure is itself a subject of some controversy. Some authors e.g. [3] have suggested that Nb remains in the intergranular region as a part of the amorphous matrix, whereas e.g., Yavari [4] suggests that Nb may enter into the Fe(Si) lattice. This controversy has motivated us to carry out a systematic study of the addition of Nb and Ta in rapidly quenched Fe–Si alloys. In our previous work [5], we reported that small additions of Nb (1.5 to 2 at%) in Fe–Si alloys caused a large increase of the coercivity H_c, as well as a displacement of X-ray lines towards lower values of 2θ. We suggested that this displacement could be attributed to the entrance of Nb into the Fe–Si lattice. More recently, we have performed high-resolution X-ray diffraction measurements on the same system, including other alloys with higher Nb content (up to 12 at%) in order to follow the microstructure evolution with increasing Nb concentration. As a result, we were led

*Corresponding author. Inst. fuer Festkörperphysik, TU Wien, Wiedner Hauptstrasse 8, A-1040, Vienna, Austria. Tel.: +4315880113153; fax: +4315880113199.
E-mail address: barbatti@ifp.tuwien.ac.at (C.F. Barbatti).

0304-8853/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jmmm.2004.11.329

to conclude that the shift in the lattice parameter with increasing Nb content arises from a reduction of the Si concentration in the α–Fe(Si) grains, and not due to the entrance of Nb atoms into the Fe–Si lattice. For all compositions, the presence of the BCC solid solution Fe(Si) embedded in an amorphous matrix was observed. For low Nb content, we have observed the presence of super-structural lines, which suggested the occurrence of DO_3-ordered phase and B2 structure. At the same time, the addition of Nb gives rise to a decrease in grain size, while it also increases the local strain within the cubic phase. Moreover, it enhances an additional crystalline phase, which can be indexed as a hexagonal phase [6].

The nuclear magnetic resonance (NMR) technique has proven to be a powerful tool in the investigation of the structure of granular systems [7], since it provides information on the local atomic environments. The NMR technique also allows one to obtain detailed magnetic information from the measurement of the local magnetic anisotropy [7]. Therefore, in the present work, NMR measurements on rapidly quenched ribbons of $Fe_{100-(x+y)}Si_xX_y$ (X = Nb, Ta) were performed in order to get more insight on the magnetic and structural properties of these materials.

Ribbons of $Fe_{100-(x+y)}Si_xNb_y$ and $Fe_{78.5}Si_{20}Ta_{1.5}$ alloys with a thickness of 30 μm and a width of 1.5 mm were prepared by the single-roller melt-spinning method. The hysteresis loop measurements were carried out at room temperature using a quasi-static hysteresigraph (0.7 Hz) with a maximum field of 180 kA/m and also an extraction magnetometer Quantum Design PPMS, with a maximum external field of 8 MA/m. NMR spectra were obtained using a broad band pulsed NMR spectrometer in the frequency range between 20 and 200 MHz, with an exception in the case of the $Fe_{89}Si_{9.5}Nb_{1.5}$ alloy, for which the measurements were extended up to 300 MHz, since no signal was observed in the previous frequency range. We applied two radio-frequency (RF) pulses to the sample, with the same width ($\tau_a = \tau_b = 0.5\,\mu s$) and separated by $\Delta\tau = 15\,\mu s$. The spin echo integral was obtained as a function of the RF frequency. The RF power was controlled by means of a variable attenuator in the range between 0 and 63 dB. The data related to the spin echo amplitude dependence on the RF power were obtained by setting the measurement at the central frequency of the dominant peaks in each spectrum, keeping the same excitation conditions described above. The experiments were performed at 4.2 K without an applied external field.

Figs. 1(a)–(c) show the spin-echo NMR spectra obtained for the as-cast $Fe_{100-x}Si_xNb_{1.5}$, $Fe_{80-y}Si_{20}Nb_y$ and $Fe_{87.9-y}Si_{12.1}Nb_y$ alloys, respectively, over the frequency range from 20 to 200 MHz. Except for the $Fe_{89}Si_{9.5}Nb_{1.5}$ alloy, in all other compositions here investigated, as well as in Finemet [7] and Fe–Nb–B

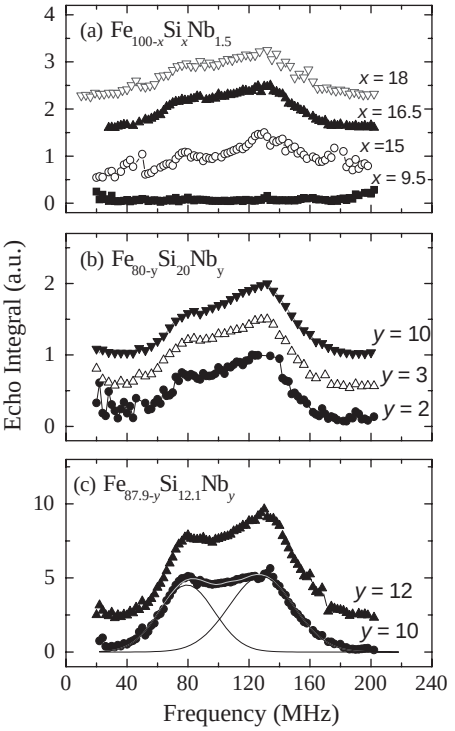

Fig. 1. NMR spectra for as-cast melt-spun ribbons of: (a) $Fe_{100-x}Si_xNb_{1.5}$, (b) $Fe_{80-y}Si_{20}Nb_y$ and (c) $Fe_{87.9-y}Si_{12.1}Nb_y$. The solid lines in (c) are related to the Gaussian fit.

ribbons [8], the spectra present very broad lines around 80 and 130 MHz (see the experimental data fitted by gaussian functions in Fig. 1(c)). These peaks are associated with the ^{93}Nb resonances in different atomic surroundings [7,8]. Generally, the highest intensity of the peak was found for the frequency of 130 MHz. For the $Fe_{89}Si_{9.5}Nb_{1.5}$ alloy, we observed a clear resonance signal (not shown here) at 230 MHz, indicating that the neighboring atoms of Nb belong to a Fe–Si phase with high concentration of Fe atoms. Since Nb is a nonmagnetic atom, the frequency of the signal tends to increase as the concentration and/or the moment of Fe in the Nb atoms neighborhood increases. The environments are characterized by a distinct number of Fe atoms in their vicinity or by the magnetic moment generated, which can be altered by the amount of nonmagnetic atoms in the surroundings of the Fe atoms. The resonance frequency and consequently the local hyperfine field depend on the number of Fe atoms in the neighborhood of the Nb atoms.

Fig. 2 shows the behavior of the spin-echo intensity as a function of the RF power for as-cast melt-spun ribbons of, for example, $Fe_{77}Si_{20}Nb_3$, $Fe_{77.9}Si_{12.1}Nb_{10}$, and $Fe_{70}Si_{20}Nb_{10}$ taken at 80 and 130 MHz. The peak

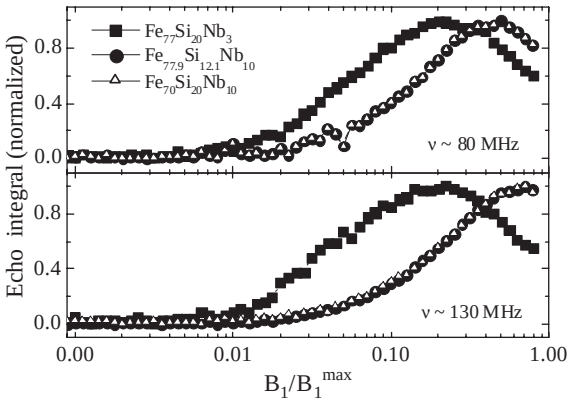

Fig. 2. Spin echo amplitude as a function of the relative power of the RF field B_1/B_1^{max} taken at approximately 80 and 130 MHz (^{93}Nb resonances) for as-cast melt-spun ribbons of $Fe_{77}Si_{20}Nb_3$, $Fe_{77.9}Si_{12.1}Nb_{10}$, and $Fe_{70}Si_{20}Nb_{10}$.

position provides a measure of the local anisotropy field [7]. The plot of the relative magnetic stiffness for 80 and 130 MHz (determined at peak) against the Nb content obtained for the as-cast $Fe_{80-y}Si_{20}Nb_y$ ribbons is shown in Fig. 3. For higher Nb content, the specimen is magnetically harder. This result agrees with the coercivity measurements, in which H_c increases with increasing Nb content (see Fig. 3). For other Nb concentrations added to the Fe–Si alloys, the proportionality between B_1/B_1^{max} and H_c was also found. For the as-cast $Fe_{78.5}Si_{20}Ta_{1.5}$ alloy, the magnetic and structural properties are very similar to those found in the as-spun $Fe_{78.5}Si_{20}Nb_{1.5}$.

The results obtained from NMR and coercivity measurements are in agreement with the previous microstructural investigations cited in the beginning of this paper and also with those found in Ref. [6]. The NMR spectra here obtained are very similar to the spectrum obtained for nanocrystalline Finemet [7], therefore indicating the existence of both amorphous and crystalline phases. A decrease in the amount of Si in the α–Fe(Si) phase results in a larger number of Fe atoms surrounding the Nb atoms, consequently the peak may undergo a shift towards higher frequencies as it occurs in the case of the $Fe_{89}Si_{9.5}Nb_{1.5}$ alloy. As for the set of alloys with increasing Nb content, one can clearly see that the echo intensity increases for the frequency of 130 MHz (see Fig. 1(b) and (c)), which means that more Nb atoms are present in this specific atomic environment (more Nb atoms in the vicinity of a region relatively richer in Fe).

The increase of magnetic stiffness with increasing Nb content can be related to the increase in the local stress, which generally increases the local anisotropy. Nevertheless, the influence of the change in size of the BCC Fe–Si grains also might be considered.

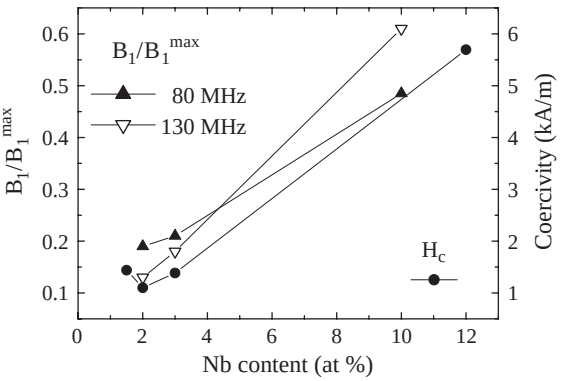

Fig. 3. Coercivity and relative magnetic stiffness (at 80 and 130 MHz) as a function of the Nb content measured on $Fe_{80-x}Si_{20}Nb_x$ as-cast ribbons.

It is then expected that if we add more Nb to Fe–Si alloys, very small grains can be obtained, which gives rise to a nanocrystalline material. Investigations of the magnetic and structural properties on Fe–Si–Nb alloys with higher concentration of Nb and also on annealed samples are in progress.

Acknowledgements

The authors thank the Brazilian funding agencies CNPq, CAPES (PROFIX and PRODOC Programs), and FAPERJ for financial support. The work was also supported by the Austrian Science Foundation under the Project Nr P15737, and also by the EC network ALFA Project Nr AML/B7-311/97/0666/II-0147-FI.

References

[1] Y. Yoshizawa, S. Oguma, K. Yamaguchi, J. Appl. Phys. 64 (1988) 6044.
[2] A. Hernando, M. Vázquez, T. Kulik, C. Prados, Phys. Rev. B 51 (1995) 3581.
[3] K. Hono, D.H. Ping, Mater. Sci. Forun. 307 (1999) 69.
[4] R. Yavari, in: M. Vázquez, A. Hernando (Eds.), Nanostructured and Non-Crystalline Materials, 1994, p. 35.
[5] R. Sato Turtelli, M. Schönhart, H. Sassik, R. Grössinger, C. Kolbeck, Vo Hong Duong, E. Ferrara, J. Magn. Magn. Mater. 226 (2001) 1498.
[6] A. Penton-Madrigal, R. Sato Turtelli, E. Estevez-Rams, H. Sassik, R. Grössinger, (2004), submitted for publication.
[7] C.F. Barbatti, E.H.C.P. Sinnecker, R.S. Sarthour, A.P. Guimarães, J. Alloys and Compounds 369 (2004) 136.
[8] E.H.C.P. Sinnecker, P. Panissod, I. Skorvánek, A.P. Guimarães, J. Magn. Magn. Mater. 242–245 (2002) 235.