Thermal Evolution of Hyperfine Fields in Fe-Zr-Si-B Nanocrystalline Alloy

A. Ślawska-Waniewska^a, J. M. Greneche^b and A. Inoue^c

^a Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland

^b Laboratoire de Physique, UPRESA CNRS 6087, Université du Maine, F72085 Le Mans, France

^c Institute for Materials Research, Tohoku University, Katahira 2-1-1, Sendai 980-77, Japan

(Received; April 7, 1998 Accepted; August 26, 1998)

Mössbauer investigations of $\text{Fe}_{87}\text{Zr}_7\text{Si}_4\text{B}_2$ nanocrystalline material were performed over the temperature range 4.2–675 K. Three well resolved spectral components have been found and attributed to bcc-Fe grains (with almost pure iron structure), residual amorphous matrix enriched with solute elements and interfaces formed at the grain–matrix boundaries. Thermal evolution of magnetic hyperfine parameters for these different structural phases are presented and discussed.

Key words: nanocrystalline alloys, soft magnetic materials, Fe-based alloys, Mössbauer spectroscopy, nanoscale bcc grains, interfaces

1. Introduction

It has recently been shown that Fe-Zr-Si-B soft magnetic nanocrystalline alloys, produced by the devitrification of amorphous ribbons, are attractive materials for applications because they exhibit simultaneously large saturation magnetization and high permeability¹⁾. These superior properties, better than found in widely studied Fe-Zr-B alloys, are ascribed to the addition of small amount of Si which results in nearly zero effective magnetostriction of the nanocrystalline state. Moreover, Si addition leads to a significant improvement of the glass forming ability of the amorphous state as well as an extension of the optimum annealing temperature range^{1),2)}. However, the role of Si in Fe-Zr-Si-B alloys is not readily understood. On the analogy of Fe-Nb-Cu-Si-B alloy, in which during annealing the crystalline α -FeSi (with 20–23 at% Si) phase is created, it was expected that in Fe-Zr-Si-B alloy silicon should also dissolve in crystalline grains. The high resolution transmission electron microscopy and nano-beam energy dispersive x-ray spectroscopy analysis has confirmed this expectation and indicated that bcc-Fe phase contains about 6 at% of Si^{1),2)}. On the contrary, the atom probe field ion microscopy has shown that silicon is enriched in the residual amorphous matrix and largely rejected from α -Fe primary crystals in which Si concentration is only about 1.5 at%^{3),4)}.

The present investigations were motivated by the desire to obtain more information about the partitioning of Si during the primary crystallization of Fe-Zr-Si-B alloy. For these studies we have used Mössbauer spectroscopy since it is one of the most sensitive method that can detect magnetic properties of various phases in the nanocrystalline material individually providing information about the short range order around Fe-atoms, in particular Si content, in the bcc-Fe grains.

It is known that in the alloys with Si-content below 10 at%, silicon dissolves in bcc-Fe lattice randomly substituting Fe atoms. The bcc-FeSi solid solutions have widely been investigated by Mössbauer spectroscopy^{5),6)}. It has been shown that three different sites of Fe atoms having 0, 1 or 2 nearest neighbor Si atoms can well be resolved in the room temperature Mössbauer spectra. The strongest sextet of these spectra has hyperfine parameters typical of pure bcc-Fe structure, whereas the additional components are observed at the hyperfine fields decreased, for each Si nearest neighbor, by about 8% of that for bcc-Fe⁵⁾. In the alloys with Si content 0.85, 3 and 4.9 at%, it was found that the intensity ratios of these three sub-spectra $I_0:I_1:I_2$ are 83:13:0%, 71:29:0% and 59:35:6%, respectively⁶⁾. These results were then used as a reference data for the nanocrystalline phase in the material studied.

2. Experimental Details

$\text{Fe}_{87}\text{Zr}_7\text{Si}_4\text{B}_2$ amorphous ribbon of about 25 μm thick and 15 mm wide was prepared by the single roller melt spinning method in an argon atmosphere. The amorphous alloy specimens were annealed at 873 K for 1 h in vacuum, i.e. at the optimum annealing conditions which lead to the best soft magnetic properties^{1),2)}. It has already been shown¹⁾⁻³⁾ that this heat treatment results in a mesoscopic structure in which randomly oriented bcc-Fe crystalline grains with a grain size of about 10–18 nm are embedded in the residual amorphous matrix. In the material studied the temperature dependence of the saturation magnetization indicates that the Curie temperature of the crystalline phase is about 1043 K, i.e. the value characteristic of bcc-Fe. Assuming that only pure bcc-Fe phase contribute to the magnetization at elevated temperatures as well as that the magnetization of small grains is the same as the one of bulk iron it was estimated that the volume fraction of this phase is about 72%.

Mössbauer investigations of the nanocrystalline sample were performed with the conventional constant acceleration spectrometer using ^{57}Co source in Rh matrix over the temperature range 4.2–675 K. The sample, with the ribbon plane perpendicular to γ -radiation, was located either in a bath cryostat or in a cryofurnace under vacuum to prevent the oxidation. The highest measuring temperature was chosen so as to avoid any structural evolution within the amorphous–crystal transformation during experiments. The Mössbauer spectra were fitted with the MOSFIT program using the procedure described in Ref. 7.

3. Results and discussion

Representative Mössbauer spectra of the nanocrystalline $\text{Fe}_{87}\text{Zr}_7\text{Si}_4\text{B}_2$ sample taken at various temperatures are shown in Fig.1. To obtain a satisfactory fit of these spectra it was necessary to take into account three sub-spectral contributions and these components can well be distinguished in the presented spectra, as shown in Fig.1. For each component, the temperature dependencies of the fitted parameters - the mean hyperfine field, the isomer shift and the relative contribution, are presented in Fig.2 a,b, and c, respectively.

In all the spectra the best resolved is a magnetically split sextet with the highest hyperfine field exhibiting sharp lorentzian lines. The hyperfine parameters of this component as well as their temperature dependencies (Fig.2a,b, curves c), are typical of bulk α -Fe (see e.g. the inset in Fig.2a which shows that the thermal evolution of the hyperfine field for the sharp sextet fits well to the one of bulk bcc-Fe). Thus, this component originates from those Fe atoms which are perfectly coordinated with another Fe-atoms in the bcc-lattice. It indicates that in $\text{Fe}_{87}\text{Zr}_7\text{Si}_4\text{B}_2$ nanostructure the well ordered crystalline phase, which can be attributed to the interior

Fig.1 Mössbauer spectra of $\text{Fe}_{87}\text{Zr}_7\text{Si}_4\text{B}_2$ nanocrystalline alloy taken at selected temperatures.

Fig.2 Thermal evolution of hyperfine parameters for crystalline *c*, amorphous *a* and interfacial *i* components (inset shows the comparison with bulk bcc-Fe).

of the grains, is formed by the pure bcc-Fe. Its relative amount is about $54 \pm 2\%$ and does not change over the measuring temperature range (Fig.2c).

The remaining two components have broad lines, characteristic of structurally disordered material, but they entirely differ in their temperature behavior. With an increase of the temperature one of them, which can be attributed to the residual amorphous matrix, collapses progressively into the quadrupolar doublet. The relative fraction of this phase is about $27 \pm 2\%$ (Fig.2c, curve *a*). However, even at the highest temperature applied, this component still exhibits a magnetic hyperfine splitting which is seen in a form of wings upon a broadened central quadrupolar contribution. It is worth noticing that in the amorphous phase this magnetic splitting is observed at temperatures that exceed the expected Curie point of the simple amor-

phous alloy with a similar composition⁸⁾. Fig. 2a shows that the average value of the hyperfine field for this component (curve *a*) decreases with increasing temperature but, over the temperature range studied, there is not any well defined ferromagnetic-paramagnetic phase transition in the amorphous matrix. In the nanocrystalline material with a high fraction of the crystalline phase, as for the present sample, the average thickness of the amorphous matrix separating the grains is about 1-3 nm. It can thus be expected that at elevated temperatures the strongly ferromagnetic grains are not magnetically isolated but they are exchange coupled through the intergranular amorphous phase inducing there a weak magnetism, as it was suggested by static magnetic measurements⁹⁾.

The third sub-spectrum, which is seen as a low-field side shoulder of the lines of the crystalline sextet does almost not change with temperature (Fig. 1). Its mean hyperfine field (Fig. 2a, curve *i*) and isomer shift (Fig. 2b, curve *i*) scale with temperature like these of the bulk part of bcc-Fe nanocrystallites (Fig. 2a, b, curves *c*). The average hyperfine field of this component is about 10% smaller whereas the isomer shift slightly more positive than these of the crystalline phase, as expected for Fe atoms partially coordinated with non-magnetic elements⁵⁾. Its relative fraction is about $19 \pm 2\%$ and does not essentially change with the temperature (Fig. 2c, curve *i*). One can consider two possible origins of this sub-spectrum: (1°) a partitioning of nonmagnetic atoms, in particular Si, into the bcc-Fe lattice and (2°) the interface that is formed at the crystalline grain-amorphous matrix boundary. As it was mentioned in the introduction, Si admixtures in the bcc-Fe structure can easily be resolved in the room temperature Mössbauer spectra, even for Si-content below 1%. The comparison between the spectrum obtained at room temperature for the present material and those for bcc-FeSi solid solutions⁶⁾ shows that the grains in the nanocrystalline material studied contain less than 1 at% of Si. Thus, the Mössbauer investigations support the atom probe field ion microscopy analysis^{3),4)} and confirm that in Fe-Zr-Si-B nanostructures Si is rejected from the bcc-Fe grains.

The additional sub-spectrum observed in $\text{Fe}_{87}\text{Zr}_7\text{Si}_4\text{B}_2$ nanocrystalline alloy can therefore be attributed to Fe atoms situated in the interfacial zone, between the crystalline and amorphous phases. Such interfacial component, with very similar hyperfine parameters and temperature behavior, has already been observed in Fe-Zr-B nanocrystalline alloys¹⁰⁾ as well as in the alloys which do not contain Zr e.g. Fe-Nb-Cr-Cu-B [11]. It arises because of the symmetry restriction and reduced coordination of Fe atoms at the grain surfaces, enhanced coordination of Fe atoms from the amorphous matrix located next to the grain boundaries¹⁰⁾ as well as enrichment of the amorphous phase near the grain surface with Zr²⁾. Although a small contribution to this component from solute elements partitioned in bcc-Fe grains can not be excluded, however, considering that Fe atoms at the grain surfaces surrounded by Zr-enriched matrix have much higher probability of having non-magnetic nearest neighbors than those inside the

grains, it is evident that the interfaces give the dominant contribution to this sub-spectrum. The thickness of the interface can be estimated from the relative contributions of different phases to the Mössbauer spectra, assuming the spherical shape of the crystals. In the material studied the average grain sizes are in the range 10–18 nm^{1),3)} and it can be found that the width of an interfacial layer surrounded the nanocrystals is about 0.5–0.9 nm corresponding to 2-3 atomic layers.

4. Conclusions

Mössbauer investigations of $\text{Fe}_{87}\text{Zr}_7\text{Si}_4\text{B}_2$ nanocrystalline material performed over a wide temperature range reveal the presence of three well resolved spectral components. They have been attributed to: (1) the interior of bcc-Fe grains (from which the solute elements, most of all Si and Zr, are largely rejected and thus with almost pure iron structure), (2) the residual amorphous matrix enriched with solute elements and (3) the interfaces formed at the grain-matrix boundaries. The interfacial layer has the thickness about 5–9 Å and it exhibits a structural disorder. It is very important to note that the interfaces remain magnetic at elevated temperatures and that their behavior does almost not depend on the magnetic state of the amorphous matrix. It can thus be expected that the magnetic properties of these boundary regions are dominated by the exchange coupling with strongly ferromagnetic grains. To the contrary, these strongly magnetic phases affect the behavior of the magnetically weaker amorphous phase, in particular being responsible for the weak hyperfine field induced in the matrix at elevated temperatures.

Acknowledgments This work was supported in part by the Committee for Scientific Research (Poland) under Grant no. 8T 11B 048 10.

References

- 1) A. Inoue, Y. Miyauchi, A. Makino, T. Masumoto: *Mater. Trans., JIM*, **37**, 78 (1996).
- 2) A. Inoue, A. Takeuchi, A. Makino, T. Masumoto: *Sci. Rep. RITU*, **A 42**, 143 (1996).
- 3) Y. Zhang, K. Hono, A. Inoue, T. Sakurai: *Appl. Phys. Lett.*, **69**, 2128 (1996).
- 4) K. Hono, Y. Zhang, A. Inoue, T. Sakurai: *Mater. Sci. & Engin. A*, **226-228**, 498 (1997).
- 5) M. B. Stearns: *Phys. Rev. B*, **129**, 1136 (1963).
- 6) L. Häggström, L. Granäs, R. Wäppling, S. Devanarayan: *Physica Scripta*, **7**, 125 (1973).
- 7) J. M. Greneche, *Hyp. Inter.*, **110**, 81 (1997).
- 8) S. Ohnuma, M. Nose, K. Shirakawa, T. Masumoto, *Sci. Rep. RITU*, **A 29**, 254 (1981).
- 9) A. Ślowska-Waniewska, P. Nowicki, H. K. Lachowicz, P. Gorria, M. Barandiaran, A. Hernando: *Phys. Rev. B*, **50**, 6465 (1994).
- 10) A. Ślowska-Waniewska, J. M. Greneche: *Phys. Rev. B*, **56**, R8491 (1997).
- 11) I. Skorvanek, M. Miglierini, P. Duhaj: *Mater. Sci. Forum*, **235-238**, 771 (1997).