ELSEVIER

Journal of Magnetism and Magnetic Materials 254–255 (2003) 495–497

Journal of magnetism and magnetic materials

www.elsevier.com/locate/jmmm

Influence of Co content on structural and magnetic properties of $Co_xFe_{84-x}Nb_7B_9$ alloys

S.N. Kane[a,*,1], A. Gupta[b], S.D. Sarabhai[a], L. Kraus[c]

[a] *Institut für Anorganische und Analytische Chimie, Johannes Gutenburg Universität Mainz, Staudinderweg 9, D-55099 Mainz, Germany*
[b] *IUC for DAE Facilities, University Campus, Khandwa road, Indore 452017, India*
[c] *Institute of Physics ASCR, Na Slovance 2, CZ-180 40, Praha 8, Czech Republic*

Abstract

Nanocrystallization of $Co_xFe_{84-x}Nb_7B_9$ ($x = 17, 25, 33$) alloys has been studied. Crystallization of specimens starts above 450°C. After annealing of specimens in the range 500–700°C, apart from amorphous component and BCC Fe-Co alloy, a non-magnetic component also appears, which is attributed to $(Fe_{1-x}Co_x)_2Nb$ phase with a relative area of about 14%. Decrease of quadrupole splitting with annealing temperature indicates some possible ordering of the non-magnetic phase.

Keywords: Nanocrystalline materials; DSC; XRD; Mössbauer spectroscopy

Fe-based nanocrystalline alloys produced by devitrification of amorphous ribbons exhibit excellent soft magnetic properties. From a number of studies, it is well accepted that the presence of Nb in the parent amorphous alloy causes inhibition of grain growth resulting in the nanocrystalline structure [1,2]. In these materials, contrary to conventional granular materials, the matrix is magnetic and its properties can be changed either by increasing the annealing temperature or by modifying chemical composition of the parent alloy. It is well known that by partial substitution of Fe by Co the saturation magnetization of Fe-based alloys can be increased [3] and changes in structural and magnetic properties can be accomplished. Magnetic properties, general crystallization behavior and magnetomechanical properties of $Co_xFe_{84-x}Nb_7B_9$ have been studied previously [4–6]; the objective of the present work is to get additional structural and magnetic information about nanocrystalline $Co_xFe_{84-x}Nb_7B_9$ ($x = 17$, 25, 33 at%) alloys from Mössbauer spectroscopy, as it is sensitive to Fe only and gives specific information about Fe sites.

Ribbons of nominal composition $Co_xFe_{84-x}Nb_7B_9$ ($x = 17$, 25 and 33), 10 mm wide and about 20 μm thick, prepared by planar flow casting method, were obtained from Slovak Academy of Sciences, Bratislava. DSC measurements were done at a heating rate of 20 K/min. Transmission Mössbauer spectra were recorded at room temperature in a constant acceleration mode, using ^{57}Co:Rh source. Mössbauer spectra were fitted with either a distribution of hyperfine fields or overlapping of amorphous and crystalline components. XRD measurements were done using Cu-K_α radiation. Samples were annealed in Ar atmosphere isochronally for 1 h in the temperature range 350–700°C to obtain various stages of crystallization.

The first crystallization temperatures obtained from DSC measurements for $x = 17$, 25 and 33 are, respectively, 500°C, 487°C and 478°C, indicating that with increase in Co content, crystallization temperature decreases. Thus, increase in Co content reduces the stability of the alloy. Fig. 1 shows the variation of Scherrer's crystallite size with annealing temperature. Perusal of Fig. 1 shows that crystallite size varies almost

*Corresponding author. Institut für Anorganische und Analytische Chimie, Johannes Gutenburg-Universität Mainz, Staudinderweg 9, D-55099 Mainz, Germany. Tel.: +49-3121-3924420; fax: +49-6131-3922-990.

E-mail address: kane@iacgu7.chemie.uni-mainz.de, kane_sn@yahoo.com (S.N. Kane).

[1] On leave from: School of Physics, D.A. University, Khandwa road Campus, Indore 452017, India.

0304-8853/03/$ - see front matter
PII: S0304-8853(02)00848-X

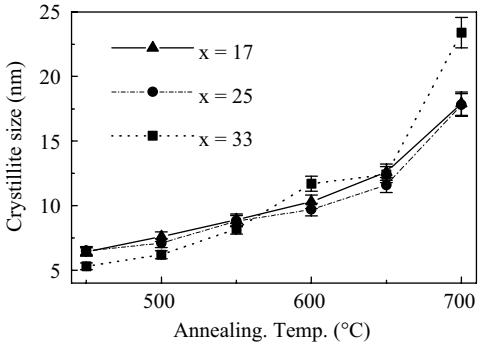

Fig. 1. Dependence of crystallite sizes of $Co_xFe_{84-x}Nb_7B_9$ for $x = 17$, 25 and 33 with annealing temperature.

linearly with annealing temperature up to 650°C and increases sharply after annealing at 700°C. Annealing at 700°C, the second step of crystallization starts, evidenced by additional crystalline peaks in XRD, deteriorating the soft magnetic properties [4].

Fig. 2(a) shows the representative Mössbauer spectra of $Co_xFe_{84-x}Nb_7B_9$ ($x = 17$) as a function of annealing temperature. Crystallization of the specimens starts at 450°C and Mössbauer spectrum consists of a crystalline (BCC-Fe-Co alloy) and an amorphous component. After annealing at higher temperatures apart from a magnetic crystalline component and an amorphous component, an additional doublet also appears which constitutes about 14% of the total area. The fact that this additional component is non-magnetic, suggests that it should be rich in Nb. Appearance of this additional phase has been evidenced in earlier studies also [7,8]. The quadrupole splitting (QS) of this non-magnetic phase decreases with increase in annealing temperature (Fig. 2b), which may be either due to a change in the composition or due to a possible ordering of the structure.

Fig. 3 shows the phase diagram of Fe–Nb [9]. Perusal of the phase diagram suggests that the non-magnetic component can be either $(Fe_{1-x}Co_x)Nb$ (μ-phase) or $(Fe_{1-x}Co_x)_2Nb$ (ε-phase). From the fitting of Mössbauer spectra one can find that the area of quadrupole doublet is 14% of the total area. That means 14% of Fe atoms in the sample are in the non-magnetic phase since in a sample, say with $x = 17$, out of 100 atoms of the sample 67 atoms are of Fe while 7 atoms are of Nb and 14% of these 67 Fe atoms, i.e. about 9.4 atoms are in non-magnetic phase. If one assumes that Fe and Co atoms go into the non-magnetic phase in the same ratio as the parent amorphous phase, then the non-magnetic phase will contain about 2.4 atoms of Co. Thus, if one further assumes that all the Nb goes into non-magnetic phase only (which is rather unlikely, as at least a part of Nb will remain in the amorphous phase), the ratio of TM:Nb will be 11.8:7 i.e. 63%:37%. From the phase

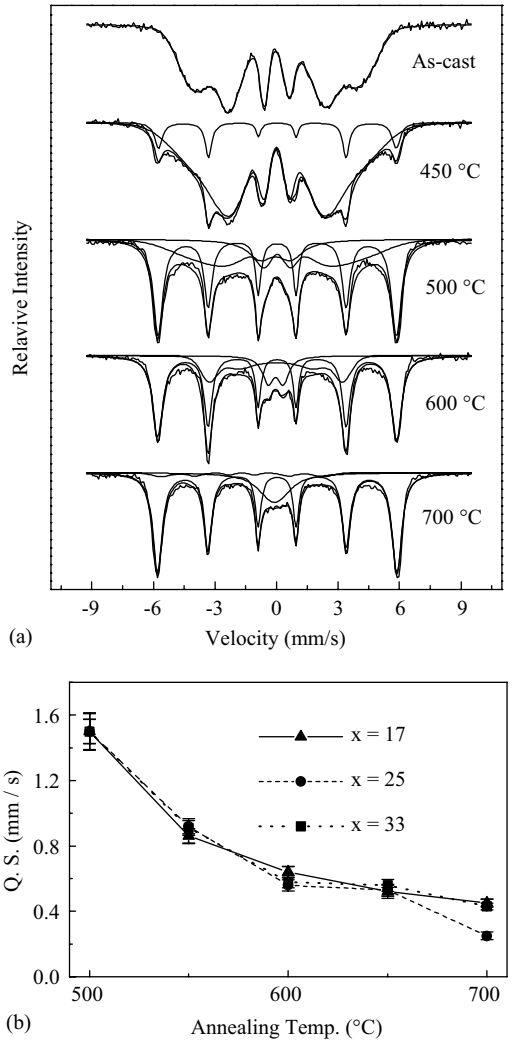

Fig. 2. (a) Representative Mössbauer spectra of samples ($x = 17$) after annealing at different temperatures; (b) variation of quadrupole splitting of the non-magnetic component with annealing temperature.

diagram of Fe–Nb one can see that the Fe–Nb phase exists over a narrow composition range 47–49% of Nb, therefore it is unlikely that the non-magnetic phase is $(Fe_{1-x}Co_x)Nb$. From the calculated stoichiometry 63:37 this phase is most likely $(Fe_{1-x}Co_x)_2Nb$, which exists over a much wider composition range, 27–39% of Nb.

Fig. 4 shows the variation of average hyperfine field, $\langle H_{cryst} \rangle$, of crystalline phase with annealing temperature. In case of the sample with $x = 33$, $\langle H_{cryst} \rangle$ remains almost constant, while in samples with $x = 17$ and 25 it increases slightly with annealing temperature. This variation in the hyperfine field with annealing temperature may be attributed to a variation in the composition of the alloy [10]. In the as-quenched amorphous alloy, the average hyperfine field, $\langle H \rangle$,

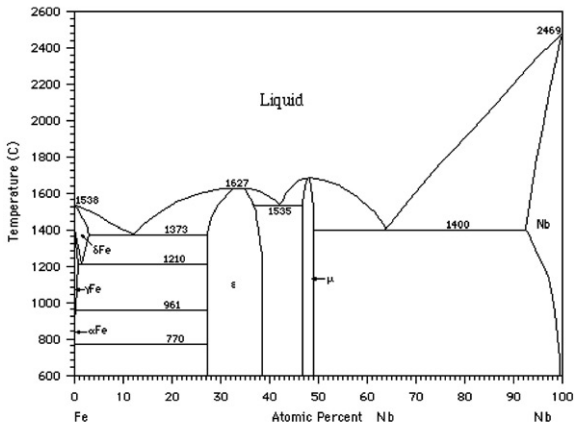

Fig. 3. Phase diagram of the Fe–Nb system showing formation of various phases of Fe and Nb.

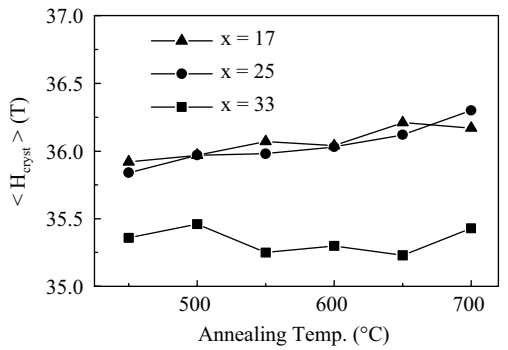

Fig. 4. Variation of average hyperfine field '$\langle H_{\mathrm{cryst}} \rangle$' of crystalline phase with annealing temperature.

goes on increasing with increasing Co concentration ($\langle H \rangle = 23.5$, 25.6 and 26.2 T for $x = 17$, 25 and 33, respectively), while 'J_s' shows an increase and then decreases ($J_s = 1.26$, 1.32 and 1.31 T for $x = 17$, 25 and 33, respectively) [4]. This different behavior of $\langle H \rangle$ and J_s may be attributed to the fact that while Mössbauer spectroscopy looks selectively at Fe atoms, in 'J_s' contribution from both Fe and Co atoms is present.

In conclusion, nanocrystallization of Co_x-$Fe_{84-x}Nb_7B_9$ ($x = 17$, 25, 33) alloys has been studied. Annealing in the range 500–700°C, apart from amorphous component and BCC Fe–Co alloy, a non-magnetic component also appears which is attributed to the $(Fe_{1-x}Co_x)_2Nb$ phase. Average hyperfine field, $\langle H_{\mathrm{cryst}} \rangle$, of crystalline phase varies with annealing temperature, which may be attributed to a variation in the composition of the alloy.

References

[1] Y. Yoshozawa, K. Yamaguchi, Mater. Sci. Eng. A 133 (1991) 176.
[2] M. Muller, N. Matterson, J. Magn. Magn. Mater. 136 (1994) 79.
[3] L. Kraus, V. Haslar, P. Duhaj, IEEE Trans. Magn. 30 (1994) 530.
[4] L. Kraus, V. Soyka, P. Duhaj, I. Matko, J. Phys. IV 8 (1998) 95.
[5] Z. Kaczkowski, L. Kraus, V. Soyka, P. Duhaj, Acta Phys. Slovaca 48 (1998) 687.
[6] Z. Kaczkowski., Z. Vertesy, L. Kraus, V. Soyka, Abstract No. P2/4B, SMM14, Hungary, 1999.
[7] L. Kraus, V. Haslar, P. Duhaj, P. Svec, V. Studnicka, Mater. Sci. Eng. A 226–228 (1997) 626.
[8] S.N. Kane, A. Gupta, L. Kraus, P. Duhaj, J. Magn. Magn. Mater. 215–216 (2000) 375.
[9] T.B. Massalski, H. Okamoto, P.R. Subramanian, L. Kacprzak, Binary Phase diagrams, Second Edition, ASM International, Materials Park, Ohio, 1990.
[10] A. Gupta, K. Ruwali, N. Paul, P. Duhaj, Mater. Sci. Eng. A 304–306 (2001) 371.