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Nanocrystallization studies of rapidly quenched $Fe_{85.4-x}Co_xZr_{6.8-y}Nb_yB_{6.8}Cu_1$ ($x = 0$ or 42.7, $y = 0$ or 1) alloys

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Abstract The microstructure of amorphous and nanocrystalline $Fe_{42.7}Co_{42.7}Zr_{6.8-x}Nb_xB_{6.8}Cu_1$ ($x = 0$ or 1) alloys was investigated. We have stated that the nanocrystalline samples consist of the crystalline α-FeCo grains about 8 nm in diameter embedded in an amorphous matrix which is rich in cobalt. From Mössbauer spectroscopy studies we have found that the crystalline α-FeCo phase in the nanocrystalline samples obtained by the conventional annealing is atomically ordered. Moreover, the order degree depends on the annealing time. As for the samples partially crystallized during rapid quenching, the crystalline α-FeCo phase is atomically disordered.

Key words Mössbauer spectra • nanocrystalline Fe-Co alloys

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Introduction

Recently, new nanocrystalline alloys of composition (Fe-Co)-M-B-Cu (M = Nb, Hf or Zr), showing the low coercivity and core losses at elevated temperatures, have been developed [2–6]. The crystalline phase in these alloys consists of α-FeCo fine grains. It has been found by X-ray diffractometry that α-FeCo phase is atomically ordered.

In this paper, we present the results of the microstructure studies for the amorphous and nanocrystalline $Fe_{42.7}Co_{42.7}Zr_{6.8-x}Nb_xB_{6.8}Cu_1$ ($x = 0$ or 1) alloys obtained by Mössbauer spectroscopy and electron microscopy. The nanocrystalline samples were obtained directly during the rapid quenching or by a conventional annealing of the amorphous ribbons.

Experimental procedure

The amorphous ribbons of the $Fe_{42.7}Co_{42.7}Zr_{6.8-x}Nb_xB_{6.8}Cu_1$ ($x = 0$ or 1) alloys, 2 mm wide and 0.020 mm thick, were prepared from high purity components by a rapid quenching method in a protective argon atmosphere.

The crystallization temperatures of the investigated alloys were determined from thermomagnetic curves measured by a force magnetometer with a heating rate of 10 K/min.

Transmission Mössbauer spectra were measured at room temperature for amorphous and nanocrystalline alloys. The nanocrystalline samples were obtained by an accumulative annealing of the as-quenched amorphous samples at 730 K for 10 and 70 min or directly during rapid solidification with two different quenching rates (samples A and B). The Mössbauer spectra were analysed using the NORMOS fitting program. Taking into account the parameters of the Mössbauer spectra corresponding to the crystalline phase, the Bragg-Williams parameter of the

long-range order for this phase was determined [1] under the assumption that the correlation between atoms is negligible. Moreover, from the results obtained from Mössbauer spectra analysis the phase compositions of the nanocrystalline samples were found, assuming the same probability of the recoil free absorption of the amorphous and crystalline phases.

The microstructure of the nanocrystalline samples after ion etching was also studied using a transmission electron microscope (JEM 3010).

Results and discussion

The crystallization temperatures of the as-quenched amorphous samples determined from the thermomagnetic curves are equal to 713 K and 725 K for the $Fe_{42.7}Co_{42.7}Zr_{6.8}B_{6.8}Cu_1$ and $Fe_{42.7}Co_{42.7}Nb_1Zr_{5.8}B_{6.8}Cu_1$ alloys, respectively. The Mössbauer spectra of the $Fe_{42.7}Co_{42.7}Zr_{6.8-x}Nb_xB_{6.8}Cu_1$ (x = 0, 1) alloys in the amorphous as-quenched state and after annealing at 730 K for 70 min, as an example, are presented in Fig. 1. The transmission Mössbauer spectra for the samples in the amorphous as-quenched state consist of sextets with broad lines characteristic of a pure amorphous state (Fig. 1 a, c). The spectra for the samples annealed at 730 K for 70 min consist of sharp sextets corresponding to the crystalline phase and the broad line features which are evidently

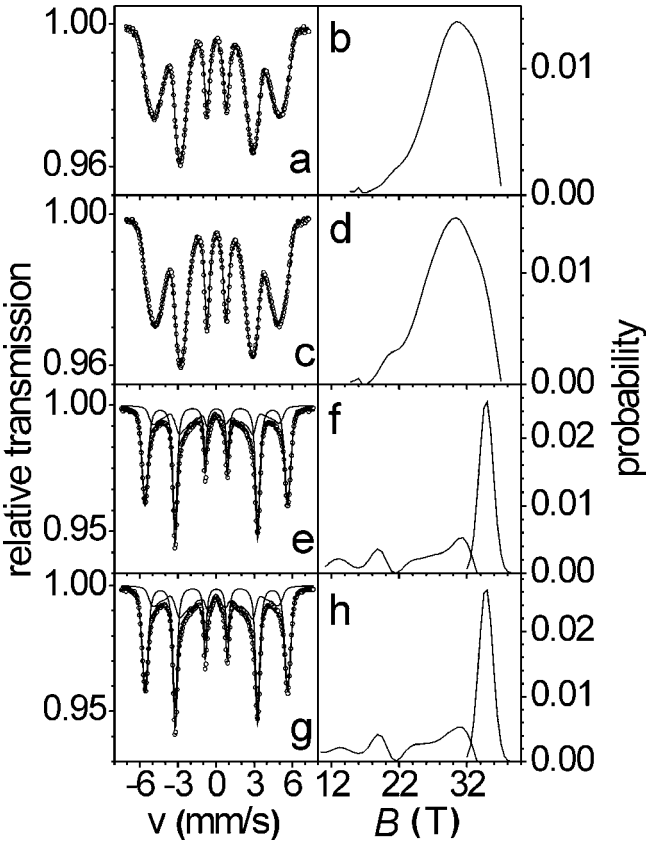

Fig. 1. Transmission Mössbauer spectra and corresponding hyperfine field distribution of the as-quenched $Fe_{42.7}Co_{42.7}Nb_xZr_{6.8-x}B_{6.8}Cu_1$ x = 0 (a, b, e, f), x = 1 (c, d, g, h) amorphous (a, b, c, d) and nanocrystalline (obtained by annealing at 730 K for 70 min) (e, f, g, h) alloys.

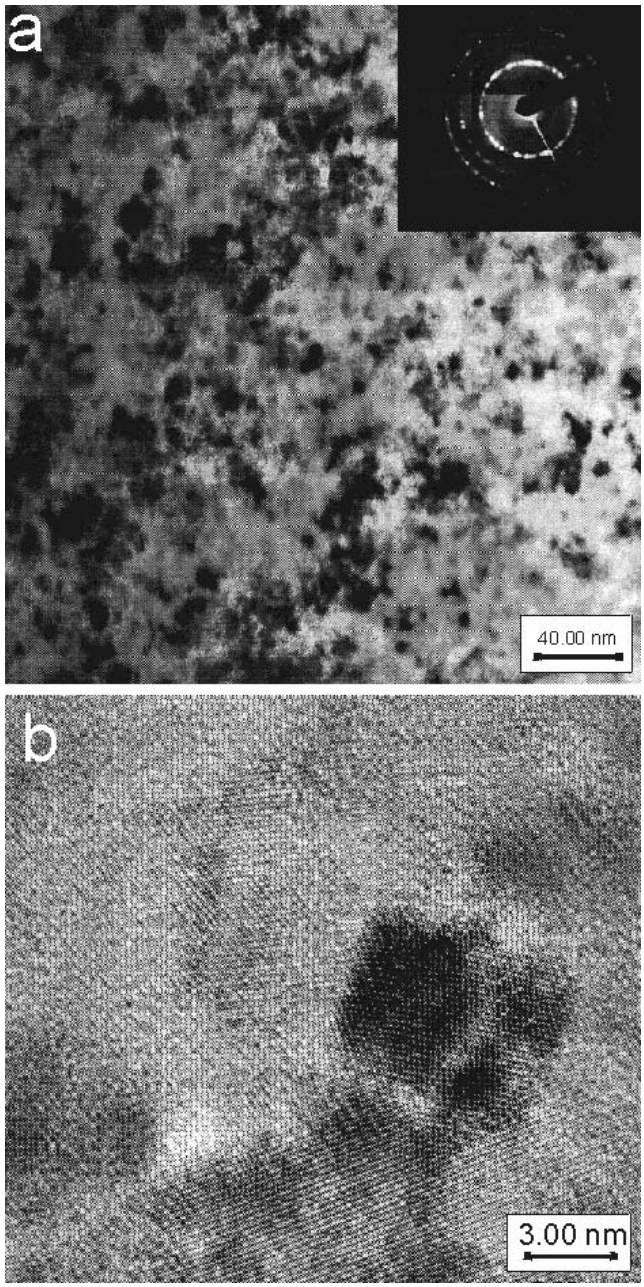

Fig. 2. Micrographs of the $Fe_{42.7}Co_{42.7}Zr_{6.8}B_{6.8}Cu_1$ alloy annealed at 730 K for 70 min: a – conventional resolution, b – high resolution.

associated with the residual amorphous phase (Fig. 1 e, g). The presence of the fine crystalline grains was also confirmed by transmission electron microscopy studies. Figure 2 shows, as an example, micrographs of the nanocrystalline $Fe_{42.7}Co_{42.7}Nb_1Zr_{5.8}B_{6.8}Cu_1$ alloy. These figures reveal the typical structure of the nanocrystalline material. One can recognize fine crystalline grains about 8 nm in diameter embedded in the amorphous matrix. From the analysis of the electron diffraction patterns of the selected area of the sample and Mössbauer studies it was stated that the crystalline phase consists of α-FeCo grains.

The Mössbauer spectra of the nanocrystalline samples obtained directly during the rapid solidification with two different quenching rates (samples A and B) are depicted in Fig. 3. The Mössbauer spectrum presented in Fig. 3 a is typical of the nanocrystalline material with a small amount

Table 1. Data obtained from Mössbauer spectra analysis for the $Fe_{42.7}Co_{42.7}Nb_xZr_{6.8-x}B_{6.8}Cu_1$ (x = 0, 1) alloys: $(B_{eff})_{am}$ – effective hyperfine field of the amorphous phase, B_{cr} – average hyperfine field of the crystalline α-FeCo phase, σ_{cr} – standard deviation of the Gaussian distribution of the hyperfine field for the crystalline phase, IS – isomer shift corresponding to the crystalline phase, V_{cr} – volume fraction of the crystalline phase, S – Bragg-Williams long range order parameter for the crystalline phase.

	Samples	$(B_{eff})_{am}$ (T)	B_{cr} (T)	σ_{cr} (T)	IS (mm/s)	Crystalline phase	V_{cr}	S
Conventional annealing				$Fe_{42.7}Co_{42.7}Zr_{6.8}B_{6.8}Cu_1$				
	as-quenched	29.51 ± 0.05						
	730 K 10 min	26.40 ± 0.1	35.24 ± 0.03	1.09 ± 0.03	0.035 ± 0.001	$Fe_{58}Co_4$	0.33	0.5
	730 K 70 min	24.70 ± 0.2	34.82 ± 0.03	1.05 ± 0.03	0.023 ± 0.001	$Fe_{58}Co_4$	0.49	0.9
				$Fe_{42.7}Co_{42.7}Zr_{5.8}Nb_1B_{6.8}Cu_1$				
	as-quenched	28.98 ± 0.05						
	730 K 10 min	26.40 ± 0.1	35.20 ± 0.03	1.13 ± 0.04	0.035 ± 0.001	$Fe_{58}Co_4$	0.32	0.5
	730 K 70 min	23.80 ± 0.2	34.79 ± 0.03	1.03 ± 0.03	0.023 ± 0.001	$Fe_{58}Co_4$	0.46	0.9
Devitrification by rapid quenching				$Fe_{42.7}Co_{42.7}Zr_{6.8}B_{6.8}Cu_1$				
	A	27.80 ± 0.1	34.70 ± 0.05	1.25 ± 0.05	0.037 ± 0.001	$Fe_{50}Co_5$	0.24	0
	B	22.70 ± 0.2	35.23 ± 0.03	1.19 ± 0.03	0.039 ± 0.001	$Fe_{54}Co_4$	0.52	0

of the crystalline phase. However, the spectrum shown in Fig. 3 c is similar to the spectra presented in Fig. 1 e, g. The data obtained from the spectra analysis are listed in Table 1. From the results listed in this Table one can conclude that the isomer shift of the crystalline α-FeCo phase depends on the way in which the nanostructure was obtained. The isomer shift of α-FeCo phase in the nanocrystalline samples received by the conventional annealing is smaller than in samples partially crystallized during the rapid quenching (Table 1). Comparing the value of the isomer shift with the results presented in [1] we have found that α-FeCo phase is atomically ordered in the nanocrystalline samples obtained by the conventional annealing of the amorphous samples. However, the large value of the isomer shift for the crystalline α-FeCo phase in the nanocrystalline samples obtained during the rapid quenching indicates that this phase is not ordered. The volume fraction of the crystalline phase increases with the annealing time at 730 K (Table 1).

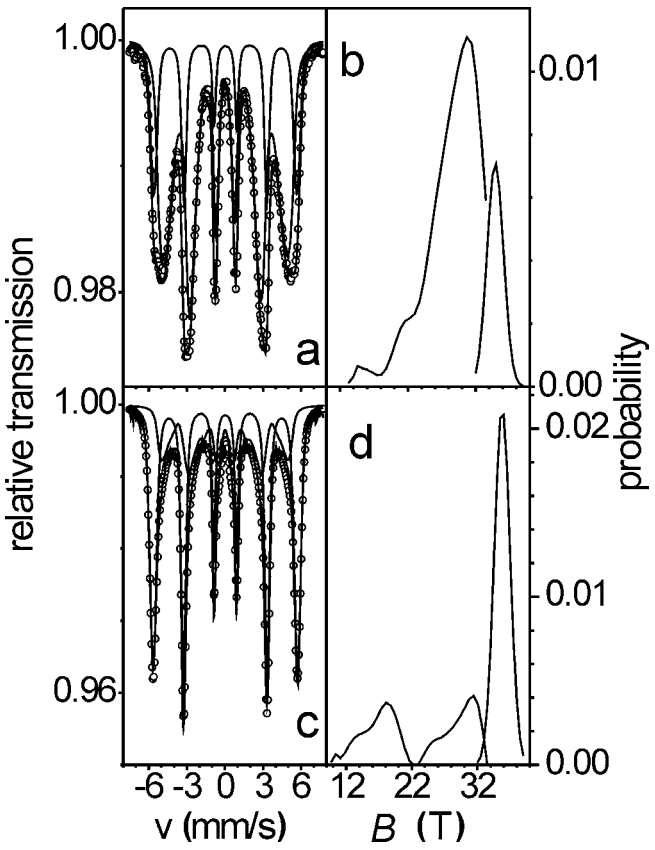

Fig. 3. Transmission Mössbauer spectra (a, c) and hyperfine field distribution (b, d) of the amorphous matrix and crystalline phase for the $Fe_{42.7}Co_{42.7}Zr_{6.8}B_{6.8}Cu_1$ alloy partially crystallized during rapid solidification with two different quenching rates (A, B).

From the Mössbauer spectra analysis of the nanocrystalline samples the following compositions were estimated:

– for the nanocrystalline samples obtained by the conventional annealing at 730 K for 70 min
$Fe_{42.7}Co_{42.7}Zr_{6.8}B_{6.8}Cu_1 \rightarrow 0.49\ Fe_{58}Co_{42} +$
$+ 0.51\ Fe_{29.5}Co_{43.5}Zr_{13.5}B_{13.5} + Cu,$
$Fe_{42.7}Co_{42.7}Nb_1Zr_{5.8}B_{6.8}Cu_1 \rightarrow 0.46\ Fe_{58}Co_{42} +$
$+ 0.54\ Fe_{30.5}Co_{43.5}Nb_2Zr_{11}B_{13} + Cu;$
– for the samples (A, B) partially crystallized during rapid solidification
A – $Fe_{42.7}Co_{42.7}Zr_{6.8}B_{6.8}Cu_1 \rightarrow 0.24\ Fe_{50}Co_{50} +$
$+ 0.76\ Fe_{41}Co_{41}Zr_9B_9 + Cu,$
B – $Fe_{42.7}Co_{42.7}Zr_{6.8}B_{6.8}Cu_1 \rightarrow 0.52\ Fe_{54}Co_{46} +$
$+ 0.48\ Fe_{31.5}Co_{39.5}Zr_{14.5}B_{14.5} + Cu.$

As can be seen from the above quoted compositions, the intergranular phase is rich in Co.

Conclusions

– In conventionally annealed samples of the $Fe_{42.7}Co_{42.7}Zr_{6.8-x}Nb_xB_{6.8}Cu_1$ (x = 0, 1) alloys the crystalline α-FeCo phase is atomically ordered.
– The value of Bragg-Williams parameter increases with annealing time at 730 K. In partially crystallized samples during the rapid quenching the crystalline α-FeCo phase is disordered.
– The intergranular phase in the nanocrystalline samples of the investigated alloys is rich in Co.

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