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Experiments on nanostructured $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ formed due to short-time annealing*

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Abstract. For technical applications the commonly used thermal processing of the amorphous $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloy consists of one-hour anneals at about 550 °C. This procedure leads to very soft magnetic properties due to the formation of the nanocrystalline Fe(Si) phase in the remaining amorphous matrix. In order to study the onset and development of the nanocrystalline phase the as-quenched amorphous samples were annealed in an Ar atmosphere at temperatures of 550 °C and 650 °C for different annealing times: 15 s, 30 s, 60 s, 90 s, 120 s, 180 s and 300 s. For sample characterization we used the conventional Mössbauer effect technique and additionally Mössbauer measurements in radiofrequency magnetic fields, which are very sensitive to magnetostriction and magnetic anisotropies. The measurements were supplemented with electron transmission microscopy and electron diffraction studies. Our short-time annealing experiments clearly show that in order to form good magnetically soft properties the annealing times of 1–2 min at 550 °C and of only 15–30 s at 650 °C are sufficient.

1. Introduction

Yoshizawa *et al* [1] first reported that a nanoscale Fe(Si) phase appears during the first crystallization stage of the amorphous $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloy. This phase, embedded in the remaining amorphous matrix, causes very soft magnetic properties of the 'nanostructured alloy'. Since this discovery a lot of research effort has been devoted to the study of the structural and magnetic properties of nanostructured alloys. The most studied system is amorphous $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$, with varying content of all the constituents, which crystallizes in two steps. The nanocrystalline phase appears at temperatures exceeding $T_{x1} = 519$ °C (792 K), which corresponds to the first exothermal peak in the differential scanning calorimetric (DSC) curve, and lower than $T_{x2} = 669$ °C (942 K) above which a complete crystallization of the amorphous phase occurs [2]. The excellent soft magnetic properties are closely related to the nanoscale structure and are well explained by the random anisotropy model [3]. Due to the small grain size the magnetocrystalline anisotropy is randomly averaged by exchange interactions. Moreover, the nanostructures reveal vanishing saturation magnetostriction. Those properties—i.e., very small anisotropy and low magnetostriction—combined with high saturation magnetization, make such materials extremely attractive for technical applications. For technical products the commonly used thermal processing of the amorphous $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloy which leads to the

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formation of the nanocrystalline Fe(Si) phase and in consequence to magnetically soft properties consists of one-hour anneals at temperatures in the region of 550 °C. Annealing at higher temperatures causes dramatic deterioration of the soft magnetic properties due to the appearance of Fe–B phases and the increase of the Fe(Si) grain size.

The Mössbauer effect was successfully used for phase identification for the annealed $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloy [4]. However, information regarding the magnetic anisotropy and magnetostriction cannot be obtained by conventional Mössbauer spectroscopy. Recently, the unconventional Mössbauer technique which makes use of the effects induced by an external magnetic radiofrequency (rf) field applied to the material investigated was used to elucidate the properties of nanocrystalline FeCuNbSiB [5] and FeZrBCu alloys [6]. The rf collapse effect is sensitive to the magnetic anisotropy and the rf sideband effect provides direct information regarding magnetostriction. Both rf effects are discussed in detail in [7, 8]. We now briefly explain this novel technique for investigating nanostructured magnetic materials, because in this work we will use it for the characterization of our differently prepared samples.

Radiofrequency magnetic fields cause two effects in the Mössbauer spectra of ferromagnetic materials: the appearance of rf sidebands and the rf collapse. The rf sideband effect is due to forced vibrations of the absorber matrix that modulate the Mössbauer resonant absorption cross section energy with the rf frequency. These vibrations, induced through magnetostriction, cause the formation of sidebands in the spectra whose positions are determined by a plus and minus integer value of the rf-field frequency beside the main spectrum. When magnetostriction vanishes the sidebands disappear.

The rf collapse effect is caused by the rf magnetic field itself. If the sample exhibits soft magnetic properties the magnetization will be switched in direction following the frequency of the applied external magnetic rf field. Because the hyperfine-field vector at the nuclei is strongly coupled to the magnetic moments of the atoms, it also starts to change its direction in response to the rf field. Now suppose that (a) the rf frequency is higher than the Larmor frequency of the nuclei in their hyperfine field and (b) the rf-field amplitude is strong enough to overcome each local anisotropy in the sample. Then the magnetic hyperfine field at the nucleus will be averaged to zero. In the spectrum we observe a single line or a quadrupole doublet. This is the complete rf collapse of the spectrum.

The advantage of the rf collapse effect is that it works locally. If the strength of the rf field is not high enough to overcome each local anisotropy we observe a partial collapse and as a consequence a more complex spectrum. For the differently prepared $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloys we are able to observe the complete collapse of the amorphous matrix and sometimes only partial collapse or no collapse of spectral components belonging to some crystallites in the sample.

The disappearance of rf sidebands together with a complete rf collapse effect (for a suitably chosen rf magnetic field strength) is our criterion used in this work for the detection of soft magnetic properties.

In this paper we discuss the formation of the nanostructures on various heat treatments of amorphous $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloy. We conclude that it is possible to obtain a good nanocrystalline phase in a simpler and less time-consuming process in which a short-time annealing is performed at 550–650 °C. The development of the nanocrystalline Fe(Si) phase is considered with respect to the annealing conditions. Mössbauer spectra collected in the conventional transmission technique and with rf magnetic fields are used for the qualitative sample characterization. In this paper we are performing Mössbauer *spectroscopy* rather then Mössbauer *spectrometry* which is the case in fitting the spectra. Only in a few cases will the results of a fit to the spectra be used as an additional argument that short-time annealing

delivers nanostructured materials, too. The Mössbauer measurements are supplemented with transmission electron microscopy (TEM) and electron diffraction studies.

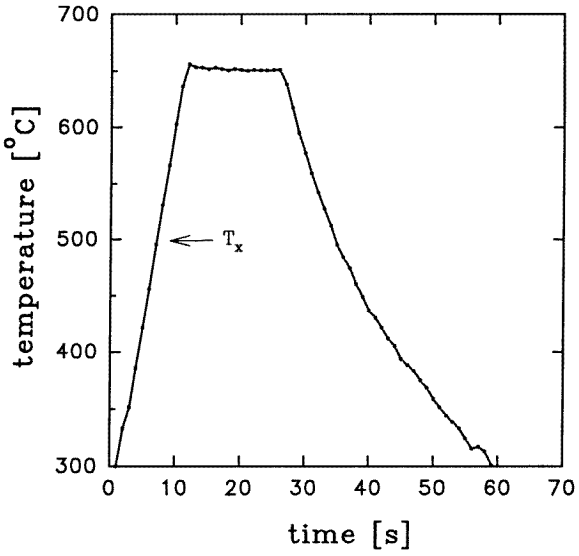

Figure 1. A typical temperature–time profile for the annealing time of 15 s at 650 °C is shown. T_x marks the onset temperature of crystallization.

2. Experimental procedure

The melt-spun amorphous $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloy was kindly provided by Vacuumschmelze GmbH, Hanau, Germany. The amorphous ribbons were 15 mm wide and about 19 μm thick. In order to study the onset and development of the nanocrystalline phase, the as-quenched amorphous samples were annealed in an argon atmosphere at temperatures of 550 °C and 650 °C for different annealing times: 15 s, 30 s, 60 s, 90 s, 120 s, 180 s and 300 s. For comparison, one-hour anneals at 550 °C and 650 °C were performed; such a thermal treatment was commonly used in earlier studies [9]. The anneals were performed using a computer-controlled AST type SHS-100 furnace in which the sample chamber was heated with halogen lamps. The desired temperature was achieved in about 10 s. The temperature was monitored with a pyrometer and a thermocouple. A typical temperature profile is shown, as an example, in figure 1 for the annealing time of 15 s at 650 °C. As can be seen from figure 1 the temperature rise-time from T_x, the crystallization temperature, to the desired annealing temperature was less than 5 s, and the temperature decrease to values below T_x after isothermal annealing took less than 9 s.

Mössbauer spectroscopy and transmission electron microscopy (TEM) were used for sample characterization. Two kinds of Mössbauer experiment were performed: (i) conventional transmission measurements and (ii) unconventional rf Mössbauer measurements in which the spectra were recorded during exposure of the samples to a rf field of 20 Oe at 60.8 MHz in a similar way to that in the earlier studies [5, 6]. The rf-field strength of 20 Oe is high enough to overcome the local magnetic anisotropy exhibited by the nanosized grains of Fe_3Si. In case (ii) a 14 mm $\times$ 16 mm sample was placed inside a coil

of a rf power generator and measured in transmission geometry. The rf field was applied in the plane of the sample, which played the role of a stationary absorber. The sample holder was water cooled in order to keep the sample temperature during the rf exposure near room temperature, which is well below the Curie point. All of the Mössbauer experiments were performed with a conventional constant-acceleration spectrometer. A ^{57}Co-in-Rh source with an activity of about 25 mCi was used. The conventional Mössbauer measurements (in the absence of the rf field, at room temperature) performed before and after rf exposure revealed that the microstructure of the sample was not affected by the rf field.

The TEM was done using a Philips CM 12 electron microscope. The magnification was 340 000. In addition to the TEM pictures being taken, the electron diffraction patterns were measured.

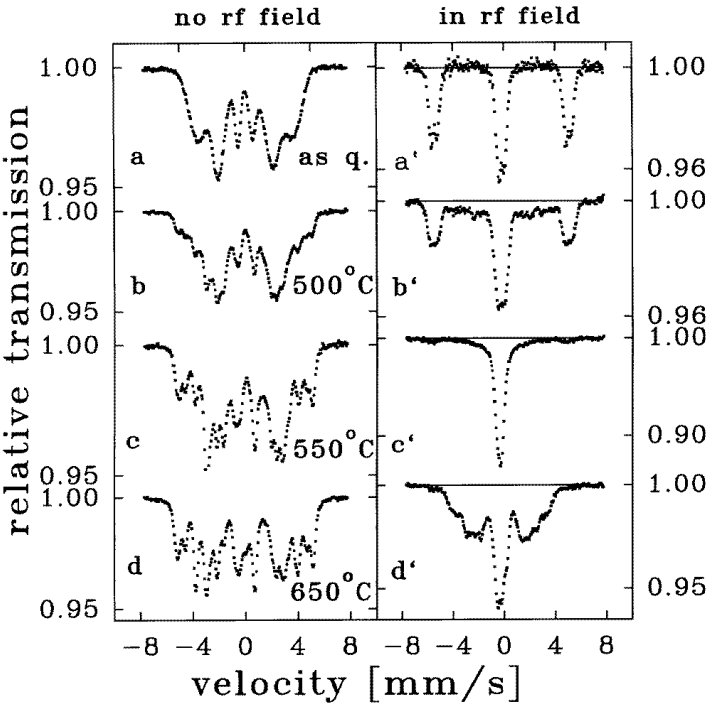

Figure 2. Mössbauer spectra recorded for $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ for conventional 1 h anneals in the temperature range from 500 °C to 650 °C without (left) and with (right) a rf field applied.

3. Results and discussion

3.1. Spectra recorded for conventional 1 h annealing at 500 °C, 550 °C and 650 °C

The Mössbauer measurements performed at room temperature both in the absence of the rf field and during the exposure to the rf field clearly show the changes in the microstructure of amorphous $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloys induced by annealing. The spectra obtained for conventional 1 h anneals in the temperature range from 500 °C to 650 °C (figure 2) will serve as a reference for comparison to the short-time-annealed samples. The preliminary results obtained for 1 h anneals were reported recently [5]. For the as-quenched

amorphous $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloy a characteristic broadened six-line pattern is observed (figure 2(a)). The application of the rf field of 20 Oe at 60.8 MHz to the as-quenched sample causes a complete collapse of the magnetic hyperfine splitting to a quadrupole doublet (QS), similar to that observed in earlier studies of amorphous alloys [10]. Strong rf sidebands which accompany the collapsed central QS doublet are due to the large magnetostriction of the as-quenched amorphous alloy (figure 2(a′)). Annealing at 500 °C causes the onset of crystallization, in agreement with the differential scanning calorimetry (DSC) data [2]. Partial crystallization of the amorphous precursor leads to the formation of the bcc-Fe(Si) phase [4]. This process is clearly observable in the conventional Mössbauer spectra as the appearance of the sextets with sharp lines (figure 2(b)). Their spectral contribution is increasing with the annealing temperature. The spectra recorded in the absence of the rf field (figures 2(c), 2(d)) can be fitted with a suitable chosen number of sextets. Four of these sextets, with hyperfine fields near the values of 31.65 T, 28.77 T, 24.36 T and 19.5 T, are characteristic of the bcc-Fe(Si) phase with DO_3 structure [11]. Broadened sextets, characterized by a distribution of hyperfine fields, correspond to the remaining amorphous phase. The fitting of the spectra is not described in detail in this contribution. Some examples are presented later in figure 5 and table 1.

The exposure to the rf field of the samples annealed at 500–650 °C causes dramatic changes in the rf Mössbauer spectra (figures 2(b′)–2(d′)). The presence of the nanocrystalline phase causes a decrease of rf sideband intensity due to the reduction of magnetostriction (figure 2(b′)). The fully rf-collapsed central QS doublet related to the remaining amorphous phase dominates in the spectrum. The noncollapsed broad spectral component corresponds to the nanocrystalline phase which starts to form in the amorphous matrix. This spectral component indicates the existence of a *local magnetic anisotropy* sufficiently large to suppress the rf collapse effect. The increase of the annealing temperature to 550 °C leads to the improvement of the soft magnetic properties of the nanocrystalline phase. The magnetic anisotropy decreases, allowing a full rf collapse of the magnetic hyperfine fields of both phases. The sidebands disappear due to vanishing magnetostriction in the nanocrystalline state (figure 2(c′)). The shape of the collapsed spectrum changes: instead of the fairly well resolved QS doublet observed for the as-quenched alloys and those annealed at 500 °C (figures 2(a′), 2(b′)), a broadened single-line-like spectrum appears (figure 2(c′)). This spectrum can be well fitted with a superposition of a QS doublet related to the amorphous phase and a single-line component corresponding to the bcc nanocrystals in the same way as in the recent study of the FeZrB alloy [12, 13]. However, from figure 2(c′) one can clearly see that in some regions of the sample the magnetic anisotropy is not negligible, as revealed by a broad triangular distortion of the nonresonant background level. Further increase of the annealing temperature causes the deterioration of soft magnetic properties due to the onset of microcrystallization. The rf Mössbauer spectrum (figure 2(d′)) consists of a collapsed central part corresponding to the retained amorphous phase and soft nanocrystalline grains in which, however, the single-line component decreased markedly, and a noncollapsed, partially resolved, magnetic hyperfine structure related to the larger magnetically harder microcrystalline particles of Fe(Si) and to Fe–B phases, detected also in the conventional spectrum in figure 2(d).

The results shown in figure 2 thus reveal that the rf Mössbauer experiment allows us to distinguish the different phases: in the nanocrystalline state both phases (the nanocrystallites Fe(Si) and the remaining amorphous matrix) have a local magnetic anisotropy low enough to allow a full rf collapse. This finally leads to a quasi-single line in the spectrum. The amorphous phase exhibits a rf-collapsed QS doublet, and from the magnetically harder Fe–B phases and bigger Fe(Si) crystallites we obtain noncollapsed, magnetically split components

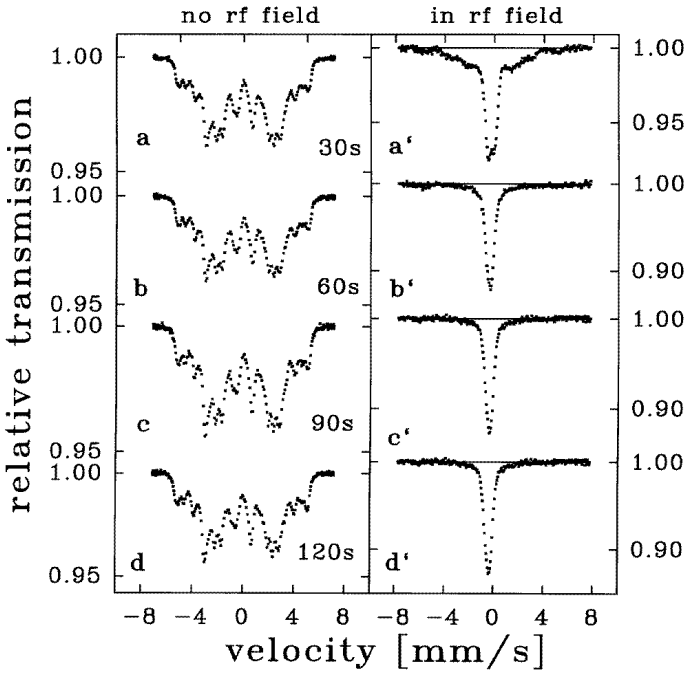

Figure 3. Mössbauer spectra recorded for $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ for samples annealed at 550 °C as a function of time from 30 s to 120 s without (left) and with (right) a rf field applied.

in the rf Mössbauer spectra. All of these components can appear simultaneously and overlap in the spectra. Such distinguishing of phases with different local magnetic anisotropies is not possible in the conventional Mössbauer experiments.

In the following short-time annealing experiments we will show that in order to form good magnetically soft nanostructured alloy the annealing time of 1–2 min at 550 °C and of only 15–30 s at 650 °C is sufficient. Our indicator for soft magnetic properties is the disappearance of the rf sideband effect.

3.2. Spectra recorded for short-time annealing at 550 °C

Investigation of the annealing of the $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloy at 550 °C as a function of time from 30 s to 120 s shows that even as little as 60 s of annealing leads to the formation of an Fe(Si) phase (figure 3(b)) which has local magnetic anisotropy small enough that full rf collapse of the magnetic hyperfine field can occur (figure 3(b′)). Shorter annealing times (30 s; figure 3(a′)) lead to the formation of an Fe(Si) phase with substantial anisotropy similar to that observed for 1 h anneals at 500 °C (figure 2(b′)). In the present case, however, the magnetostriction is greatly decreased as is evident from the disappearance of rf sidebands in figure 2(a′). Annealing at 550 °C for 60–120 s produces a very soft nanocrystalline phase as revealed by the spectra recorded during the rf-field exposure (figures 3(b′)–3(d′)) which each consist of a broadened single-line-like pattern, similar to that observed in figure 2(c′). Some triangular distortion of a nonresonant background level is, however, still evident. As can be seen from figure 3 only the rf Mössbauer experiment is sensitive enough to the changes in the magnetic properties (anisotropy) related to the microstructure of nanoscale

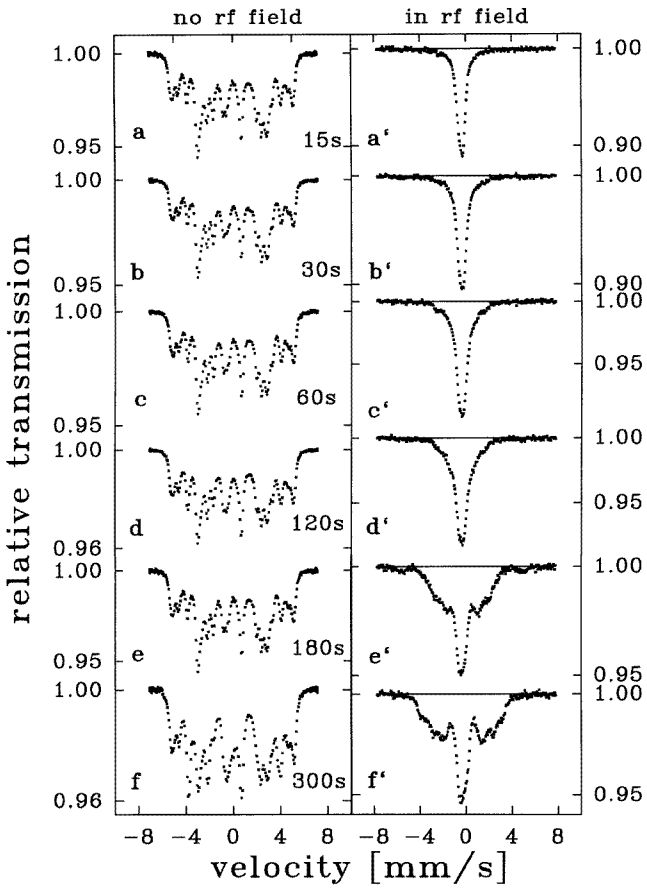

Figure 4. Mössbauer spectra recorded for $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ for samples annealed at 650 °C as a function of time from 15 s to 300 s without (left) and with (right) a rf field applied.

grains. The conventional spectra, recorded in the absence of the rf field (figures 3(a)–3(d)) do not differ much from each other.

3.3. Spectra recorded for short-time annealing at 650 °C

A nanocrystalline phase can also be formed with further shortening of the annealing time at higher temperature; 15 s annealing at 650 °C is sufficient (figure 4(a′)). The rf-collapsed spectra recorded for the annealing times of 15 s and 30 s at 650 °C reveal the formation of a nanocrystalline phase causing soft magnetic properties of the nanostructured alloy. These spectra (figures 4(a′), 4(b′)) each consist of a superposition of a single line and a QS doublet as discussed above (figure 2(c′)). However, longer annealing times, exceeding 60 s, caused an increase of magnetic anisotropy and deterioration of the soft magnetic properties, as is evident from the increase of the triangular distortion and broadening of collapsed spectra (figures 4(c′), 4(d′)). As before, the conventional Mössbauer experiment (figures 4(a)–4(d)) is not sensitive enough to exhibit such changes in the microstructure of the nanophase. Annealing times longer than 180 s at 650 °C result in the formation of magnetically harder Fe(Si) and Fe–B phases. The noncollapsed component appears in the rf

Table 1. Fitting parameters for the Mössbauer spectra of figure 5 recorded for two samples of $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ annealed at 650 °C for $t_a = 15$ s and $t_a = 300$ s. A and D represent sites for Fe atoms in the ordered DO_3 structure typical for the Fe–Si nanocrystals. The AN with $N = 4$, 5, 6, 7 and 8 indicate the sites and numbers of the nearest-neighbour Fe atoms. The D site always exhibits eight nearest-neighbour Fe atoms. 'Fe-rich' indicates bcc-iron with a small amount of solved silicon; 'Param.' indicates an as-yet unidentified phase characterized by a broad single line; 'Others' indicates phases with a hyperfine field of about 27 T.

	Hyperfine fields of crystalline phases (T)							
t_a (s)	A4	A5	A6	A7, A8, D	Fe_2B	Fe-rich	Param.	Others
15	19.52	24.52	28.92	31.77	—	31.90	—	28.07
300	19.41	24.10	28.69	31.74	23.69	32.02	0.21	27.18
	Isomer shifts of crystalline phases (mm s) with respect to ^{57}Fe in rhodium							
t_a (s)	A4	A5	A6	A7, A8, D	Fe_2B	Fe-rich	Param.	Others
15	0.17	0.09	0.03	0.07	—	−0.82	—	−0.13
300	0.13	0.14	0.01	0.08	−0.02	−0.10	−0.02	−0.86
	Relative amount of phases (%)							
t_a (s)	Fe_3Si	Fe_2B	Fe-rich	Param.	Others	Amorphous		
15	47.14	—	14.93	—	7.44	30.49		
300	49.66	16.74	13.61	15.12	4.87	—		

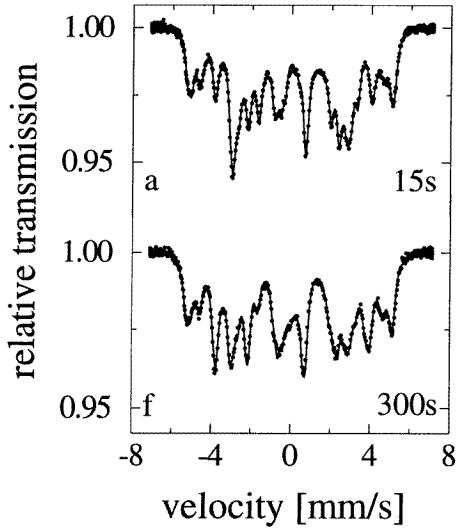

Figure 5. Conventional transmission Mössbauer spectra recorded for $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ for two samples annealed at 650 °C for 15 s (a) and 300 s (f). The solid line represents the fit to the spectra. The parameters are summarized in table 1.

Mössbauer spectra (figures 4(e′), 4(f′)). The formation of microcrystalline Fe–B phases is so pronounced that it can be readily detected in the conventional Mössbauer measurements (figure 4(f)). In order to show that the spectrum belonging to the 15 s anneal at 650 °C

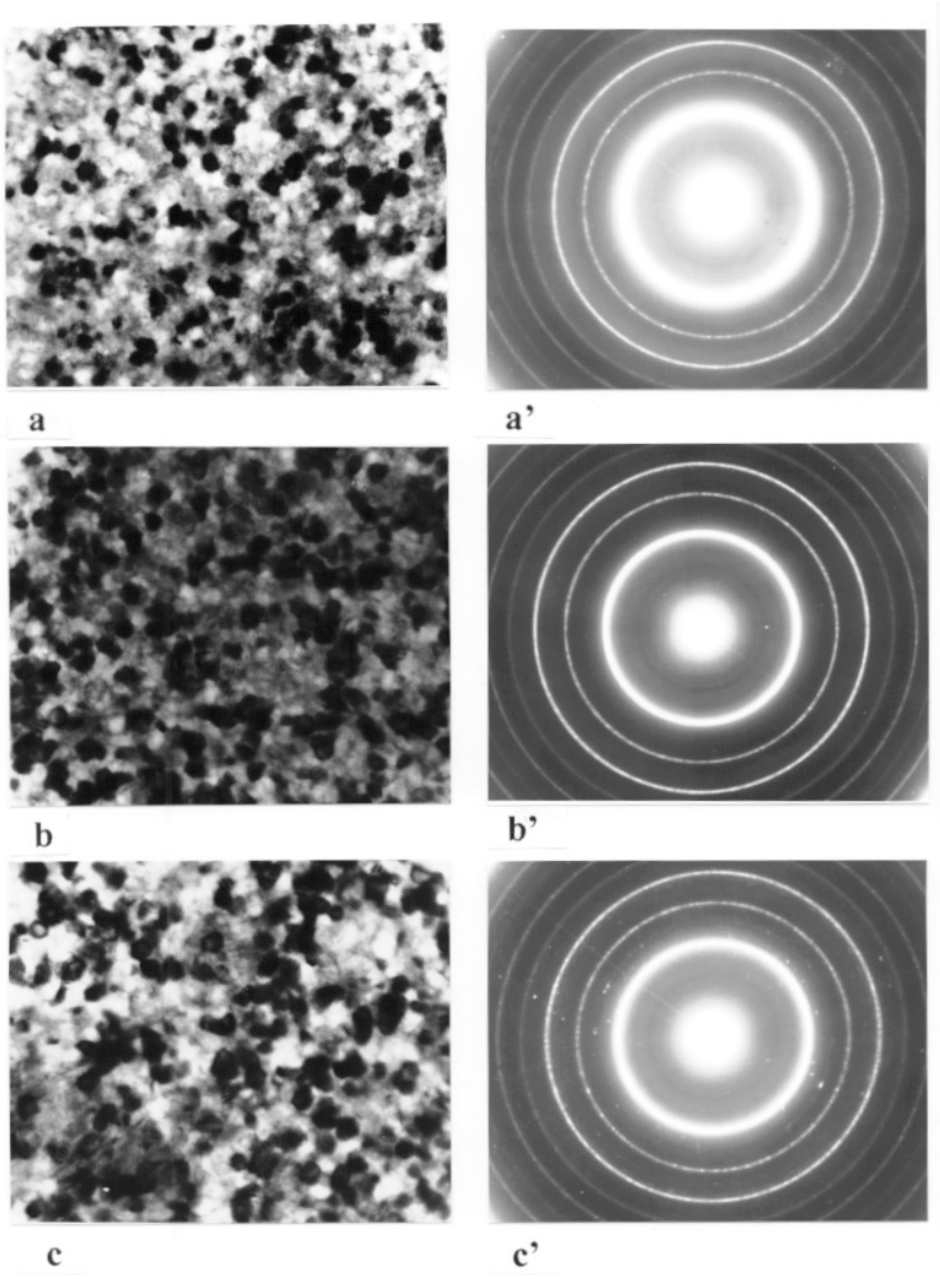

Figure 6. Transmission electron microscope pictures ((a), (b), (c)) and the corresponding electron diffraction patterns ((a′), (b′), (c′)) for $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$: (a) 550 °C, 30 s; (b) 650 °C, 15 s; (c) 650 °C, 120 s. For details, see the text.

really exhibits the nanostructure necessary for soft magnetic properties, we performed a fit to the spectrum presented in figure 4(a) and we compare it with a fit to a spectrum for a long-time-annealed sample (30 min) in figure 4(f). Both spectra together with the fit are

redrawn in figure 5. The relevant fit parameters are summarized in table 1. From these it is obvious that the parameters for the sample annealed for 15 s at 650 °C fit very well to the results characteristic for ideal soft magnetic properties previously described in [9]. On the other hand the parameters for the alloy annealed for 300 s at 650 °C indicate the formation of microcrystalline Fe–B phases. This is so pronounced that it can be directly seen from the changes in the shape in the Mössbauer spectrum (figure 5).

To obtain additional confirmation about the nanostructure produced by short-time annealing at 650 °C the Mössbauer experiments were supplemented with TEM and electron diffraction measurements (figure 6). The TEM pictures obtained for the samples annealed at 550 °C for 30 s (figure 6(a)) and at 650 °C for 15 s (figure 6(b)) show great similarity to each other. Clearly, nanocrystalline grains with the average size of 11–13 nm are formed. Also the shape of the grains is very similar: the grains are almost spherical and well separated from each other. These TEM pictures do not explain the differences clearly detected in the rf Mössbauer experiment (compare figure 3(a′) and figure 4(a′)). Also the electron diffraction patterns are very similar (figures 6(a′), 6(b′)). Since the nanocrystalline grains display in the two cases similar shapes and sizes, it seems that the markedly larger anisotropy in the sample annealed for 30 s at 550 °C (figure 3(a′)) is related to the stress. Despite the average magnetostriction in this sample being rather small (there are no rf sidebands in figure 3(a′)), the local magnetostriction may not be negligible, thus allowing the stress related to the onset of crystallization to induce a local magnetic anisotropy large enough to prevent a rf collapse of the magnetic hyperfine structure in some parts of the sample (figure 3(a′)). Further annealing may relax the stresses and decrease the anisotropy. Longer annealing at 650 °C (figure 6(c)) causes an increase of the grain size. The electron diffraction pattern contains a number of clear spots corresponding to larger crystalline grains (figure 6(c′)). The grains start to join, thus forming larger crystallites with irregular shapes. The magnetic anisotropy of such regions increases both due to the shape (shape anisotropy) and the larger size of the grains (the magnetocrystalline anisotropy may not be negligible). This effect is clearly seen in the rf Mössbauer spectra (figures 4(d′)–4(f′)).

4. Conclusions

Our study shows that the nanostructured alloy consisting of nanocrystalline bcc-Fe(Si) phase in the remaining amorphous matrix with excellent soft magnetic properties and vanishing magnetostriction can be formed in $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloy via short-time annealing at 550–650 °C. This finding is important from the point of view of technical applications of such materials. Long, one-hour annealing seems to be unnecessary, thus making the process of the forming of nanocrystals simpler and less time-consuming.

The unique rf Mössbauer technique is very sensitive to the changes in the microstructure of the alloy studied and allows the determination of the magnetic properties (anisotropy, magnetostriction) of the phases formed due to the annealing, thus allowing the distinguishing between the magnetically soft amorphous and nanocrystalline phases, and magnetically harder microcrystalline grains. This technique is clearly superior to conventional Mössbauer studies, which only allow the identification of phases. However, information concerning the absolute sizes of the grains cannot be directly extracted from the Mössbauer studies. The TEM measurements are indispensable for grain size determination. However, the TEM technique does not allow the identification of the composition of the phases formed and of their magnetic properties. A systematic study with the use of complementary methods is necessary to achieve a better understanding of the structural and magnetic properties of the nanocrystalline phases appearing in the course of annealing the amorphous precursor.

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