

Crystallization Process of Amorphous Alloys $(\text{Co}_{1-x}\text{Fe}_x)_{74.5}\text{Si}_{13.5}\text{B}_{12}$ of $x=0.06, 0.5$ and 1.0 : Mössbauer and X-ray diffraction measurements

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Abstract

The crystallization processes of amorphous alloys $(\text{Co}_{1-x}\text{Fe}_x)_{74.5}\text{Si}_{13.5}\text{B}_{12}$ of $x=0.06, 0.5$ and 1.0 have been studied by using the Mössbauer and the X-ray diffraction measurements. Each sample is annealed near its crystallization temperature isothermally. For the three kinds of samples, as the annealing time is increased, firstly the metallic phases precipitate and then the metalloid phases follow. For the sample of $x=0.06$, some amount of Si atom which once dissolved in the precipitated metallic phase is found to be expended when the metalloid Si compound precipitates. On the other hand, for the samples of $x=0.5$ and $x=1.0$, the Si atoms stay in the precipitated metallic phase and no Si compound is detected during the heat-treatment. The number of sites of Fe atoms in the precipitated metallic phases is found to be one for the samples of $x=0.06$ and $x=0.5$ but five for the sample of $x=1.0$.

1 Introduction

The Co-based amorphous alloy $(\text{Co}_{0.94}\text{Fe}_{0.06})_{74.5}\text{Si}_{13.5}\text{B}_{12}$ has been known to be an excellent soft magnetic material[1,2]. It has the properties of high permeability, low coercive force and small magnetostriction. Such properties are considered to be closely related to the amorphous structure.

Since amorphous materials are in metastable state due to the process of the super rapid cooling, there are possibilities of losing the properties by some heat treatments. Lots of researchers have studied thermal stabilities of amorphous materials using various experimental methods, in which the Mössbauer spectroscopy has played an important role for investigating the microscopic state of the amorphous structure.

However, except for one group[3], the Mössbauer study on Co-based amorphous alloys has not been done, because the alloys contain only a small amount of Fe. So we have done the Mössbauer measurement by preparing the amorphous alloy $(\text{Co}_{0.94}\text{Fe}_{0.06})_{74.5}\text{Si}_{13.5}\text{B}_{12}$ enriched with ^{57}Fe . For this alloy, we have observed the transition from amorphous state to crystalline state[4], the magnetic anisotropy induced by field-annealing and the directional distribution of the magnetization axis[5,6].

In this paper, we report on the crystallization processes of amorphous alloys $(\text{Co}_{1-x}\text{Fe}_x)_{74.5}\text{Si}_{13.5}\text{B}_{12}$ of $x=0.06, 0.5$ and 1.0 during various heat-treatments, where samples of $x=0.5$ and $x=1.0$ with large concentrations of Fe are prepared anew for this investigation [7]. Parallel to the Mössbauer spectra, we also measured the X-ray diffraction patterns in order to identify the crystalline phase precipitated in the crystallization process.

The present paper consists of four sections. In section 2, the preparation, annealing conditions and how to determine the crystallization temperature of samples will be presented. In section 3, characteristics common to the three kinds of samples during the crystallization, distinctive characteristics of each sample and finally the characteristics of fully crystallized samples will be presented. In section 4, main features of our results are summarized. In Appendix, we will describe some results obtained for the several kinds of crystalline compounds, which are utilized in this paper in order to identify the precipitated crystalline phases in the crystallization process.

2 Experimental

The ferromagnetic amorphous alloys $(\text{Co}_{1-x}\text{Fe}_x)_{74.5}\text{Si}_{13.5}\text{B}_{12}$ of $x=0.06, 0.5$ and 1.0 were made by the single roller quenching method. They were in the long-ribbon form of 5 mm wide and $\sim 20 \mu\text{m}$ thick. In the alloy of $x=0.06$, an iron was enriched to 30 % with ^{57}Fe to make the Mössbauer measurements easy. The ribbons were cut in ~ 20 mm long and were annealed in argon atmosphere at the annealing temperature T_a for the

annealing time t_a . Hereafter, we denote the sample $(\text{Co}_{1-x}\text{Fe}_x)_{74.5}\text{Si}_{13.5}\text{B}_{12}$ annealed at the temperature T_a for the time t_a as the sample- $x(T_a, t_a)$.

The Mössbauer spectra were measured using a constant acceleration spectrometer of a conventional design. The velocity was calibrated with Fe-metal. The source was ^{57}Co in Rh and γ -rays were incident perpendicularly to the ribbon plane.

The X-ray diffraction patterns were observed using Fe- $K\alpha$ radiation filtered with Mn foil. The scattering angles 2θ ranged from 20° to 152° . Both the Mössbauer and the X-ray diffraction measurements were done at room temperature.

We determined the crystallization temperature T_x of the sample of $x=0.06$ as 799 K by using a differential thermal analyzer, where the temperature of sample was elevated with a heating rate of $16^\circ\text{K}/\text{min}$. When annealed at T_x , the sample-0.06(799 K, 1.5 min) showed the Mössbauer spectrum still consisting of the six broad absorption lines characteristic of the amorphous phase, while the X-ray diffraction pattern of this sample showed very small but visible structures superimposed on a broad halo peak.

In order to find T_x 's of the samples of $x=0.5$ and 1.0 , we annealed the samples at temperatures with intervals of 5 K above 750 K for a constant time of 1.5 min (isochronal annealing) and quenched them to room temperature. We observed the Mössbauer spectrum and the X-ray diffraction pattern for the samples, until we could discern similar characteristics to those observed for the sample-0.06(799 K, 1.5 min). The sample-0.5(755 K, 1.5 min) and the sample-1.0(805 K, 1.5 min) showed the satisfactory patterns and we deduced the T_x 's for the sample of $x=0.5$ and 1.0 to be 755 K and 805 K, respectively.

In order to observe the development of the crystallization, we annealed the sample of $x=0.6$ around its T_x : 799 K and 873 K, the sample of $x=0.5$ at 760 K and the sample of $x=1.0$ at 805 K.

As the annealing time, we chose firstly the short time of 1.5 min and 5 min for the three kinds of samples to observe the initial stage of the crystallization. Secondly, in order to investigate the middle stage of the crystallization, we repeated the 2 h-annealing at 799 K and the 15 min-annealing at 873 K for the sample of $x=0.06$. At every stage of annealing, samples were quenched to room temperature where both the Mössbauer and X-ray diffraction measurements were done. The sample, in which the 2 h-annealing was repeated eleven times, showed the similar spectrum to that observed for the sample annealed continuously for 22 h. Therefore, for the samples of $x=0.5$ and $x=1.0$, the continuous annealings for a long time were done.

In order to observe the final stage of the crystallization and to examine the role of the annealing temperature T_a , we also annealed the samples at temperatures much higher than T_x for a long time: they were the sample-0.06(873 K, 20 h), the sample-0.5(900 K, 20 h) and the sample-1.0(900 K, 20 h).

3 Results and Discussion

The Mössbauer spectra observed for samples $(\text{Co}_{1-x}\text{Fe}_x)_{74.5}\text{Si}_{13.5}\text{B}_{12}$ of $x=0.06$, 0.5 and 1.0 at room temperature are shown in Fig.1 A, B and C, in which figures (a) show the spectra observed for the respective "as-prepared" samples and Figures (b)-(f) show the spectra observed for "annealed" ones for various annealing time at temperatures 799 K, 760 K and 805 K (isothermal annealing). Representative X-ray diffraction patterns of each sample are shown in Fig.2 A, B and C.

We will now indicate some general characteristics of our results. Figures (a) in Fig.2 show only halo patterns in which any structure due to the crystalline phases is not observed. This fact means that the "as-prepared" samples of $x=0.06$, 0.5 and 1.0 are completely in an amorphous state. The corresponding Mössbauer spectra in Fig.1 also consist of six broad absorption lines characteristic of the amorphous alloy. This indicates that there exist some distributions in the hyperfine field H_{hf} . The average values of the H_{hf} are estimated to be 242 kOe, 261 kOe and 245 kOe for the samples of $x=0.06$, $x=0.5$ and $x=1.0$, respectively.

Figures (b) in Fig.1 show the Mössbauer spectra for the samples annealed for a short time of 1.5 min at each temperature. It is clear that the intensity ratios are considerably different from the respective spectra of the "as-prepared" sample, although the positions of the absorption lines are almost similar to those in Fig.(a).

Generally, the relative intensity of the Mössbauer absorption lines depends on the angle ϕ between the direction of the incident γ -rays and that of H_{hf} as $I_{1,6}:I_{2,5}:I_{3,4}=3:\alpha:1$, where $I_{i,j}=I_i=I_j$ and I_i stands for the intensity of i -th absorption line from the left side. Furthermore,

$$\alpha=4\sin^2\phi/(1+\cos^2\phi). \quad (1)$$

Note that α equals zero at $\phi=0$ and attains its maximum value of 4 at $\phi=90^\circ$. As the γ -rays are incident perpendicularly to the ribbon plane, a small value of α means that the direction of H_{hf} rises up with a large

angle from the ribbon plane. The obtained values of α are listed in Table 1. We already reported on them for the sample of $x=0.06$ [6] and for the sample of $x=0.5$ [7].

For the "as-prepared" sample of $x=1.0$ and the sample-1.0(805 K, 1.5 min), we obtained the value of $\alpha=2.9$. It means that the average direction of H_{hf} of the as-prepared sample of $x=1.0$ rises up $\sim 23^\circ$ from the ribbon plane and it does not change by the annealing-(805 K, 1.5 min), in contrast to the sample of $x=0.06$ and $x=0.5$.

Table 1. The values of $\alpha=4\sin^2\phi/(1+\cos^2\phi)$ for three samples, where ϕ means the angle between the direction of the incident γ -rays and that of H_{hf} .

	sample	α
x=0.06	as-prepared	3.9
	(799 K, 1.5 min)	2.0
x=0.5	as-prepared	3.0
	(760 K, 1.5 min)	2.5
x=1.0	as-prepared	2.9
	(805 K, 1.5 min)	2.9

In Figures (c)~(f) of Fig.1 the Mössbauer spectra for samples annealed at various times up to ~ 20 h are shown. From the change of these spectra, we can see that the crystalline phases precipitate one after another as t_a is increased

At the first stage of the crystallization ($t_a \sim 5$ min), the metallic phase (Co_{1-x}Fe_x) precipitates in the three kinds of samples. These phases can be identified from the X-ray diffraction patterns. In Figs. 1 A and 1 B, the positions of the absorption lines in the spectra of the precipitated metallic phase are indicated by the solid bars. The positions of the inner four absorption lines are estimated from those of the well resolved outermost absorption lines on the assumption that a quadrupole splitting is zero. In Fig.1 C, the spectra of the precipitated metallic phase are too complicated to analyze at this stage.

At the second stage of the crystallization ($5 \text{ min} < t_a < 20 \text{ h}$), the metalloid compound precipitates. In the boron compounds, (Co_{1-x}Fe_x)₂B phases precipitate in the three kinds of samples. The positions of the absorption lines in the spectra of this compound are indicated by broken bars. Those of the boron compound precipitated in the sample of $x=0.06$ are indicated by referring to the Mössbauer spectra obtained for a crystalline compound (Co_{0.99}Fe_{0.01})₂B prepared for identification [8] (see Appendix below). On the other hand, those of the boron compound precipitated in the samples of $x=0.5$ and $x=1.0$ are indicated by referring to the values reported in papers for the crystalline compounds (Co_{0.5}Fe_{0.5})₂B and Fe₂B [8,9,10].

For the silicon compounds, it has become clear from X-ray patterns that a {Co(Fe)}₂Si phase precipitates only in the sample of $x=0.06$, and does not precipitate in the samples of $x=0.5$ and $x=1.0$. The positions of the absorption lines of the {Co(Fe)}₂Si phase in Mössbauer spectra are indicated by the solid bars near the velocity of 0 mm/s (Fig. 1A(f)), here the spectrum of a compound (Co_{0.99}Fe_{0.01})₂Si prepared for identification is referred to (see Appendix). In the following sub-sections, distinctive characteristics in the crystallization process of the three kinds of samples will be described separately.

3-1 The sample of $x=0.06$

The remarkable property appearing in the Mössbauer spectra during the crystallization process of the sample of $x=0.06$ is that the values of H_{hf} in the precipitated metallic phase depend on both the annealing temperature T_a and the annealing time t_a [9]. From the interval of the two outermost absorption lines of the Mössbauer spectra shown in Fig.1 A(c)~(f), we can estimate the values of H_{hf} in the metallic phase Co_{0.94}Fe_{0.06}.

Figures 3(a) and (b) show the values of H_{hf} in the metallic phase precipitated at the 799 K-annealing and the 873 K-annealing as the function of t_a . The solid lines drawn in each figures show the ranges of annealing time

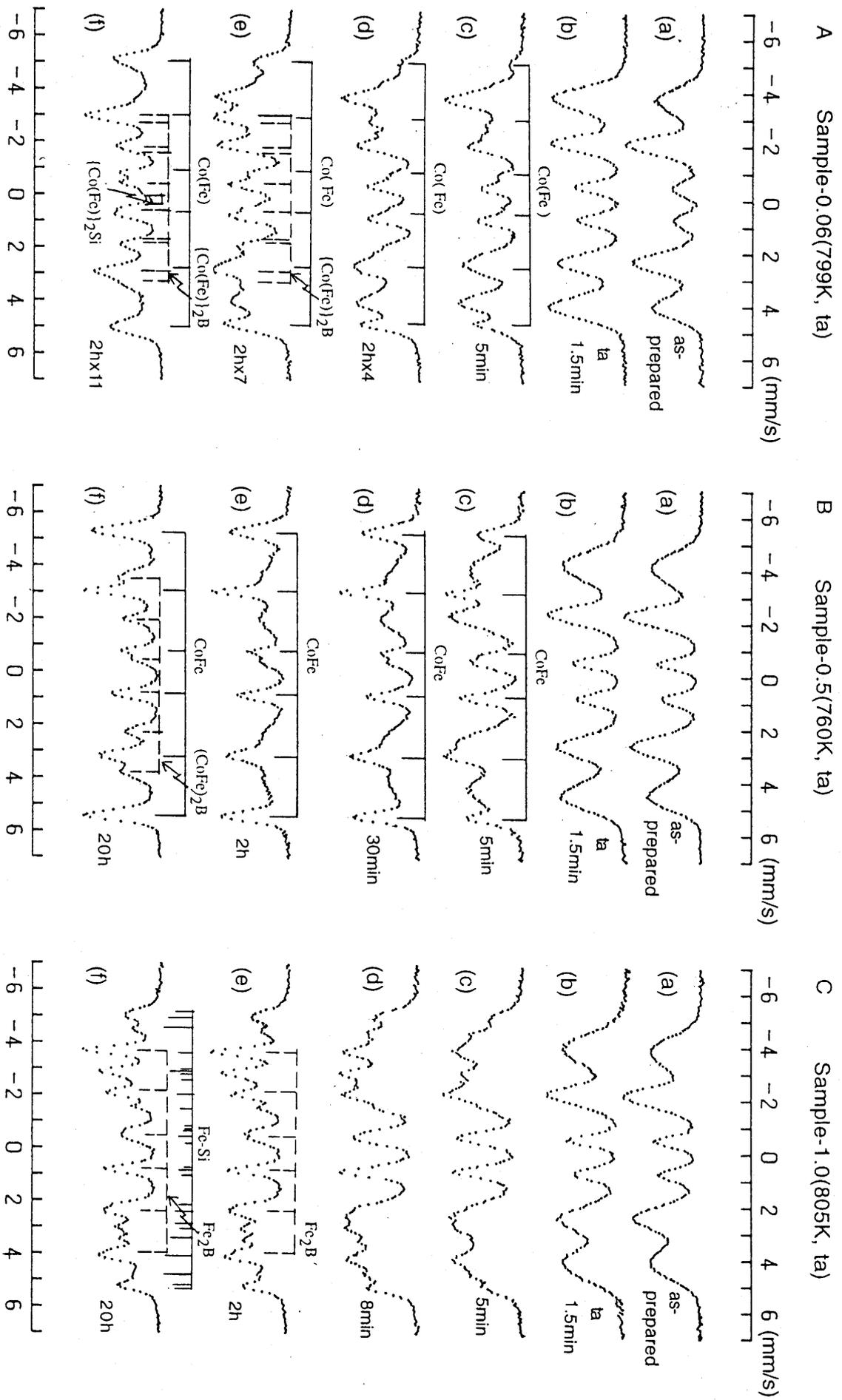


Fig. 1. The temperature dependence of Mössbauer spectra observed for samples $(\text{Co}_{1-x}\text{Fe}_x)_{74.5}\text{Si}_{13.5}\text{B}_{12}$ (A) $x=0.06$, (B) $x=0.5$ and (C) $x=1.0$.

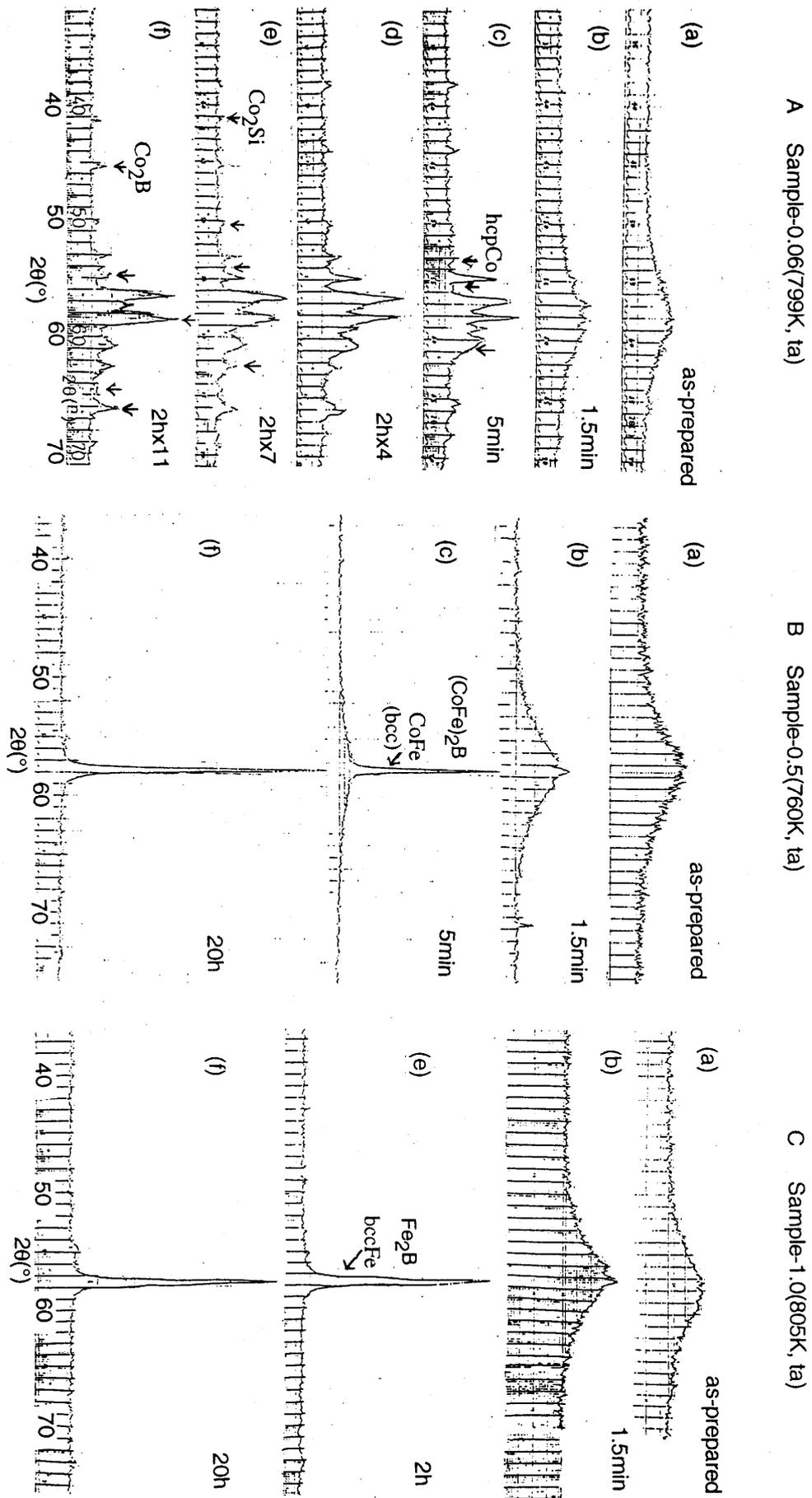


Fig. 2. The temperature dependence of X-ray diffraction patterns for samples ($\text{Co}_{1-x}\text{Fe}_x$)_{74.5}Si_{13.5}B₁₂ (A) $x=0.06$, (B) $x=0.5$ and (C) $x=1.0$.

where crystalline phases indicated are detected by the X-ray diffraction measurement. The existence of the amorphous phase was determined by the Mössbauer spectra. The values of H_{hf} in the metallic phase $Co_{0.94}Fe_{0.06}$ precipitated at the early stage of crystallization are 303 kOe in 799 K-annealing and 284 kOe in 873 K-annealing. Both of them show the values smaller than those of H_{hf} (325 kOe and 315 kOe) which have been reported for the fcc Co and the hcp Co metals including a small amount of Fe[10].

It should be noticed that $(Co_{0.94}Fe_{0.06})_2B$ and $(Co_{0.94}Fe_{0.06})_2Si$ phases precipitate at the annealing times where the values of H_{hf} in the $Co_{0.94}Fe_{0.06}$ phase begin to increase. On the other hand, it has been known that a nonmagnetic impurities in Fe metal cause a decrease of the value of H_{hf} [11]. In our case, it can be considered that the metallic phase $Co_{0.94}Fe_{0.06}$ precipitates by taking in some amount of metalloid as an impurity. The increase of H_{hf} in the $Co_{0.94}Fe_{0.06}$ phase means the decrease of the metalloid concentration in this phase. Therefore, it is suggested that some amount of the metalloid dissolved in the $Co_{0.94}Fe_{0.06}$ phase at the early stage of the crystallization is expended when $(Co_{0.94}Fe_{0.06})_2Si$ phase or $(Co_{0.94}Fe_{0.06})_2B$ phase precipitates and grows.

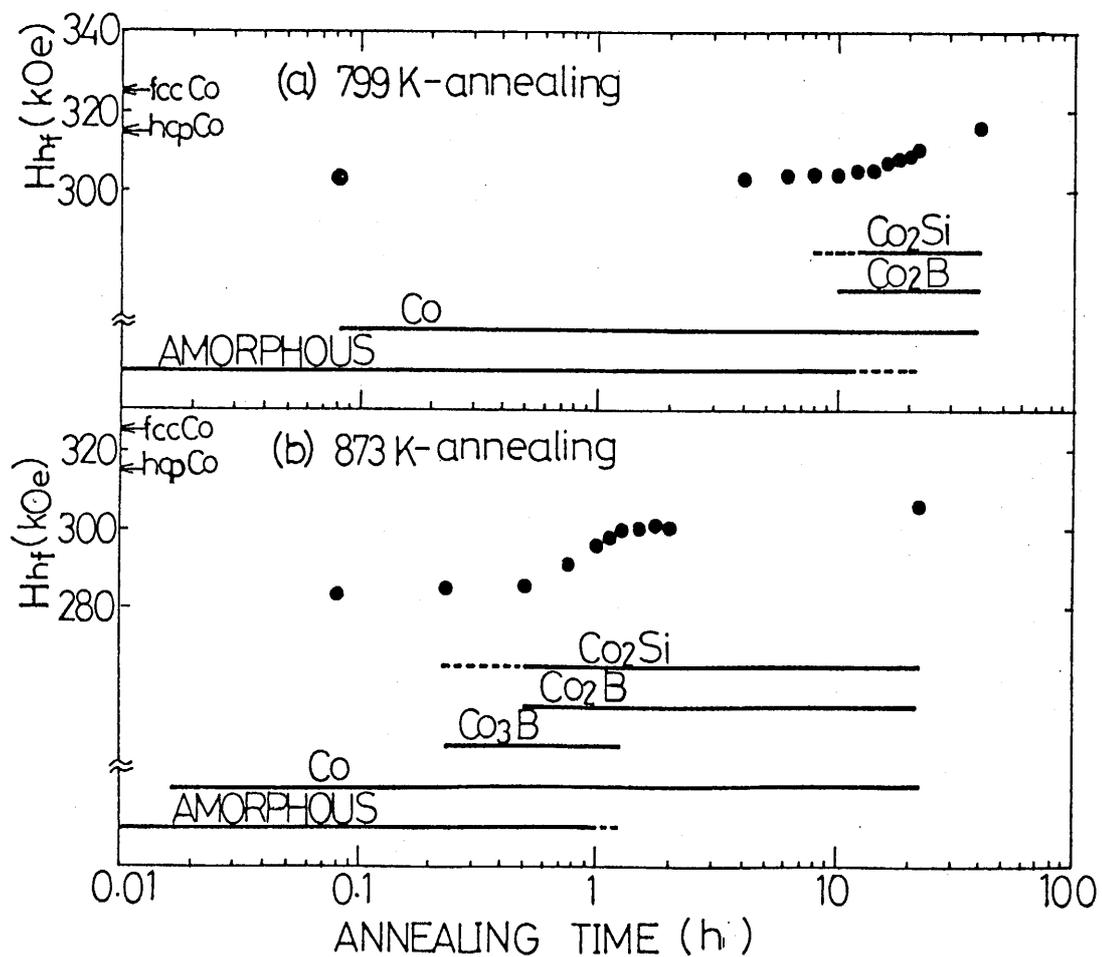


Fig. 3. The values of H_{hf} in the metallic phase precipitated (a) at the 799 K-annealing and (b) at the 873 K-annealing as the function of annealing time t_a . The solid lines drawn in each figures show the ranges of annealing time where crystalline phases indicated are detected by the X-ray diffraction measurement. The existence of the amorphous phase was determined by the Mössbauer spectra.

As the next remarkable property, a Si compound precipitates in the crystallization process only for this sample of $x=0.06$. As seen in Fig.2 A(e) and (f), the peaks corresponding to the compound (Co_{0.94}Fe_{0.06})₂Si appear on the X-ray diffraction patterns of the samples-0.06(799 K, 2 h x 7) and -(799 K, 2 h x 11) (short arrows in Fig.2 A(e)). From the X-ray diffraction patterns, the amount of the precipitated compound (Co_{0.94}Fe_{0.06})₂Si is estimated to be nearly the same as that of the precipitated compound (Co_{0.94}Fe_{0.06})₂B. On the other hand, the absorption area of the Mössbauer spectrum corresponding to the (Co_{0.94}Fe_{0.06})₂Si is much smaller than that corresponding to the (Co_{0.94}Fe_{0.06})₂B as seen in Fig.1 A(f). This fact means that Fe atom is hard to dissolve in a compound Co₂Si.

J.Wolny et al. have studied the crystallization of a sample with a similar composition to ours [3]. They reported that the peaks corresponding to the (Co_{0.94}Fe_{0.06})₂Si were observed in the X-ray diffraction pattern, but its absorption lines were not detected in the Mössbauer spectrum. A reason for this fact given by them is that Fe atom does not substitute for Co atom in Co₂Si due to an instability of Fe₂Si structure.

In our case, it was confirmed by the Mössbauer measurement that Fe atoms slightly dissolved in the compound Co₂Si precipitated in the crystallization process and also dissolved in the compound Co₂Si prepared for identification (see Appendix). In the Mössbauer spectra of the sample annealed at 873 K, the absorption lines of (Co_{0.94}Fe_{0.06})₂Si were also observed. The difference between the results of J.Wolny et al. and ours is probably to originate in the annealing condition: we annealed our samples in an argon atmosphere but they annealed their sample in vacuum.

As the third remarkable property, the compound (Co_{0.94}Fe_{0.06})₃B precipitates in the sample of $x=0.06$ only when it is annealed at 873 K for periods between 0.25 h and 1.25 h. In the Mössbauer spectrum, the (Co_{0.94}Fe_{0.06})₃B is hard to be identified because it shows the complicated spectrum. In the X-ray diffraction pattern, on the other hand, the lines corresponding to the (Co_{0.94}Fe_{0.06})₃B can be identified. As the annealing time is increased, the compound (Co_{0.94}Fe_{0.06})₃B disappears. It is probable that the compound (Co_{0.94}Fe_{0.06})₃B resolves into the (Co_{0.94}Fe_{0.06})₂B and the Co_{0.94}Fe_{0.06}.

3-2 The sample of $x=0.5$

As seen in Fig.2 B(c), the X-ray diffraction pattern for the sample-0.5(760 K, 5 min) shows sharp lines corresponding to a bcc structure superimposed on a halo pattern. This fact means that a considerable amount of the metallic phase Co_{0.5}Fe_{0.5} with the bcc structure precipitates in the amorphous phase. As seen in Fig.1 B(c), the Mössbauer spectra of this sample can be decomposed into six broad absorption lines corresponding to the amorphous phase and six sharp absorption lines corresponding to the metallic phase. In this sample, the relative area of the absorption lines corresponding to the metallic phase is smaller than that corresponding to the amorphous phase. As the annealing time is increased to 2 h, the relative area of the absorption lines corresponding to the metallic phase becomes large (Fig.1 B(d),(e)).

In the spectrum for the sample-0.5(760 K, 20 h), the amorphous phase completely disappears and a new compound appears. This compound was identified as an inter-metallic compound (Co_{0.5}Fe_{0.5})₂B (Fig.1 B(f)). We decomposed this spectrum by using the Lorentzian line fitting and estimated the intensity ratio of the inter-metallic phase to the metallic phase to be 1:0.59. On the other hand, if the amorphous phase (Co_{0.5}Fe_{0.5})_{74.5}Si_{13.5}B₁₂ is decomposed into a metallic phase including Si, Co_{0.5}Fe_{0.5}-Si, and an inter-metallic phase (Co_{0.5}Fe_{0.5})₂B (as shown later, a Si compound does not precipitate), the intensity ratio of two phases becomes 1:0.48 as

$$(Co_{0.5}Fe_{0.5})_{74.5}Si_{13.5}B_{12}=50.5(Co_{0.5}Fe_{0.5}-Si)+12(Co_{0.5}Fe_{0.5})_2B. \quad (2)$$

The intensity ratio of the inter-metallic phase to the metallic phase obtained by the Lorentzian line fitting is larger than this value by 20 %. Although the difference is a little larger than the experimental error, we may conclude that all B atoms have been expended to make a compound (Co_{0.5}Fe_{0.5})₂B and have not stayed in the metallic phase.

In contrast to the sample of $x=0.06$, a Si compound is not detected in both the Mössbauer spectra and the X-ray diffraction patterns. This fact means that all Si atoms dissolve in the metallic phase and stay there during the heat treatments.

The value of H_{hf} for the precipitated metallic phase shows a constant value of 331 kOe independent of annealing time at 760 K-annealing. Generally, in a Co_{0.5}Fe_{0.5} alloy, it is known that an order state and a disorder one exist depending on the cooling rate from high temperature, and the values of H_{hf} corresponding to the order and the disorder states are 350 kOe and 342 kOe at room temperature, respectively[12] The values of

H_{hf} of the metallic phase precipitated in our sample are small by 10~20 kOe as compared with those values. Also from this fact, it became clear that Si atoms dissolve in a metallic phase. It is likely that Si atoms once dissolved in the metallic phase do not precipitate as the compound differently from the case of the sample of $x=0.06$, but still stay in the metallic phase for any annealing process tried in our case.

3-3 The sample of $x=1.0$

As seen in Fig.1 C(c) ~ (f), the Mössbauer spectra observed for the samples of $x=1.0$ annealed at 805 K($=T_x$) are very complicated. In the X-ray diffraction patterns of the sample-1.0(805 K, 2 h) and the sample-1.0(805 K, 20 h), a sharp line at the scattering angle $2\theta \sim 57.5^\circ$ corresponding to both the bcc Fe metal and the compound Fe_2B , and several weak lines corresponding to the compound Fe_2B are observed. No lines corresponding to Si compound exist. It is probable that Si atoms in these samples have dissolved in a precipitated bcc Fe metal similarly to the case of the sample of $x=0.5$.

Therefore, such complicated Mössbauer spectra as in Fig.1 C(f) may be decomposed into the sub-spectra corresponding to the metal Fe-Si including Si atoms and those corresponding to the inter-metallic compound Fe_2B . After the sub-spectra of Fe_2B are subtracted from the observed ones, the residual consists of five sets of sub-spectra of the metal Fe-Si by referring to the values reported in the paper[13]. The positions of the absorption lines of this residual spectra are indicated by the solid bars in Fig.1 C(f). The five sets of sub-spectra are considered to be the spectra corresponding to the Fe atoms which are surrounded by the different number of Si atoms in the metal. H.N.Ok et al. have decomposed the spectra of crystalline phase precipitated in the crystallization process of an amorphous alloy $Fe_{74.5}Si_{14.5}B_{10.4}$, which has a similar composition to our sample, into the spectra corresponding to an Fe_2B phase and the five sets of Fe-Si phase[13]. Their result agrees well with ours.

3-4 Completely crystallized samples

So far, the crystallization of the samples annealed at temperatures near T_x was described for various annealing times up to 22 h. In order to examine whether the crystalline phases precipitated in the samples annealed at temperatures near T_x for ~22h are different from those annealed at higher temperatures or not, we annealed the samples at higher temperatures than T_x by ~100 K for ~22 h. Figures 4 and 5 show the Mössbauer spectra and the X-ray diffraction patterns of these samples, respectively. By comparing the spectra in Fig.4 with the respective spectra in Fig.1 (f), we notice that the Mössbauer spectra are similar to each other except for a small difference in the intensity ratios. The lines of the X-ray diffraction patterns for the three kinds of samples in Fig.5 become more sharp as compared with those in Fig. 2(f). This fact means that the precipitated crystals grow up in size by the annealing at higher temperature.

By comparing Fig.5 (a) with Fig.2 A(f), the X-ray diffraction patterns of the sample of $x=0.06$, it is worth noticing that the relative intensity corresponding to the compound with a hcp structure (marked by short arrows) decreases and that with a fcc structure (marked by long arrows) increases, with increasing T_a .

This fact was confirmed in the following way: as seen in Fig.5 (a), the (100) and (101) reflections for the hcp Co appear as isolated lines. On the other hand, the (111) and (200) reflections for the fcc Co superimpose on one of the reflections for Co_2Si and one of the reflections for Co_2B . In order to examine isolated reflections at high angles for the fcc Co, we took the back reflection X-ray photographs. The photographs of the sample-0.06(873 K, 22 h) showed clearly the isolated reflections (222) and (311) corresponding to the fcc structure. These reflections became more sharp and intense compared to those of the sample-0.06(799 K, 22 h). This fact means that a part of the hcp structure changes to the fcc structure when T_a increases from 799 K to 873 K. Such a change in the structure of the metallic phase in the sample of $x=0.06$ is considered to be related to the increase of H_{hf} in this phase as T_a is increased.

In Table 2, the precipitated phases in the crystallization process for the three kinds of samples and their Mössbauer parameters are listed. As seen in Table 2, there is only one kind of H_{hf} in the precipitated metallic phase for the samples of $x=0.06$ and $x=0.5$. On the other hand, there are five kinds of H_{hf} for the sample of $x=1.0$. According to Stearns[11], the value of H_{hf} in an Fe-Si alloy depends on the numbers of Si atoms surrounding Fe as the nearest neighbors. The precipitated metallic phase in the sample of $x=0.5$ shows the bcc structure similar to the case of the sample of $x=1.0$, but the value of H_{hf} is one kind. Such one-kindness of H_{hf} for the sample of $x=0.5$ seems to originate in the Co atoms which exist as the nearest neighbors.

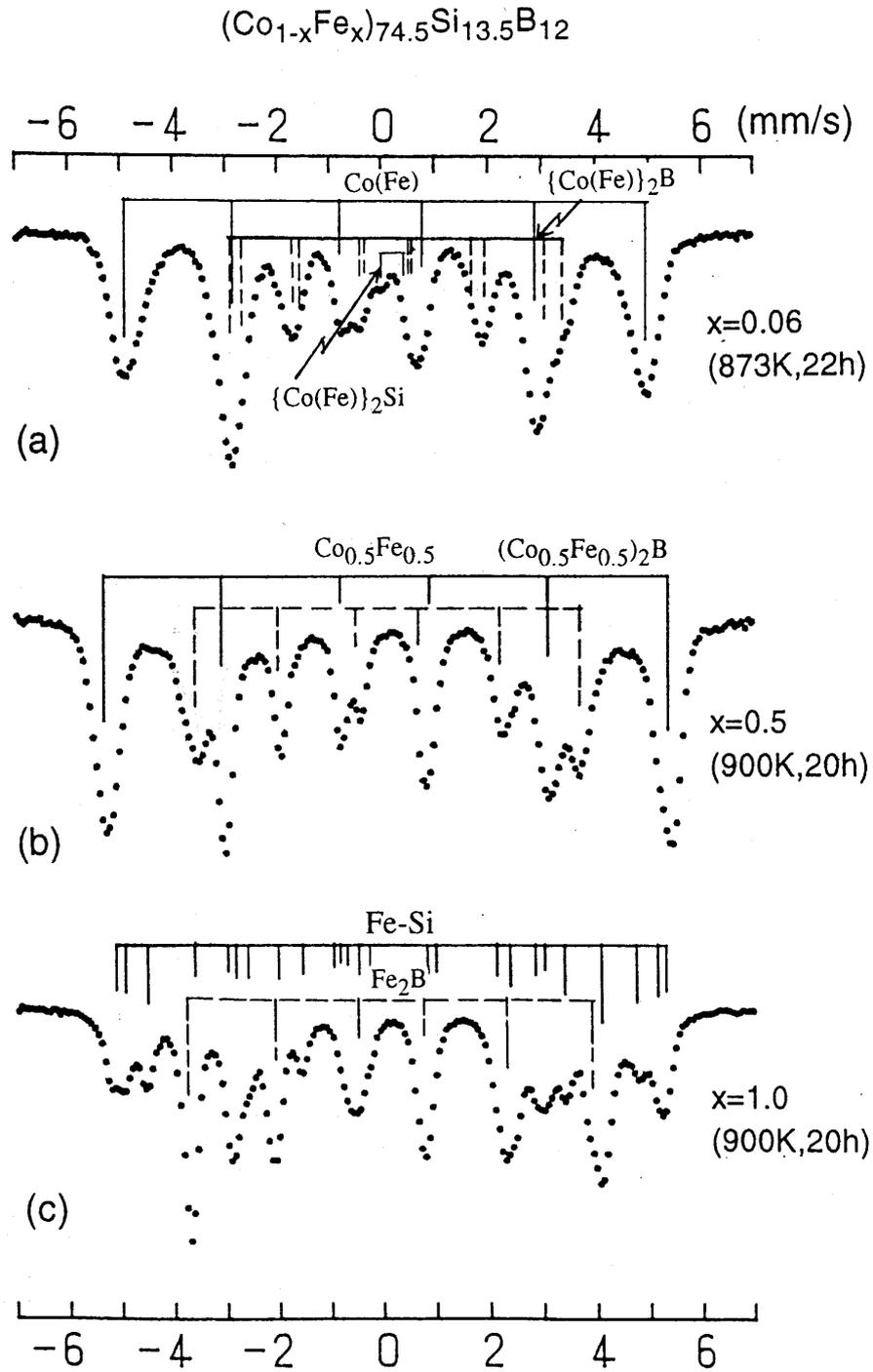


Fig.4. The Mössbauer spectra of completely crystallized samples : (a)-0.06(873 K, 22 h) (b)-0.5(900 K, 20 h) (c)-1.0(900 K, 20 h).

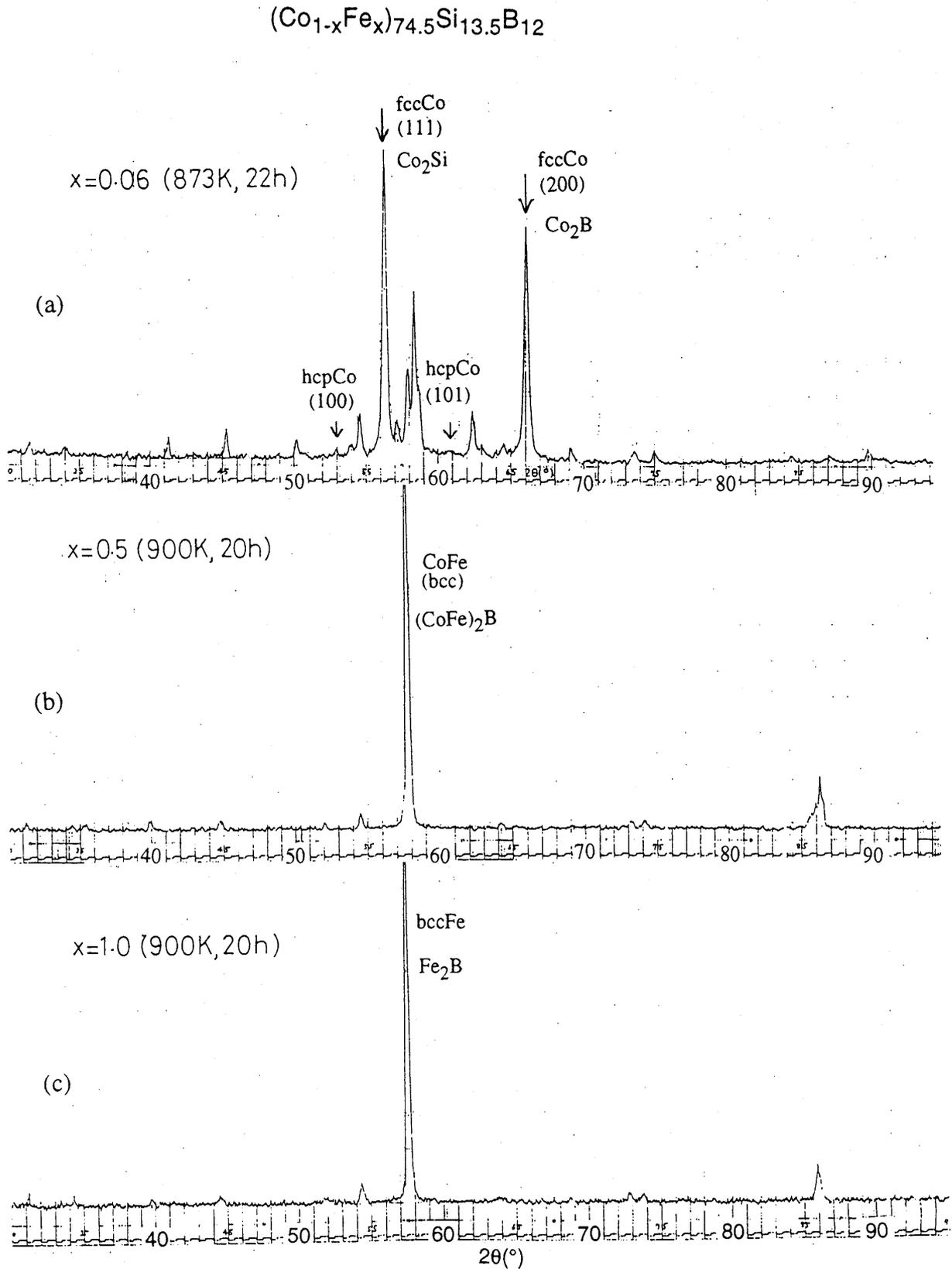


Fig. 5. The X-ray diffraction patterns of completely crystallized samples : (a)-0.06(873 K, 22 h) (b)-0.5(900 K, 20 h) (c)-1.0(900 K, 20 h).

Table 2. The precipitated phases in the crystallization process in the three samples and their Mössbauer parameters.

sample x (T _a , t _a)	crystals precipitated by heat-treatment		
0.06 (873 K, 22 h)	Co _{0.94} Fe _{0.06} , H _{hf} =306 kOe ΔE=0	(Co _{0.94} Fe _{0.06}) ₂ B, H _{hf} =194 kOe 178 kOe ΔE=0.095 mm/s 0.03 mm/s	(Co _{0.94} Fe _{0.06}) ₂ Si H _{hf} =0 ΔE=0.5 mm/s
0.5 (900 K, 20 h)	Co _{0.5} Fe _{0.5} , H _{hf} =332 kOe ΔE=0	(Co _{0.5} Fe _{0.5}) ₂ B H _{hf} =226 kOe ΔE=-0.05 mm/s	
1.0 (900 K, 20 h)	Fe-Si, H _{hf} =323.5 kOe 314 kOe 290 kOe 241 kOe 195 kOe all ΔE=0	Fe ₂ B H _{hf} =237 kOe ΔE=0.03 mm/s	

4 Conclusions

The present work clarifies the following points about the crystallization process of the amorphous alloys (Co_{1-x}Fe_x)_{74.5}Si_{13.5}B₁₂ of x=0.06, 0.5 and 1.0. The characteristics common to the crystallization process of three kinds of samples are as follows. (1) At the first stage of the crystallization, a metallic phase precipitates and then a metalloid phase follows. (2) The precipitated metallic phase contains a small amount of Si atoms, not B atoms.

Differences among the crystallization process of three kinds of samples are as follows.

(1) For the sample of x=0.06, the values of H_{hf} of the precipitated metallic phase depend on the annealing time t_a and the annealing temperature T_a. At the initial stage of the crystallization, the value of H_{hf} in the metallic phase is smaller than that in the metal Co_{0.94}Fe_{0.06}. At the middle stage of the crystallization, the (Co_{0.94}Fe_{0.06})₂Si precipitates and the values of H_{hf} in the metallic phase increase. This fact means that Si atoms in the metallic phase are expended for the formation of (Co_{0.94}Fe_{0.06})₂Si, so that, Si concentration in the metallic phase decreases. In contrast, for the samples of x=0.5 and x=1.0, the values of H_{hf} in the precipitated metallic phase are smaller than those in a Co_{0.5}Fe_{0.5} alloy and a pure Fe metal, respectively, and keep constant during the heat-treatments. The Si compounds do not precipitate. This fact means that the Si atoms dissolve in the metallic phase and stay in the phase during the heat-treatments tried.

(2) There exist five kinds of H_{hf} in the metallic phase including some amounts of Si atoms for the sample of x=1.0. On the other hand, there exists only one kind of H_{hf} in the metallic phase for the samples of x=0.5 and x=0.06.

As described above, the characteristics of the crystallization process for these amorphous alloys were able to be caught only by a combination of the Mössbauer and X-ray diffraction measurements.

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References

- [1] Kikuchi, M., Fujimori, H., Obi, Y. and Masumoto, T. : *Jpn.J.Appl.Phys.* **14** (1975) 1077.
 [2] Shiiki, K., Watanabe, T. and Kudo, M. : *J.Appl.Phys.* **50** (1979) 5419.
 [3] Wolny, J., Zajac, W. and Calka, A. : *Nuclear Instruments and Methods* **199** (1982) 179.
 [4] Morimoto, S., Torikai, E., Ito, A., Shiiki, K. and Kudo, M. : *Proc.4th Int.Conf.on Rapidly Quenched Metals* (Sendai, 1981) 695.
 [5] Torikai, E., Ito, A., Morimoto, S., Shiiki, K. and Kudo, M. : *Proc.4th Int.Conf.on Rapidly Quenched Metals* (Sendai, 1981) 1129.
 [6] Ito, A., Torikai, E., Morimoto, S., Shiiki, K. and Kudo, M. : *Jpn.J.Appl.Phys.* **20** (1981) 797.
 [7] Morimoto, S. and Ito, A. : *Nuclear. Instrum. Methods* **B76** (1993) 68.
 [8] Morimoto, S. and Ito, A. : *Hyperfine Interactions* **41** (1988) 451.
 [9] Morimoto, S., Torikai, E., Ito, A., Shiiki, K. and Kudo, M. : *J.Magn. Magn.Mater.* **31-34** (1983) 1519.
 [10] Nasu, S., Murakami, Y., Nakamura, Y. and Shinjo, T. : *Scripta Metallurgica* **2** (1968) 647.
 [11] Stearns, M. B. : *Phys.Rev.* **147** (1966) 439.
 [12] Vincze, I., Campbell, I.A. and Meyer, A. J. : *Solid State Commun.* **15** (1974) 1495.
 [13] Ok, H. N., Baek, K. S. and Kim, C. S. : *Phys.Rev.B* **24** (1981) 6600.
 [14] Onozuka, T., Yamaguchi, S., Hirabayashi, M. and Wakiyama, T. : *J.Phys.Soc.Jpn.* **33** (1972) 857.

Appendix

In order to identify the precipitated crystalline phase during the heat treatment in the sample $(\text{Co}_{1-x}\text{Fe}_x)_{74.5}\text{Si}_{13.5}\text{B}_{12}$ of $x=0.06$, we prepared the compounds $\{\text{Co}(\text{Fe})\}_2\text{B}$, $\{\text{Co}(\text{Fe})\}_3\text{B}$ and $\{\text{Co}(\text{Fe})\}_2\text{Si}$ containing about 1 atomic % Fe (partially enriched with ^{57}Fe), and observed the Mössbauer spectra and the X-ray diffraction patterns. The Mössbauer spectra for these compounds observed at room temperature are shown in Fig.6.

Figure 6(a) shows the spectra observed for $\{\text{Co}(\text{Fe})\}_2\text{B}$, which can be decomposed into two sets of the six-line-patterns with the equal intensity ratio indicated by the solid and broken bars[8]. The values of H_{hf} and quadrupole splittings ΔE are listed at the top column in Table 3, in which we assume that $H_{\text{hf}} // V_{\text{zz}}$ (z indicates the tetragonal axis of the crystal Co_2B).

Figure.6(b) shows the spectra observed for $\{\text{Co}(\text{Fe})\}_3\text{B}$, which also consist of two sets of the six-line-patterns. The positions of absorption lines are indicated by the solid and the broken bars. The values of the Mössbauer parameters of two sets are listed at the middle column in Table 3. In Fig.6(b), we notice the small outermost absorption lines. The value of H_{hf} obtained from the outermost position of the absorption lines is estimated to be 319 kOe, which agrees well with that in the hcp $\text{Co}(\text{Fe})$ (see 3-1). The corresponding X-ray diffraction pattern supports that the $\text{Co}(\text{Fe})$ phase has not the fcc structure but the hcp structure.

Figure 6(c) shows the Mössbauer spectrum observed for the compound $\{\text{Co}(\text{Fe})\}_2\text{Si}$, which shows an asymmetric doublet. This spectrum is decomposed into a pair of doublets having the values of the Mössbauer parameter listed at the lowest column in Table 3. The Mössbauer spectrum for a compound $\{\text{Co}(\text{Fe})\}_2\text{Si}$ in which Co atoms is substituted for Fe atoms has not been observed before our experiment because a compound Fe_2Si is unstable as described in 3-1.

Table 3. The Mössbauer parameters obtained for three compounds.

compound	$H_{\text{hf}}(\text{kOe})$	$\Delta E(\text{mm/s})$
$\{\text{Co}(\text{Fe})\}_2\text{B}$	195	0.07
	177	0.03
$\{\text{Co}(\text{Fe})\}_3\text{B}$	262	0.16
	216.5	0.065
$\{\text{Co}(\text{Fe})\}_2\text{Si}$	0	0.54
	0	0.31

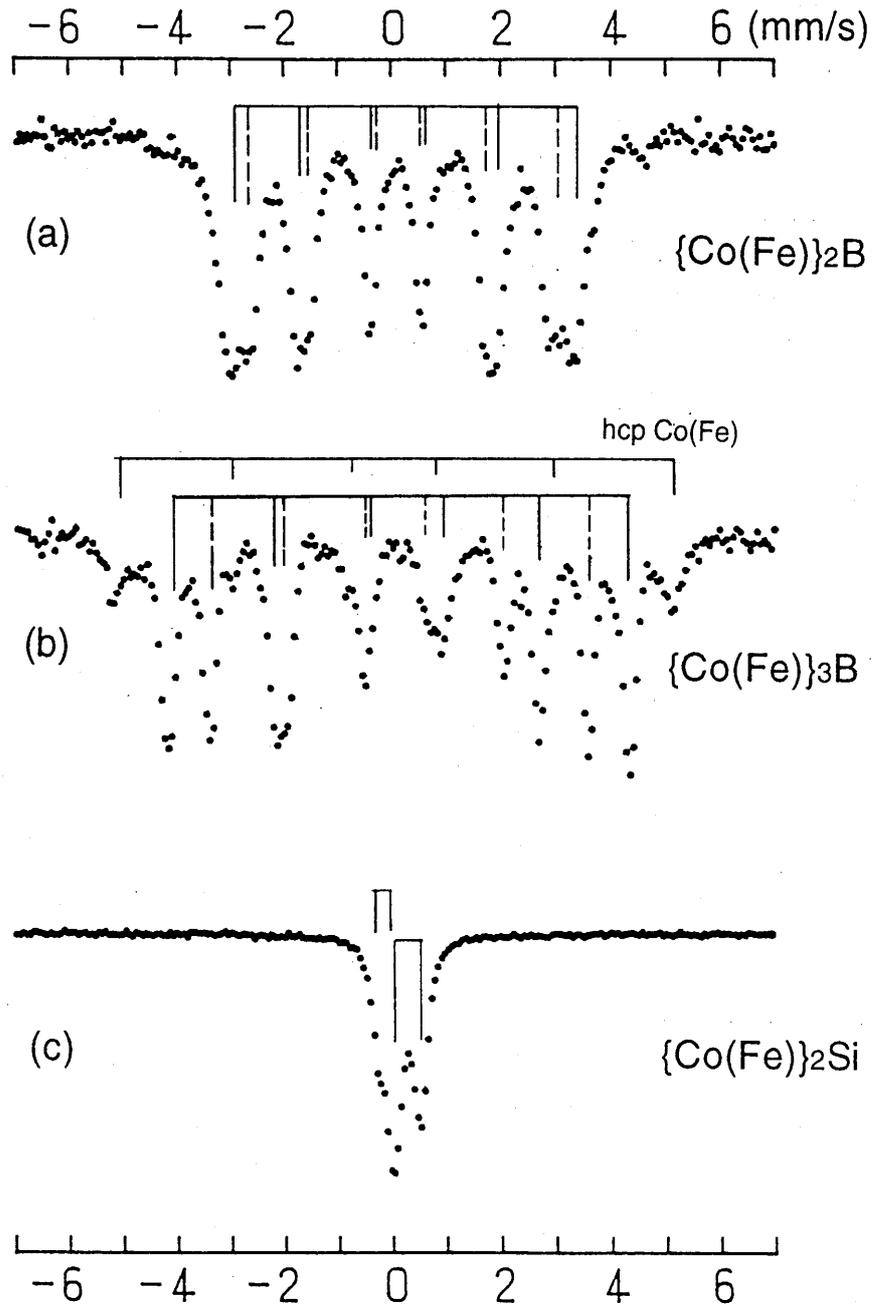


Fig. 6. The Mössbauer spectra of compounds (a) $\{Co(Fe)\}_2B$, (b) $\{Co(Fe)\}_3B$ and (c) $\{Co(Fe)\}_2Si$.