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Mössbauer study of products of low energy milled $\text{Fe}_{30}\text{Si}_{70}$

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Abstract

Measurements of x-ray diffraction pattern and Mössbauer spectra show that $\beta\text{-FeSi}_2$ is produced in an $\text{Fe}_{30}\text{Si}_{70}$ powder sample by low energy ball milling, and its proportion increases step by step as the milling time increases until the milling time reaches 60 h; after that this solid reaction reaches saturation. Within the final products, there is over 90% $\beta\text{-FeSi}_2$ and a little Fe and Si remnants. The remnant Fe exists in two forms: one is powder and the second is enveloped by $\beta\text{-FeSi}_2$. When using hydrochloric acid to treat the as-milled sample, the first form of Fe is removed but the second form of Fe still remains. When the sample is annealed at 600 °C, the proportion of $\beta\text{-FeSi}_2$ is close to 99% in the final products.

1. Introduction

$\beta\text{-FeSi}_2$ is a useful semiconductor material with a direct gap of 0.87 eV [1] and Hall coefficient depending on the temperature [2, 3], so that the research of its structure, properties and productivity is of great interest.

There are many ways to produce $\beta\text{-FeSi}_2$, such as ion implantation [4–9], pulsed laser deposition [10] and chemical vapour deposition [11] in which $\beta\text{-FeSi}_2$ thin film can be produced on Si substrate.

The method based on the classical melting process to make $\beta\text{-FeSi}_2$ does not yield a homogeneous $\beta\text{-FeSi}_2$ bulk product directly because of the eutectic (1212 °C) and peritectoid (982 °C) transformations. A very long period of annealing at nearly 982 °C is required after the solidification of the $\alpha\text{-FeSi}_2$ and $\varepsilon\text{-FeSi}$ eutectic structure. Mechanical ball-milling is an advanced method to synthesize iron disilicide.

The energy states of $\beta\text{-FeSi}_2$, $\alpha\text{-FeSi}_2$ and $\gamma\text{-FeSi}_2$ are calculated [12] showing that $\beta\text{-FeSi}_2$ has a lower energy state than $\alpha\text{-FeSi}_2$ and $\gamma\text{-FeSi}_2$. When ball milling the power with same contents, the composition of end products is in correlation with the rotation speed (shock energy) and ball milling time [13, 14]. The shock energy is proportional to $\Omega^2 R$ (Ω is the rotation speed; R is the rotation radius). When ball milling for 3 hours, with Ω as high

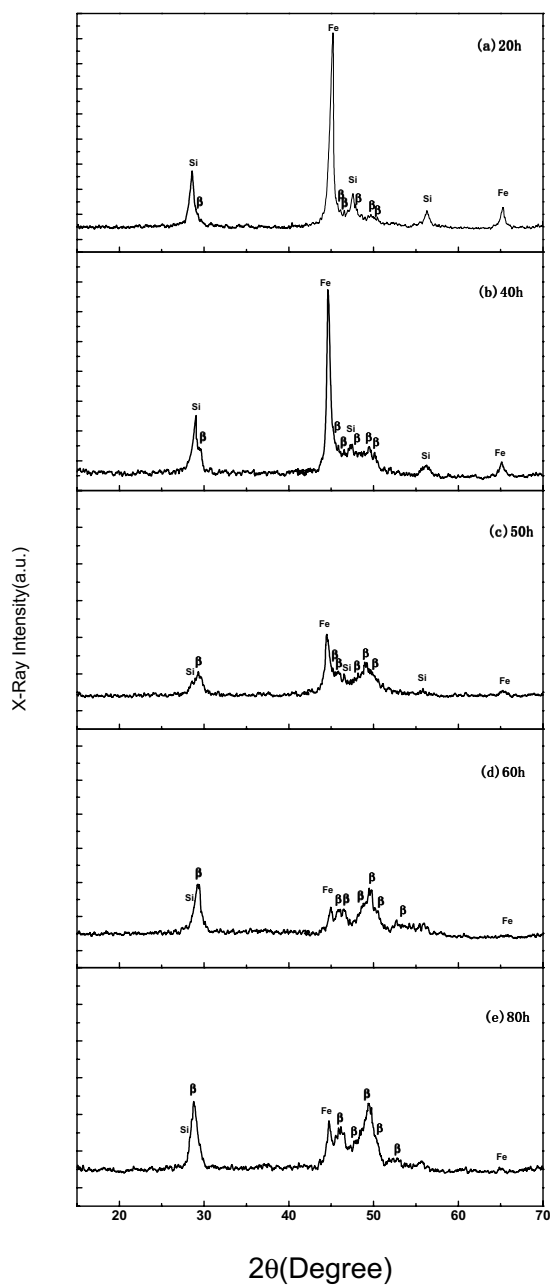


Figure 1. X-ray diffraction pattern of $\text{Fe}_{0.3}\text{Si}_{0.7}$ milled for t hours (a) $t = 20$ h (b) $t = 40$ h (c) $t = 50$ h (d) $t = 60$ h (e) $t = 80$ h.

as 700 r min^{-1} and $R 6.75 \text{ cm}$, which means $\Omega^2 R$ is equal to 362.4 m s^{-2} , the end product is very complex, including $\beta\text{-FeSi}_2$, $\alpha\text{-FeSi}_2$, $\varepsilon\text{-FeSi}$, Fe, Si and some $\text{Fe}_x\text{Si}_{1-x}$ amorphous phases [13]. However, when ball milling for 80 hours, with Ω as low as 200 r min^{-1} and $R 10.5 \text{ cm}$, which means $\Omega^2 R$ is equal to 45.9 m s^{-2} , the end-product consists of only three

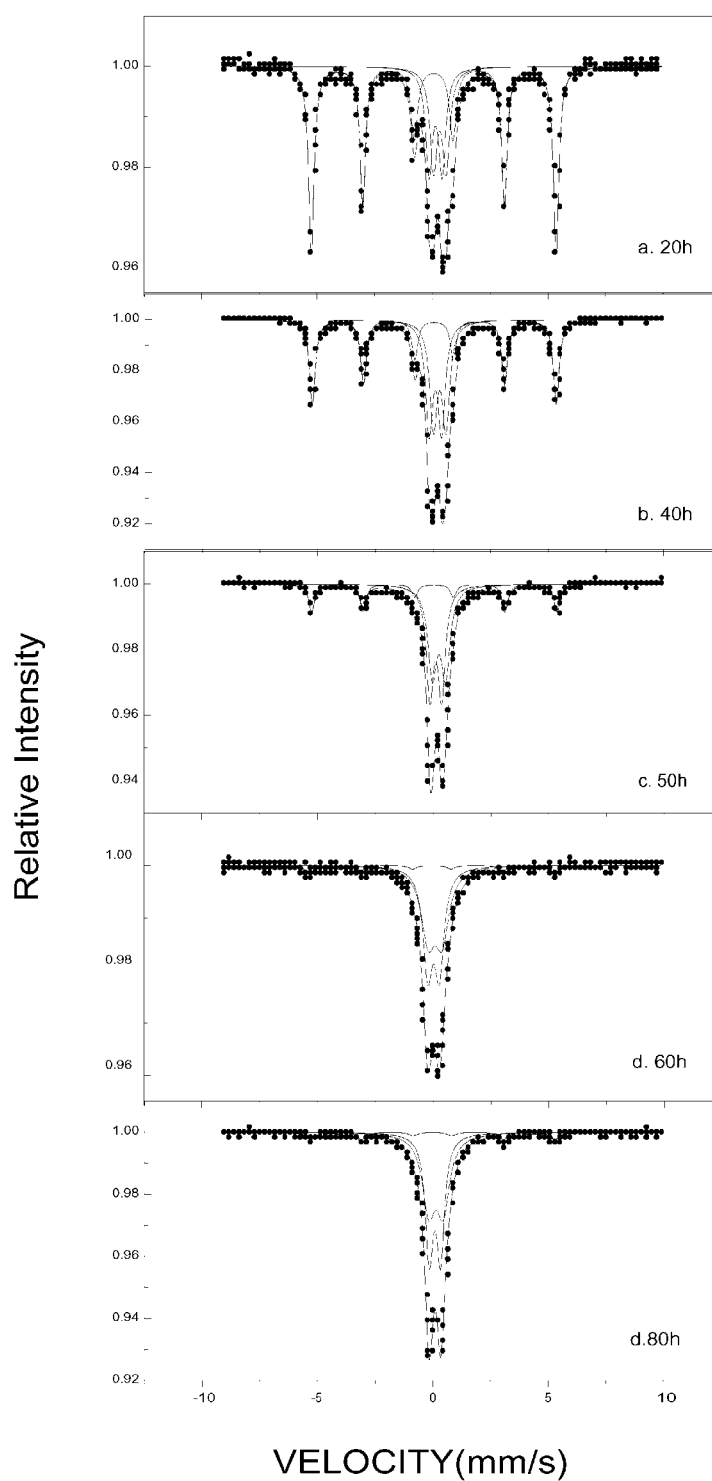


Figure 2. RT experimental Mössbauer spectra of $\text{Fe}_{0.3}\text{Si}_{0.7}$ milled for t hours (a) $t = 20$ h (b) $t = 40$ h (c) $t = 50$ h (d) $t = 60$ h (e) $t = 80$ h. Dots: experiment data, lines: sub-spectra.

Table 1. Mössbauer parameters of as-milled samples (20, 40, 50, 60, 80 h).

Milling								
Time (h)	Phase	IS (mm s ⁻¹)	QS (mm s ⁻¹)	H (kOe)	Area (%)	HWH (mm s ⁻¹)		
20	α -Fe	0.05	0.01	330.1	61.6	0.14	0.14	0.17
	β -FeSi ₂	0.32	0.54		19.2	0.19		
		0.14	0.57		19.2	0.18		
40	α -Fe	0.05	0.01	329.2	41.2	0.15	0.15	0.15
	β -FeSi ₂	0.29	0.54		29.4	0.20		
		0.11	0.54		29.4	0.19		
50	α -Fe	0.05	0.01	330.1	20.0	0.15	0.15	0.15
	β -FeSi ₂	0.12	0.51		40.0	0.19		
		0.25	0.57		40.0	0.23		
60	α -Fe	-0.05	0.00	330.1	6.8	0.23	0.22	0.21
	β -FeSi ₂	0.02	0.50		46.6	0.24		
		0.09	0.60		46.6	0.36		
80	α -Fe	0.00	0.02	329.8	7.4	0.23	0.22	0.21
	β -FeSi ₂	0.10	0.49		46.3	0.20		
		0.14	0.62		46.3	0.33		

Table 2. Mössbauer parameters of Fe₃Si₇(80 h) after HCl treatment.

Condition	Phase	IS (mm s ⁻¹)	QS (mm s ⁻¹)	H (kOe)	Area (%)	HWH (mm s ⁻¹)		
No annealing	α -Fe	-0.01	0.04	330.1	4.4	0.23	0.22	0.21
	β -FeSi ₂	0.07	0.51		47.8	0.25		
		0.13	0.58		47.8	0.35		
Annealing at 600 °C	ϵ -FeSi	0.74	0.35		1.2		0.12	
	β -FeSi ₂	0.05	0.43		49.4	0.18		
		-0.05	0.45		49.4	0.18		
Annealing at 800 °C	ϵ -FeSi	0.35	0.31		8.0		0.13	
	β -FeSi ₂	0.23	0.45		46.0	0.15		
		0.39	0.48		46.0	0.18		
Annealing at 950 °C	ϵ -FeSi	0.36	0.47		14.2		0.15	
	β -FeSi ₂	0.48	0.50		19.6	0.16		
		0.58	0.52		19.6	0.15		
		α -FeSi ₂	0.71		0.58	46.6	0.21	

phases: β -FeSi₂, Fe and Si. So in contrast with 700 r min⁻¹, the latter is considered as low energy ball milling. The experiments will be discussed later in detail.

2. Preparation of samples

The purities of Fe and Si power are better than 99.8%, and the mesh size is 200. The Fe and Si powder were mixed in 3:7 atomic proportions and the mixture was placed into a hardened steel vial with steel balls (50 balls with diameter 1 cm and 20 balls with diameter 0.5 cm). All

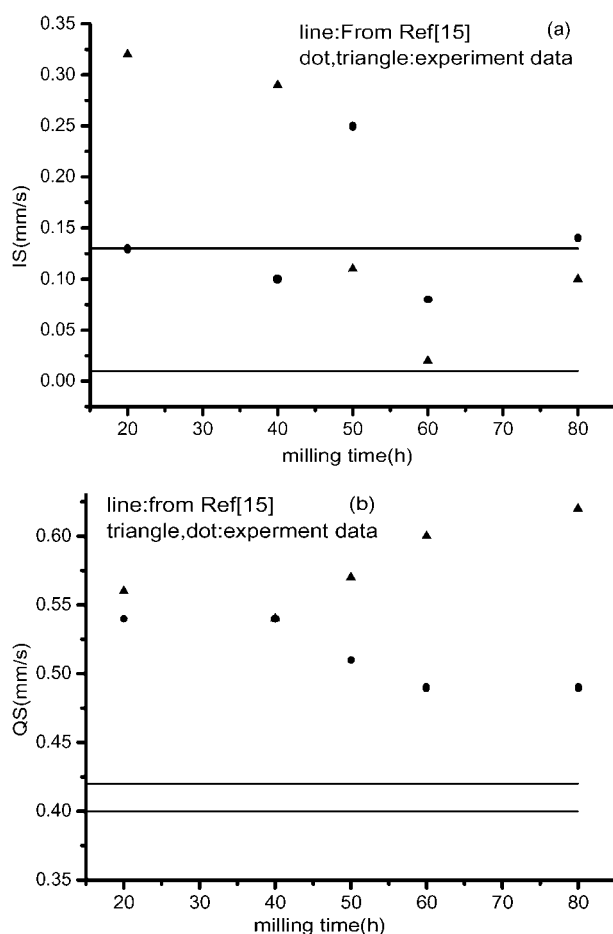


Figure 3. Isomer shift (IS) and quadruple splitting (QS) of β -FeSi₂ in Fe₃₀Si₇₀ samples milled for different times.

samples were milled separately with the rotation at 200 r min^{-1} and rotation radius 10.5 cm. The mass ratio of the balls to the mixture was 20 to 1. The vial was sealed under an argon atmosphere to prevent oxidation of the samples. The samples were milled for 20, 40, 50, 60 and 80 h separately. The samples are denoted Fe₃₀Si₇₀(20 h), Fe₃₀Si₇₀(40 h), Fe₃₀Si₇₀(50 h), Fe₃₀Si₇₀(60 h) and Fe₃₀Si₇₀(80 h).

The inductively coupled plasma–atomic emission spectroscopy (ICP-AES) was used to study the proportion of impurities (mainly Ni and Cr) produced in the ball-milling procedure. In the Fe₃₀Si₇₀(60 h) sample, the proportion of Cr and Ni is only 0.23 wt% and 0.13 wt%, respectively, and the ratio of Fe:Si does not change.

3. Experiments and results

The samples were measured with a Rigaku-Max- γ A rotation target x-ray diffractometer (Cu K α ; $\lambda = 0.154 \text{ nm}$). Mössbauer spectra were recorded using an MS-500 Mössbauer spectrometer and ⁵⁷Co/(Pd) radiation source, 25 mCi, at room temperature (RT).

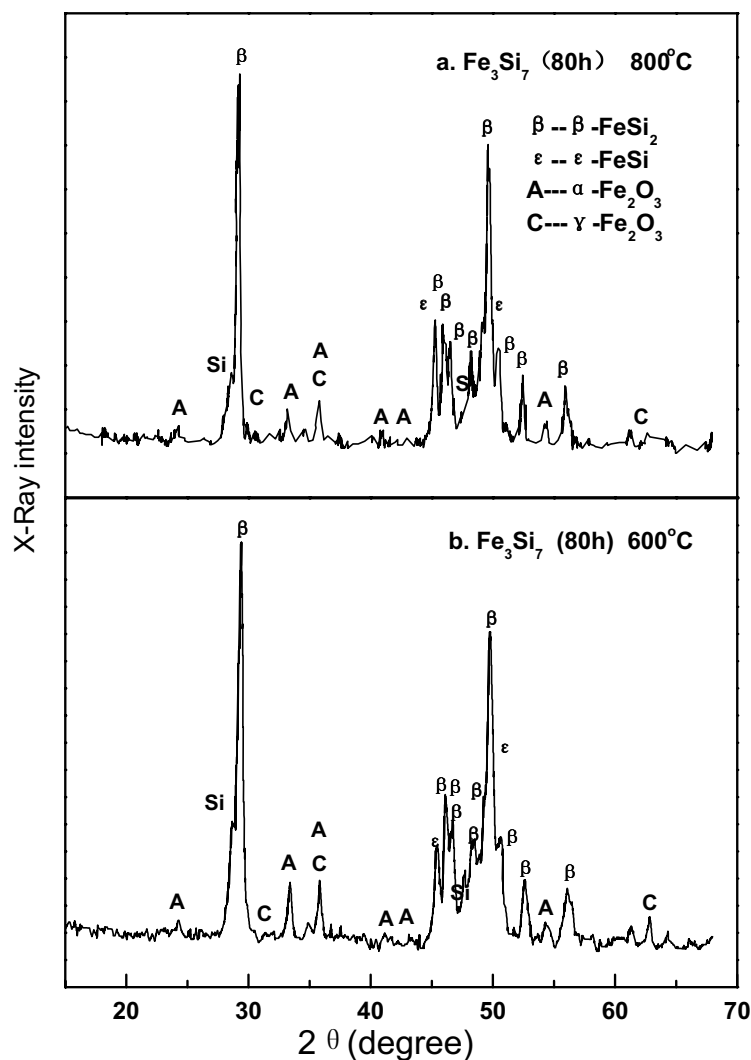


Figure 4. X-ray diffraction pattern of Fe₃₀Si₇₀ (80 h) sample annealing in a Muffle furnace for 1 h at (a) 800 °C (b) 600 °C.

3.1. As-milled samples

The x-ray diffraction (XRD) patterns of the as-milled samples are represented in figure 1. It can be found that after being milled for 20 h, the compound β -FeSi₂ appears clearly and the intensities of its peaks increase quickly as milling time increases; at the same time the intensity of crystalline Fe and Si peaks in the same samples decreases rapidly with increasing milling time. Neither Fe nor Si are exhausted however. At $2\theta = 44.7^\circ$, the Fe peak is still observed.

Figure 2 represents the RT experimental Mössbauer spectra as well as their fitting results (dots: experimental data). The experimental spectra were fitted by the Gauss–Newton method. The ISs are referred to α -Fe. Apparently the sextet is from α -Fe and the doublet is from β -FeSi₂.

β -FeSi₂ crystal is an orthorhombic structure with a primitive cell containing as many as

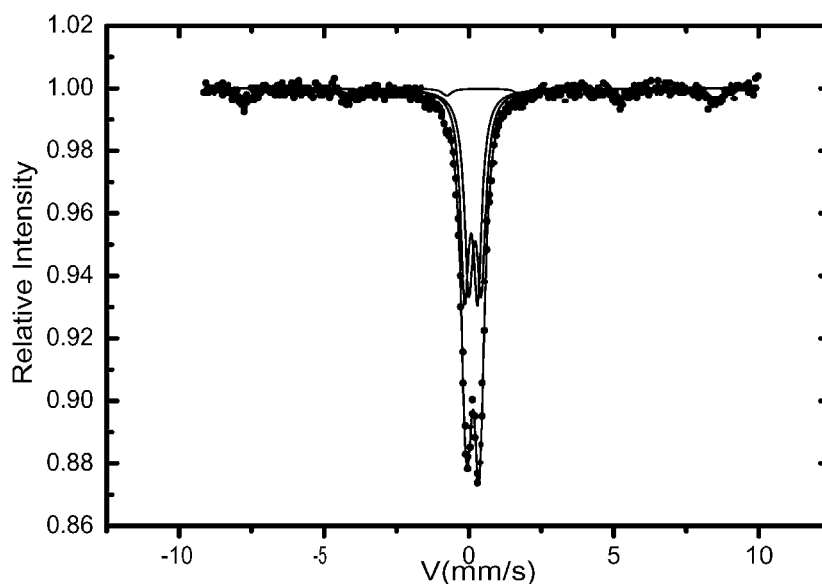


Figure 5. Mössbauer spectra of Fe₃Si₇ (80 h) annealed at 600 °C (without HCl treatment).

48 atoms. The iron atoms are located in two different Fe sites (Fe1 and Fe2), both surrounded by eight Si atoms forming distorted cubes. Hence the Mössbauer spectra of β -FeSi₂ is fitted by two doublet sub-spectra, only limiting the area ratio of the two doublets to 1:1 according to the atom ratio of Fe1 and Fe2. Mössbauer fitting parameters are shown in table 1. From the area ratio of sextet and doublets in table 1, the proportion of β -FeSi₂ increases with the milling time and that of α -Fe decreases rapidly; this is in agreement with the results of XRD. At 60 h the proportion of β -FeSi₂ is more than 90% and the proportion of α -Fe is less than 10%. After that, the proportion of β -FeSi₂ does not rise obviously with milling time, which means the solid reaction between Fe and Si reaches saturation.

Figure 3 describes the relationship of isomer shift (IS) and quadrupole splitting (QS) of β -FeSi₂ with the milling time. Wandji *et al* reported that a vapour deposited β -FeSi₂ single crystal showed a QS of 0.42 and 0.40 mm s⁻¹ [15], which are also plotted in figure 3. The average QS of as-milled samples changes between 0.54 and 0.56 mm s⁻¹.

3.2. Annealed sample in a muffle furnace

From the above results, the Fe₃₀Si₇₀(80 h) sample is taken as the final product, hence annealing the Fe₃₀Si₇₀(80 h) sample in a muffle furnace for 1 hour at 600 °C and 800 °C respectively.

XRD patterns of these samples are represented in figure 4(a) (600 °C) and figure 4(b) (800 °C), in which ϵ -FeSi apparently exists in addition to Fe₂O₃.

Figure 5 shows the Mössbauer spectra of Fe₃Si₇(80 h) annealed at 600 °C, in which the wide sextet (with $H = 497$ kOe and $QS = -0.183$ mm s⁻¹) is clearly from Fe₂O₃, that is apparently produced from Fe and O₂ when the as-milled sample is annealed.

3.3. Treating as-milled sample with HCl then annealing in a muffle furnace

In order to prevent the remnant α -Fe from reacting with O₂ during thermal treatment, hydrochloric acid (5% HCl) was used to remove the α -Fe in this sample. These 'HCl treated

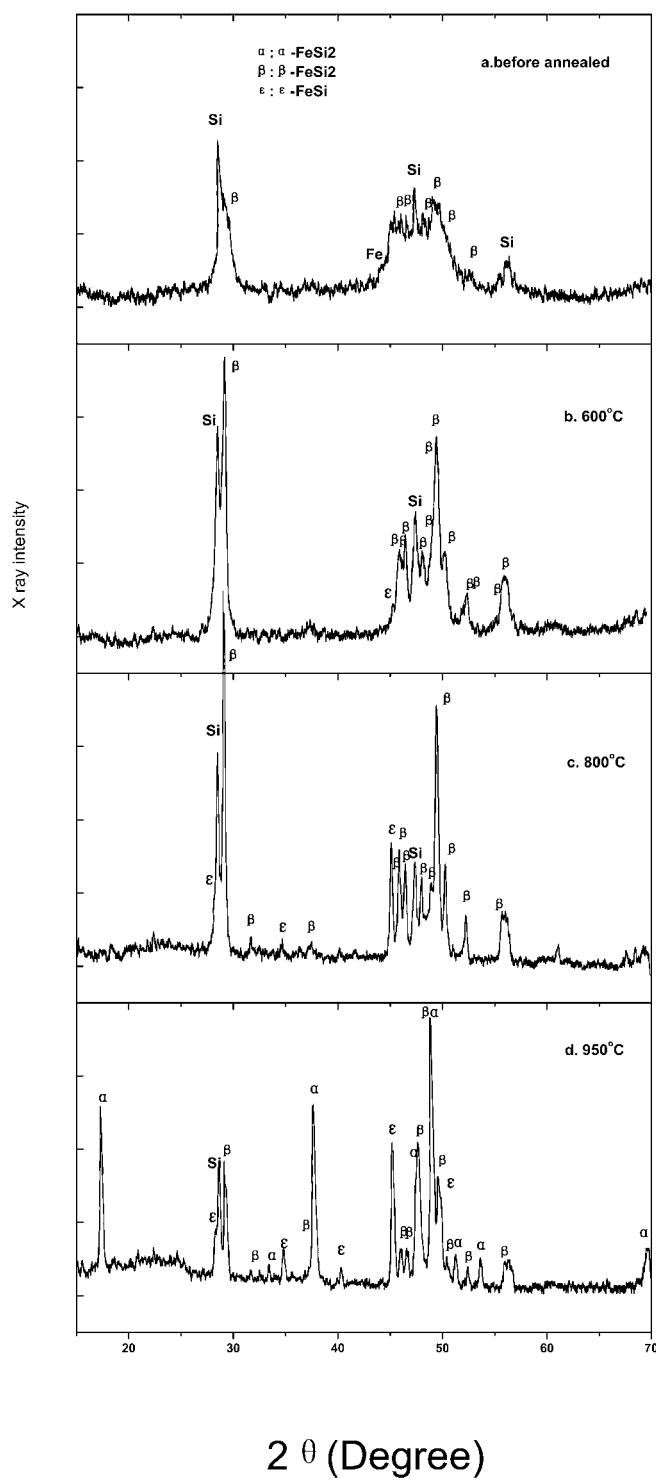


Figure 6. X-ray diffraction pattern of the HCl treated $\text{Fe}_{0.3}\text{Si}_{0.7}$ samples (a) no annealing (b) 600 °C (c) 800 °C (d)950 °C.

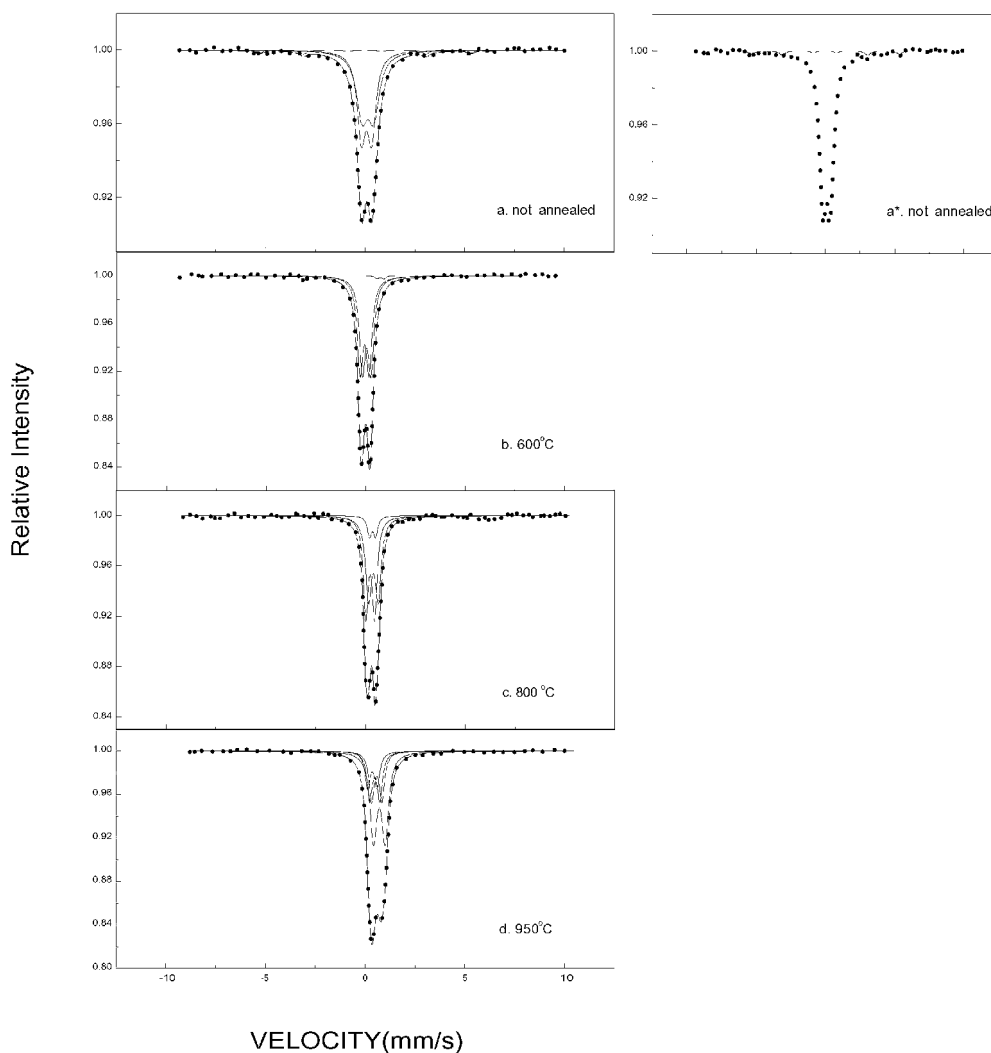


Figure 7. Mössbauer spectra of HCl treated-annealing sample of Fe₃Si₇ (80 h) at RT (a), (a*) no annealing (a weak sextet of α -Fe is shown in a*). (b) 600 °C (c) 800 °C (d) 950 °C. Dots: experimental data, lines: sub-spectra.

samples' are annealed in a muffle furnace for 1 h at 600 °C, 800 °C and 950 °C separately.

Figure 6(a) shows the XRD pattern of the 'HCl treated sample' in which a weak peak of α -Fe could be observed (at $2\theta = 44.7^\circ$), of course the peaks of β -FeSi₂ and Si are clear. Figures 6(b)–(d) show the XRD patterns of the samples for 600 °C, 800 °C and 950 °C annealings separately, in which no α -Fe peaks are observed. In figure 6(b) (600 °C) the main peak of ϵ -FeSi is very weak, but in figure 6(c) (800 °C) the peaks of ϵ -FeSi are clearly seen. Especially, in figure 6(d) (950 °C) a series of peaks of α -FeSi₂ are observed.

Figure 7 shows the experimental Mössbauer spectra of the HCl treating–annealing sample at room temperature as well as fitted sub-spectra (the fitting parameters are listed in table 2). Figures 7(a) and 7(a*) (no annealing) show one weak sextet of α -Fe with proportion 4% and two doublets of β -FeSi₂. Figures 7(b) (annealing at 600 °C) and 7(c) (800 °C) show three

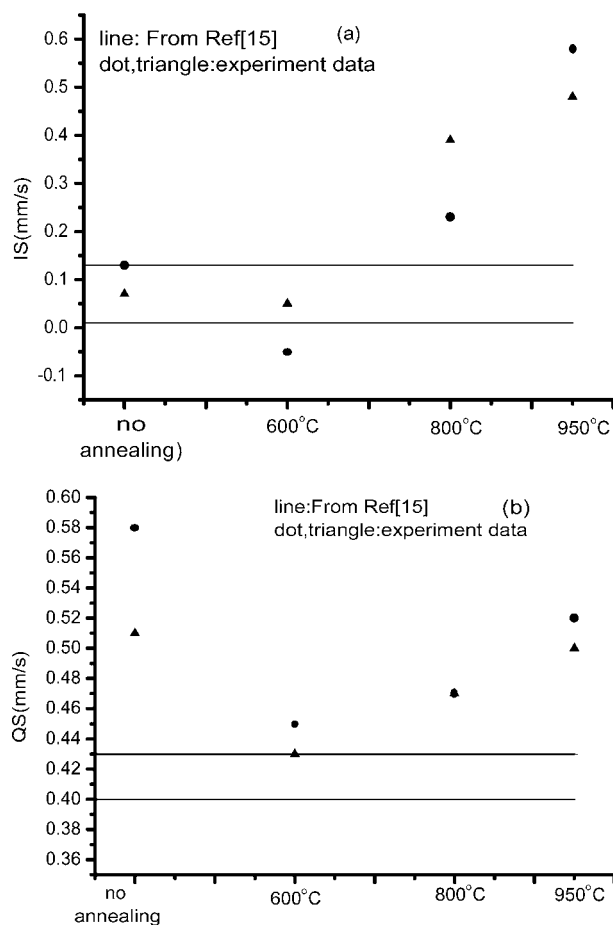


Figure 8. Isomer shift and quadruple splitting of β -FeSi₂ in sample Fe₃₀Si₇₀ (80 h). (a) no annealing (b) annealing at 600 °C (c) at 800 °C (d) at 950 °C.

doublets (two for β -FeSi₂ and one for ε -FeSi—distorted NaCl structure). In figure 7(d) one more doublet of α -FeSi₂, tetragonal symmetry, appears.

Figure 8 shows the experimental IS and QS of β -FeSi₂ and that from [15]. It can be seen that the experimental value of QS of β -FeSi₂ in the samples annealed at 600 °C and at 800 °C is 0.43–0.47 mm s⁻¹, which is close to 0.40–0.42 mm s⁻¹ [15]. In addition, the proportion of β -FeSi₂ in the sample annealed at 600 °C is close to 99%, which is noticeable.

4. Discussion

The β -FeSi₂ is produced after ball milling of Fe₃₀Si₇₀, although the ratio of Fe:Si (3:7) is smaller than that in β -FeSi₂ (1:2), remnant α -Fe still exists with a proportion about 7% (less than 10%) in the sample. From the XRD patterns and Mössbauer spectra, it can be seen that in the HCl treatment sample the α -Fe still exists, with the proportion of about 4%, which shows Fe could not be removed completely by using HCl treatment. However, in the above annealed samples, neither α -Fe nor Fe₂O₃ is found, while in the annealed sample without HCl treatment, Fe₂O₃ is found apparently from both the XRD pattern and Mössbauer spectra.

Comparing these two cases, it can be assumed that the remnant Fe exists in two forms: the first lies in powder in the sample; the second is surrounded by β -FeSi₂. During HCl treatment, the first form of Fe joins in the reaction with hydrochloric acid and is used up, but the second form of Fe still remains. When annealing the sample after HCl treatment, the second form of Fe, enveloped by β -FeSi₂, produces β -FeSi₂ and a little ϵ -FeSi by diffusion of atomic Fe and Si. When the annealing temperature is 600 °C the proportion of ϵ -FeSi is 1.2%, and when the annealing temperature is increased to 800 °C the proportion of ϵ -FeSi also increases to 8%. However when annealing at 950 °C, because of the phase transition (β -FeSi₂ to α -FeSi₂), the case is changed.

5. Conclusion

The results reported in this paper show that β -FeSi₂ is produced in Fe₃₀Si₇₀ powder using low energy ball milling and the proportion of β -FeSi₂ in these as-milled samples increases step by step as the milling time increases until the milling time reaches 60 h, after this the solid reaction reaches saturation. Within the final products, there is over 90% β -FeSi₂ and a little Fe and Si remnants. The remnant Fe exists in two forms: one is in powder and the second is enveloped by β -FeSi₂. When using hydrochloric acid to treat the as-milled sample, the first form of Fe is removed but the second form of Fe still remains. No Fe₂O₃ is formed when annealing the sample with HCl treatment. Good periodicity and a large proportion of β -FeSi₂ (close to 99%) are found in the sample annealed at 600 °C.

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