

Formation of β -FeSi₂ and the remanent α -Fe

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2002 J. Phys.: Condens. Matter 14 5449

(<http://iopscience.iop.org/0953-8984/14/21/318>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.104

The article was downloaded on 18/05/2010 at 06:44

Please note that [terms and conditions apply](#).

Formation of β -FeSi₂ and the remanent α -Fe

Li Yuzhi, Zhu Chenhui, Zhu Sanyuan, Liu Xianming and Li Gongpu

Structure Research Laboratory, University of Science and Technology of China, Hefei 230026, People's Republic of China

E-mail: liyz@ustc.edu.cn

Received 5 February 2002, in final form 15 April 2002

Published 16 May 2002

Online at stacks.iop.org/JPhysCM/14/5449

Abstract

Measurement of x-ray diffraction patterns, Mössbauer spectra, Raman scattering spectra and HRTEM/EDAX for β -FeSi₂ obtained by milling Fe₃₀Si₇₀ and HCl treatment shows that the Fe is not exhausted in the final product. There are two reactions during the ball milling process: one is the surface reaction to produce β -FeSi₂ between Fe and Si by driving force; some α -Fe is surrounded by β -FeSi₂. Another process is that Si diffuses through the β -FeSi₂ layer and reacts with Fe inside. However, this cannot exhaust all the Fe inside the grain, so the α -Fe still exists although there is little. The two processes coexist during the ball milling procedure, but the first process plays the main role for the first 50 h, then the second process mainly influences the proportion of α -Fe.

1. Introduction

β -FeSi₂ has been widely studied for its great potential to be applied into industry. In recent years, many properties have been found, such as its direct energy gap of 0.88 eV [1], the Hall coefficient depending on the temperature [2], its decrease in resistance and thermoelectromotive forces that are hardly changed when doped with Ag [3, 4] etc.

There are many ways to produce β -FeSi₂, such as ion implantation [5–10], pulsed laser deposition [11] and chemical vapour deposition [12], in which β -FeSi₂ thin film can be produced on a substrate. Ball milling is another simple and easy way. With Fe (30 at.%) and Si (70 at.%) powder we produced β -FeSi₂ by this method, and we found there is always Fe power left after ball milling no matter how long the milling time is. A recent study shows some of the remnant Fe is surrounded by β -FeSi₂ [13].

Here we shall study this in detail.

2. Preparation of samples

The purities of Fe (Shanghai Chemical Reagent Company) and Si powder (China Medicine Company, Beijing) are better than 99.8%, and the mesh sizes are 200. The Fe and Si powders

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 samples were milled separately with rotation at 200 revolutions min^{-1} and rotation radius 10.5 cm. The ratio by mass 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, and are called as-milled samples.

3. Experiments and results

The samples were measured with a Rigaku Max- γ A rotation target x-ray diffractometer (Cu $K\alpha$; $\lambda = 0.154$ nm). Mössbauer spectra were recorded using an MS-500 Mössbauer spectrometer and $^{57}\text{Co}/(\text{Pd})$ radiation source, 25mCi, at room temperature (RT). Raman spectra were measured using a Spex-1043 laser Raman scattering spectrometer ($\lambda = 514.5$ nm). High-resolution transmission electron microscopy (HRTEM) and energy dispersive analysis x-ray (EDAX) were also performed using a JEOL-2010 (accelerating voltage 200 kV; Cliff–Lorimer method).

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 $\beta\text{-FeSi}_2$ 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 decreases rapidly with increasing milling time. However, neither Fe nor Si is exhausted for milling time is as long as 80 h. (At $2\theta = 44.7^\circ$, the Fe peak is still observed).

Figure 2 shows the Raman scattering spectra of as-milled samples in which the peak at about 514 cm^{-1} originates from the distorted Si crystal and the intensity of this peak decreases as the milling time increases, which is in agreement with the result of XRD (figure 1).

Figure 3 represents the RT experimental Mössbauer spectra as well as their fitting results. The experimental spectra were fitted by the Gauss–Newton method. The isomer shifts (ISs) are referred to $\alpha\text{-Fe}$. Apparently the sextet from $\alpha\text{-Fe}$ could be observed besides the two doublets from $\beta\text{-FeSi}_2$.

Mössbauer fitting parameters are shown in table 1. The area of sextets to that of doublets is proportional to the number of Fe atoms in $\alpha\text{-Fe}$ to that in $\beta\text{-FeSi}_2$.

3.2. HCl-treated samples

The as-milled samples were treated with hydrochloric acid (5% HCl) to obtain HCl-treated samples.

Figure 4 shows the XRD pattern of the HCl-treated samples, in which a weak peak at $2\theta = 44.7^\circ$ from $\alpha\text{-Fe}$ could be observed besides the apparent peaks of $\beta\text{-FeSi}_2$ and Si.

Figure 5 shows the experimental Mössbauer spectra of HCl-treated samples at RT as well as fitted sub-spectra. The fitting parameters are listed in table 2.

4. Analysis and discussion

From the Mössbauer result, the area ratio of $\alpha\text{-Fe}$ and $\beta\text{-FeSi}_2$ is obtained, which is the same as the Fe atom number ratio (in $\alpha\text{-Fe}$ and $\beta\text{-FeSi}_2$), supposing the no-recoil fractions of both are the same. During HCl treatment, the $\alpha\text{-Fe}$ that is not surrounded by $\beta\text{-FeSi}_2$ reacts with

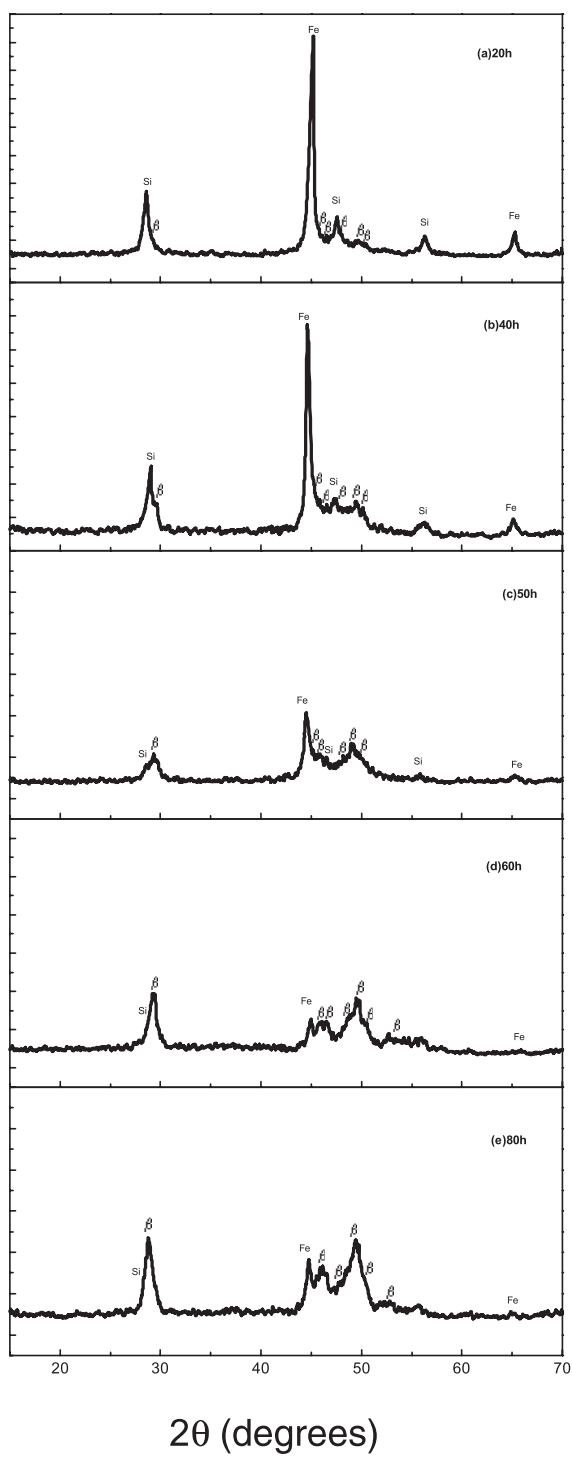


Figure 1. XRD pattern of Fe₃₀Si₇₀ as milled for t hours: $t = 20$ h (a); 40 h (b); 50 h (c); 60 h (d) and 80 h (e).

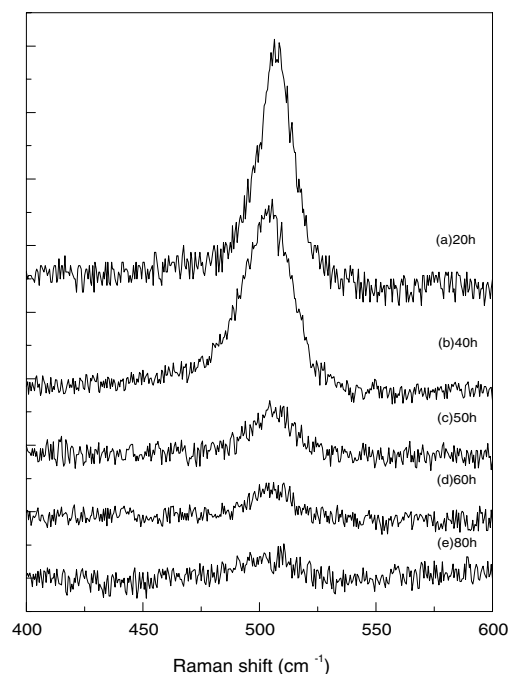


Figure 2. Raman scattering spectra of $\text{Fe}_{30}\text{Si}_{70}$ as milled for t hours: $t = 20$ h (a); 40 h (b); 50 h (c); 60 h (d) and 80 h (e).

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	

HCl, but β -FeSi₂ does not react with HCl, hence the total number of Fe atoms changes after HCl treatment. In order to make comparisons, define variables x and y as the following.

- (a) x is the fraction of α -Fe in the as-milled samples (table 1).
- (b) y is the fraction of α -Fe in the HCl-treated samples (table 2).

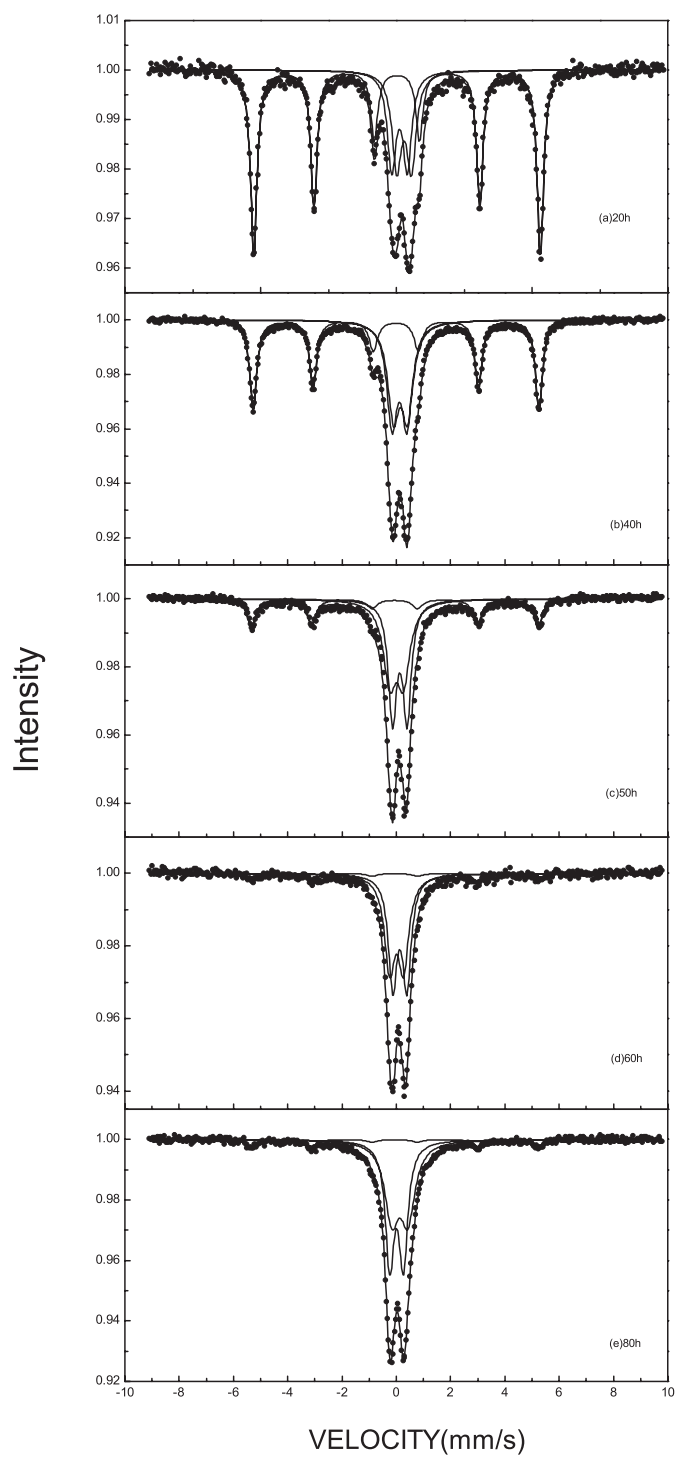


Figure 3. Mössbauer spectra of Fe₃₀Si₇₀ as milled for t hours: $t = 20$ h (a); 40 h (b); 50 h (c); 60 h (d) and 80 h (e).

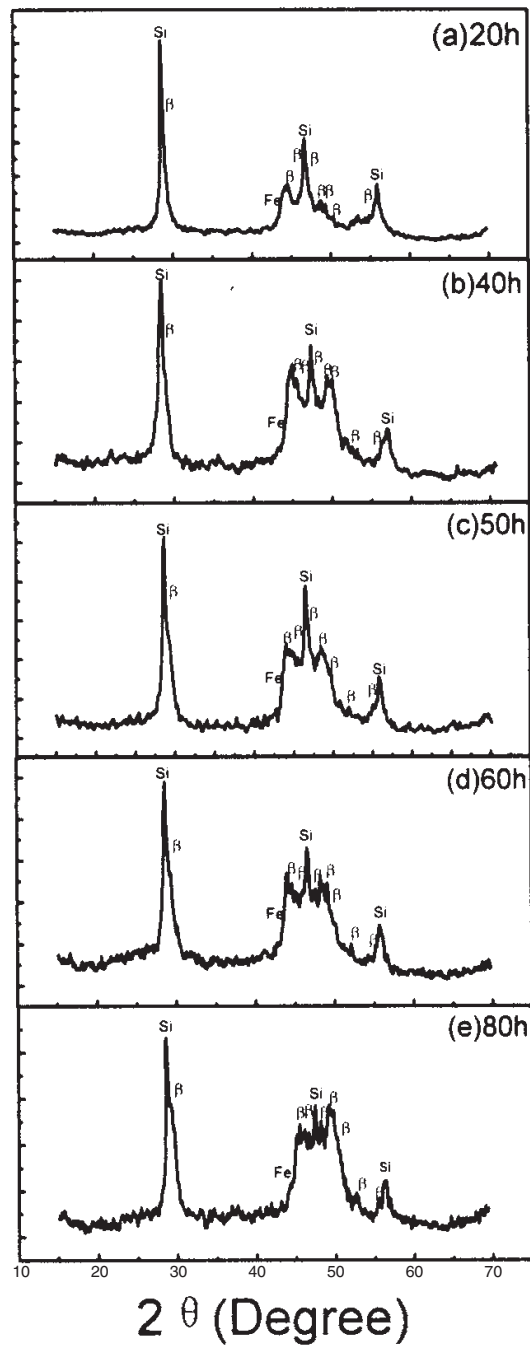


Figure 4. XRD pattern of the HCl-treated $\text{Fe}_{30}\text{Si}_{70}$ samples milled for t hours: $t = 20$ h (a); 40 h (b); 50 h (c); 60 h (d) and 80 h (e).

So from the results for the HCl-treated samples, the fraction of Fe atoms in α -Fe surrounded by β - FeSi_2 in the as-milled sample is obtained:

$$M = (1 - x) * y / (1 - y). \quad (1)$$

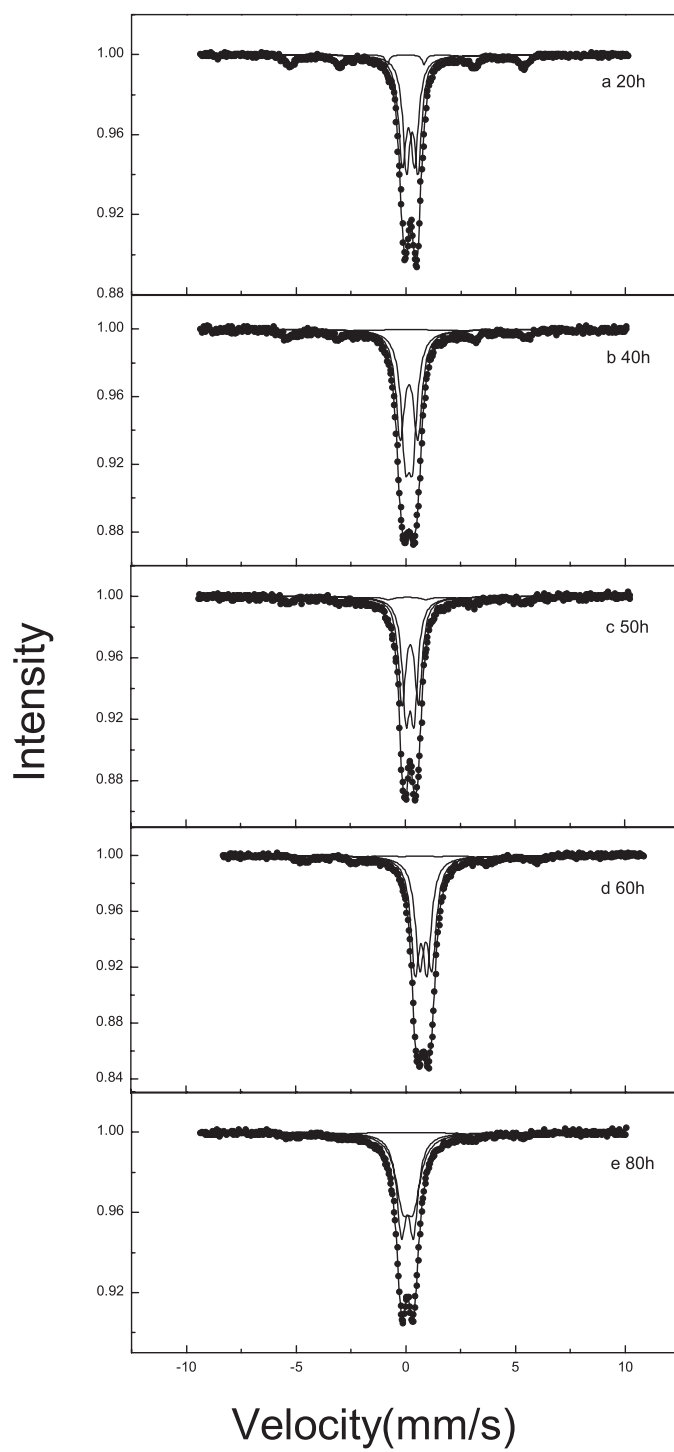


Figure 5. Mössbauer spectra of the HCl-treated Fe₃₀Si₇₀ samples milled for t hours: $t = 20$ h (a); 40 h (b); 50 h (c); 60 h (d) and 80 h (e).

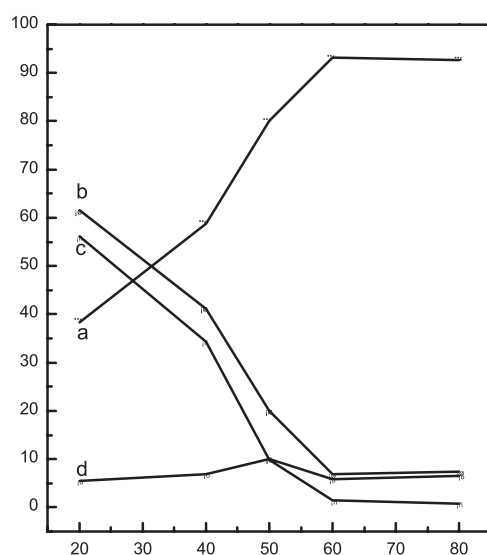


Figure 6. Relationship between Fe atom number and milling time: (a) β -FeSi₂; (b) remanent Fe; (c) remanent Fe not surrounded by β -FeSi₂ and (d) remanent Fe surrounded by β -FeSi₂.

Table 2. Mössbauer parameters of HCl-treated 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	0.01	0.05	329.4	12.6	0.19	0.28	0.10
	β -FeSi ₂	0.11	0.56		43.7		0.21	
40	α -Fe	0.02	0.03	336.1	10.6	0.34	0.28	0.97
	β -FeSi ₂	0.15	0.80		44.7		0.24	
50	α -Fe	0.06	-0.04	331.9	11.2	0.30	0.62	0.29
	β -FeSi ₂	0.22	0.75		44.4		0.21	
60	α -Fe	0.66	0.03	325.8	5.8	0.14	0.44	0.39
	β -FeSi ₂	0.70	0.54		47.1		0.23	
80	α -Fe	0.29	-0.01	330.0	6.6	0.24	0.58	0.50
	β -FeSi ₂	0.11	0.50		46.7		0.38	
		0.08	0.55		46.7		0.25	

The result is plotted in figure 6(d). In figure 6, curve a shows the fraction of Fe atoms in β -FeSi₂ with milling time, b shows the fraction of Fe atoms in α -Fe with milling time and c shows the relationship of quantity of α -Fe which is not surrounded by β -FeSi₂ with milling time. It is clear that when milling time is close to and longer than 60 h, the quantity of α -Fe which is not surrounded by β -FeSi₂ is close to zero.

From figure 6(a), the fraction of β -FeSi₂ increases as milling time increases, until milling time reaches 60 h, but figure 6(d) shows that the change of fraction of Fe surrounded by β -FeSi₂ is not the same: a maximum (10.1%) appears at 50 h; the fraction increases from 5.5 to 10.1% with milling time 20–50 h, then decreases from 10.1 to 6.6% with milling time 50–80 h.

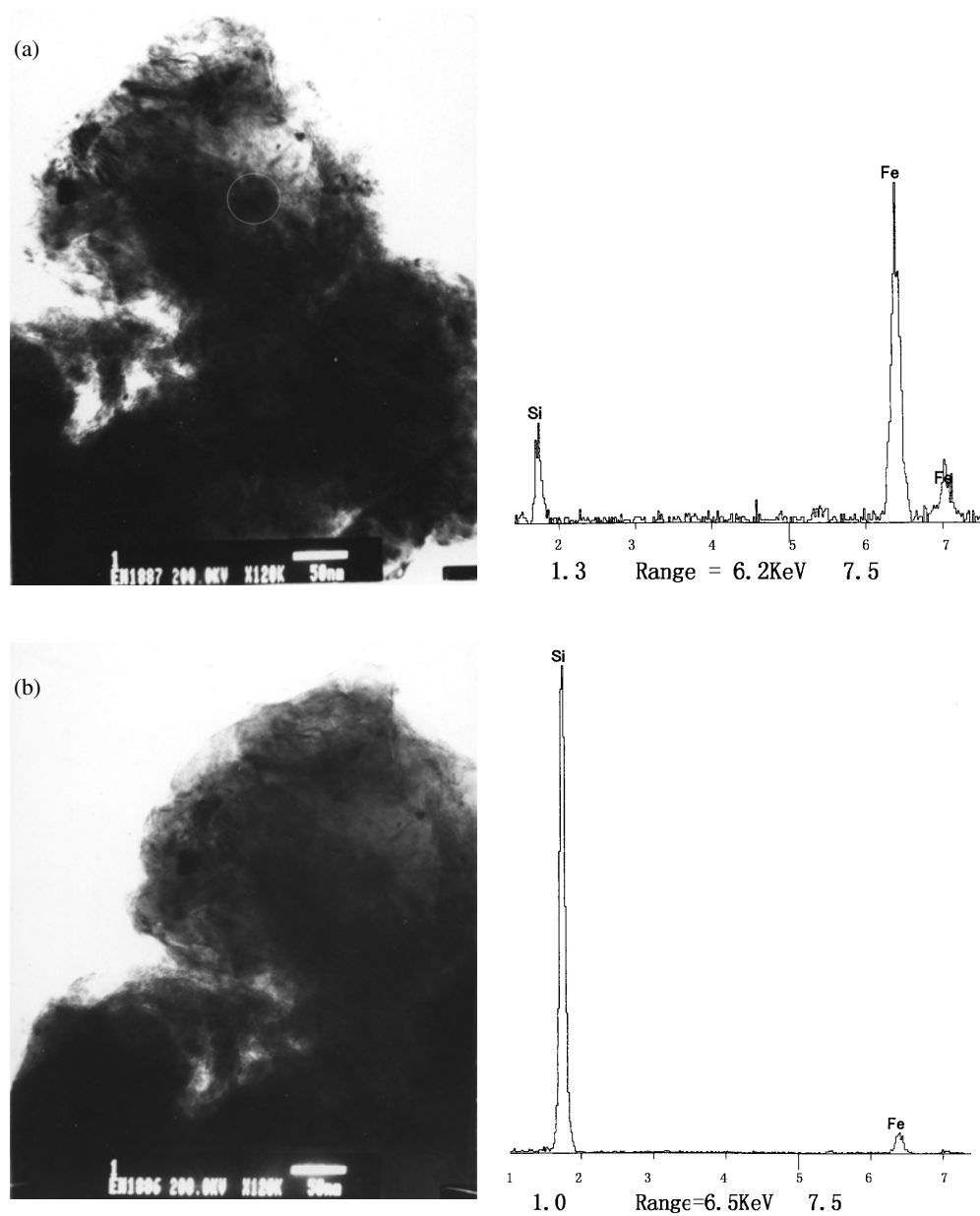


Figure 7. SEM/EDAX of HCl-treated Fe₃₀Si₇₀ (50 h). (a) (right) is the EDAX spectrum of the circled zone in (a) (left). (b) (right) is the EDAX spectrum of the grey zone in (b) (left).

We suggest that there are two processes.

During ball milling of Fe₃₀Si₇₀, the drive will make Fe and Si produce β -FeSi₂ by surface reaction and some Fe grains will be surrounded by β -FeSi₂. As milling time increases, the number of Fe grains surrounded by β -FeSi₂ increases. This is the first process. At the same time, the Si will diffuse through the β -FeSi₂ layer and react with α -Fe inside due to the steel balls' collision. This is the second process, during which the proportion of α -Fe inside will

decrease. Competition of the two results in a maximum, 10.1%, in curve figure 6(d) at 50 h. The diffusion process is therefore always slower than the second one. As result, there is always some α -Fe left.

The HRTEM/EDAX spectrum of the HCl-treated $\text{Fe}_{30}\text{Si}_{70}$ sample is illustrated in figure 7. Several different zones of our sample are studied but we only choose two typical zones' HRTEM photos and their corresponding EDAX spectra (figures 7(a) and (b)). From the HRTEM photo of figure 7(a) (left), we can see many small relatively black particles (for example, the circled zone) on the grey background. In the EDAX spectrum of the circled zone (figure 7(a) (right)), Fe and Si signals could be observed of which the Fe element is 77.4 at.%. This shows that Fe is the principal element of the black particle. This result therefore provides direct evidence for the existence of α -Fe and that Fe exists as small particles surrounded by β - FeSi_2 , which is in agreement with the Mössbauer result (figure 5). In figure 7(b) (right), the EDAX focus zone is the grey zone (seen in figure 7(b) (left)), and signals of 4 at.% Fe element and 96 at.% Si element are observed, which means that Si is the main phase in this focus zone in addition to a little β - FeSi_2 .

5. Conclusion

We can obtain β - FeSi_2 by milling $\text{Fe}_{30}\text{Si}_{70}$, but the remanent Fe is not exhausted. There are two reactions during the ball milling process: one is the surface reaction to produce β - FeSi_2 between Fe and Si by driving force; some α -Fe is surrounded by β - FeSi_2 . Another process is that Si diffuses through the β - FeSi_2 layer and reacts with Fe inside, but it cannot exhaust all the Fe inside the grain, so the α -Fe still exists although in small amount [14, 15]. The two processes coexist during the ball milling procedure, but the first process plays the main role before 50 h, then the second process mainly influences the proportion of α -Fe.

References

- [1] Milosavljevic M, Shao G, Bibic N, McKinty C N, Jeynes C and Homewood K P 2001 *Appl. Phys. Lett.* **79** 1438
- [2] Tani J and Kido H 2001 *Japan. J. Appl. Phys.* **140** 3236
- [3] Watanabe T and Hasaka M 2001 *J. Japan Inst. Met.* **63** 508
- [4] Ito M, Nagai H, Harimoto D, Katsuyama S and Majima K 2001 *J. Alloys Compounds* **322** 226
- [5] Jin S, Li X N, Zhang Z, Dong C, Gong Z X, Bender H and Ma T C 1996 *J. Appl. Phys.* **80** 3306
- [6] Reuther H and Dobler M 1996 *Appl. Phys. Lett.* **69** 3176
- [7] Kruijjer S, Keune W, Dobler M and Reuther H 1997 *Appl. Phys. Lett.* **70** 2696
- [8] Shao G, Yang Z, Nguyen Manh D and Homewood K P 1998 *J. Mater. Sci. Lett.* **17** 1243
- [9] Desimoni J, Sanchez F H, Fernandez van Raap M B, Lin X W, Bernas H and Clerc C 1996 *Phys. Rev. B* **54** 12 787
- [10] Kruijjer S, Keune W, Dobler M and Reuther H 1997 *Appl. Phys. Lett.* **70** 2696
- [11] Zhengxin Liu, Okoshi M and Hanabusa M 1999 *J. Vac. Sci. Technol. A* **17** 619
- [12] Zhao Jian-Hua, Li Yan-Chu, Liu Ri-Ping, Zhang Xiang-yi, Zhou Zhen-Hua, Wang Chao-Ying, Xu Ying-Fan and Wang Wen-Kui 1999 *Chin. Phys. Lett.* **16** 208
- [13] Li Yuzhi, Zhu Chenhui, Zhu Sanyuan and Zhou Guien 2001 *J. Phys.: Condens. Matter* **13** 6019
- [14] Malhouroux-Gaffet N and Gaffet E 1993 *J. Alloys Compounds* **198** 143
- [15] Gras C, Gaffet E, Bernard F and Niepce J C 1999 *Mater. Sci. Eng. A* **264** 94