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Phases in ball-milled $\text{Fe}_{0.6}\text{Si}_{0.4}$

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Abstract. Phases in $\text{Fe}_{0.6}\text{Si}_{0.4}$ ball milled for different lengths of time have been investigated by means of x-ray diffraction, Mössbauer spectroscopy and Raman scattering spectroscopy. It was found that the high-temperature phase Fe_5Si_3 can be formed by ball milling $\text{Fe}_{0.6}\text{Si}_{0.4}$ at room temperature. In the milling procedure the compounds FeSi and Fe_3Si were also formed.

1. Introduction

Much attention has been directed to ball milling because of its technical applications as well as the fundamental research since Koch *et al* [1] prepared amorphous $\text{Ni}_{0.6}\text{Nb}_{0.4}$ by mechanical alloying in 1983. Recently, it has been found that high-energy ball milling can form not only non-equilibrium phases, e.g. amorphous, nanocrystalline, quasi-crystalline [2–6], but also some special compounds [7, 8].

As a important system for practical use, Fe–Si alloys have been investigated for a long time [9–14]. Some properties of the metallic compounds have been discovered. In figure 1, part of the phase diagram is given [11]. It can be seen that the compound Fe_5Si_3 is a stable phase only in the narrow temperature region between 825 and 1030 °C. Shinjo *et al* [10] have studied the Mössbauer spectrum of Fe_5Si_3 at 77 K by alloying Fe–Si powders at 950 °C and quenching to 0 °C.

Recently, Escorial *et al* [7] have studied the ball-milled nominal compositions $\text{Fe}_{0.95}\text{Si}_{0.05}$, $\text{Fe}_{0.75}\text{Si}_{0.25}$ (Fe_3Si), $\text{Fe}_{0.625}\text{Si}_{0.375}$ (Fe_5Si_3) and $\text{Fe}_{0.5}\text{Si}_{0.5}$ (FeSi). They found the compound FeSi in all as-milled samples, and also traces of Fe_2Si in $\text{Fe}_{0.625}\text{Si}_{0.375}$ and of Fe_2Si , Fe_5Si_3 and FeSi_2 in $\text{Fe}_{0.5}\text{Si}_{0.5}$. More recently, Umemoto [8] studied an Fe–Si system near the composition FeSi_2 by ball milling. He found that, after milling for a substantially long time, the pre-mixed powder of nominal composition $\text{Fe}_{0.3}\text{Si}_{0.7}$ (approximately FeSi_2) transforms to a homogeneous β - FeSi_2 phase.

These new studies seem to present the possibility of forming the compound Fe_5Si_3 by ball milling at room temperature (RT). In this paper, $\text{Fe}_{0.6}\text{Si}_{0.4}$ which is near the composition of the compound Fe_5Si_3 was chosen and investigated for different ball-milling times. On the basis of the results from x-ray diffraction, Mössbauer spectroscopy and Raman scattering spectroscopy, the existence of the compounds Fe_5Si_3 , FeSi and Fe_3Si was confirmed. In the phase formation procedure, Fe and Si reacted and produced the compound FeSi first, and then Fe_3Si and Fe_5Si_3 appeared gradually.

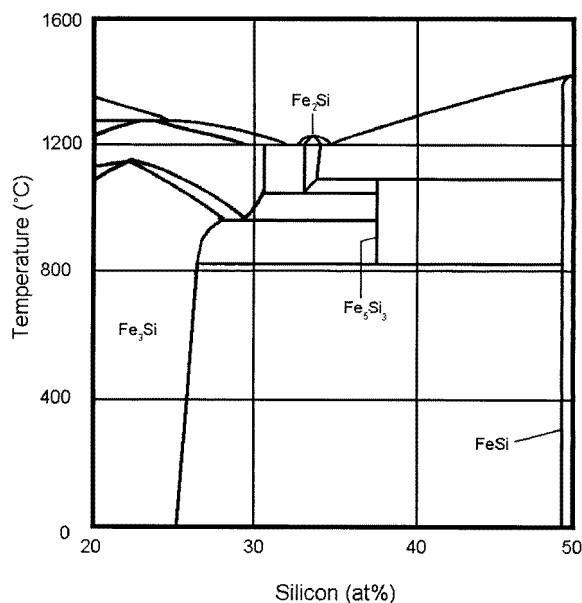


Figure 1. Phase diagram for the Fe–Si system.

2. Experiment

The purities of the Fe and Si powders are better than 99.8%, and the mesh sizes are 200. The Fe and Si powders were mixed in 6:4 atomic proportions and the mixture was placed into a hardened steel vial with steel balls. All samples were milled separately. The mass ratio of the balls to the mixture was 10 to 1. The vial was sealed under an argon atmosphere to prevent oxidation of the samples. The samples were milled for 10, 20, 30, 40 and 60 h separately.

The samples were measured with a Rigaku-Max- γ A rotating target x-ray diffractometer (Cu K α ; $\lambda = 0.154$ nm) and a Spex-1403 laser Raman scattering spectrometer ($\lambda = 514.5$ nm). Mössbauer spectra were recorded using a MS-500 Mössbauer spectrometer and $^{57}\text{Co(Pd)}$ radiation source at RT. The Mössbauer spectrum of the sample milled for 60 h was also taken at 85 K.

3. Results and discussion

The x-ray diffraction patterns of the samples are represented in figure 2. It can be found that the intensities of crystalline Fe and Si peaks decrease rapidly with increasing milling time, and the crystalline Si peaks disappear when the milling time reaches 40 h. After being milled for 20 h, the compound FeSi appears obviously in figures 2(c)–2(f). In the samples milled for 40 h or more, the diffraction peaks of Fe₃Si and Fe₅Si₃ can also be found in the patterns. However, in the phase diagram of the Fe–Si system shown in figure 1, Fe₅Si₃ is a high-temperature phase at equilibrium, which is stable only within a narrow temperature range from 825 to 1030 °C. Hence, although figures 2(e) and 2(f) show the main peak and the other peaks from Fe₅Si₃ [15], it is still necessary to confirm whether there is really some Fe₅Si₃ in these samples.

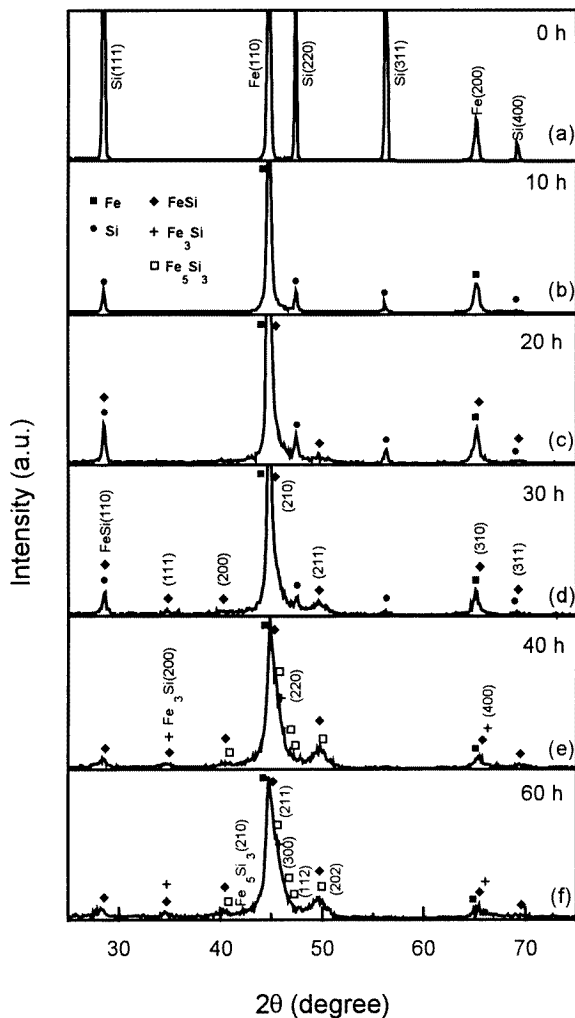


Figure 2. X-ray diffraction patterns of the $Fe_{0.6}Si_{0.4}$ milled for different times (a.u., arbitrary units). The crystal plane indices in (d) are those of FeSi, in (e) those of Fe_3Si and in (f) those of Fe_5Si_3 .

As far as we know, the structure of Fe_5Si_3 is of a hexagonal Mn_5Si_3 type. Its projection onto the basal plane is illustrated in figure 3 [10]. (The errors in the original picture have been corrected in this figure.) This structure has two inequivalent sites of Fe. The nearest neighbours of the Fe(I) site are two Fe(I) and their distance is very small (2.35 Å). In contrast with Fe(I), Fe(II) has two Si at a distance of 2.35 Å, one Si atom at 2.50 Å and two Si at 2.62 Å as nearest neighbours. Every unit cell of Fe_5Si_3 has four Fe(I), six Fe(II) and six Si; so the atom ratio of Fe(I) to Fe(II) is 2 to 3 in this compound. This compound is ferromagnetic at RT because its Curie point is at 100 °C [10].

Figures 4(a)–4(f) represent the RT experimental Mössbauer spectra as well as their fitting results. Figure 4(g) is the spectra of the sample milled for 60 h taken at 85 K. The experimental spectra were fitted by the Gauss–Newton method, and the fitting parameters are listed in table 1.

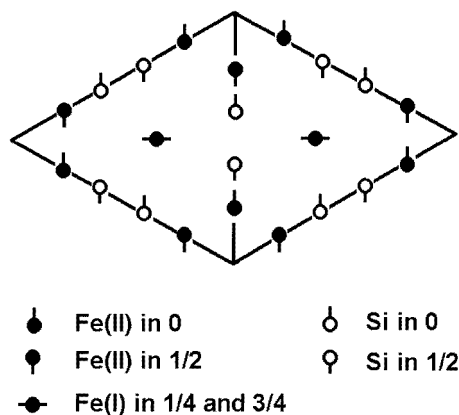


Figure 3. The structure of Fe_5Si_3 projected onto the basal plane.

In figure 4, the most outstanding subspectra are the sextet I and the doublet. Certainly, sextet I is from α -Fe, which exists in all samples, and its decreasing proportion is in agreement with the result of the x-ray diffraction patterns.

The doublet appears in figure 4 in the samples milled for 10 h and increases rapidly with increasing milling time up to 40 h, while the x-ray result shows that the diffraction peaks from the compound FeSi appear in the samples milled for more than 20 h. In figure 1, FeSi shows a homogeneity region extending from 49.0 to 50.8 at.% Si at RT. The structure of the FeSi is the distorted NaCl type [16]; all Fe sites in this compound are physically equivalent, and it is a paramagnetic phase. In general, this means that the Mössbauer spectrum of FeSi is a doublet. Elsukov *et al* [14] have studied the different compositions of iron–silicon alloys by Mössbauer spectroscopy at 77 K, and they obtained an almost pure FeSi compound in $\text{Fe}_{0.5}\text{Si}_{0.5}$. Its isomer shift (IS) and quadruple splitting (QS) are about 0.26 mm s^{-1} and 0.62 mm s^{-1} , respectively, which agree quite well with the parameters that we get for the samples milled for 60 h at 85 K, namely 0.24 mm s^{-1} and 0.62 mm s^{-1} .

As the compound Fe_5Si_3 has two inequivalent Fe sites and it is ferromagnetic at RT, the Mössbauer spectrum of this compound should be two sextets at RT and 85 K. Shinjo *et al* [10] have obtained the Mössbauer spectrum of Fe_5Si_3 in 77 K; some Fe_3Si exists in their sample, and they obtained magnetic fields of 230 and 130 kOe; the IS and QS of Fe(I) are 0.3 mm s^{-1} and 0.15 mm s^{-1} , and those of Fe(II) are 0.2 mm s^{-1} and -0.3 mm s^{-1} . From table 1, it can be seen that at 85 K the magnetic fields of sextets IV and V, which are at about 235 kOe and 126 kOe, respectively, are similar to those obtained by Shinjo *et al*, especially the value that we found for the sextet V which is almost equal to that for Fe(II) obtained by Shinjo *et al*. Furthermore, the area ratio of the sextet IV to the sextet V is 12 to 17 which is about 2 to 3, i.e. the atom ratio of Fe(I) to Fe(II). Moreover, the area ratios of these two sextets are 3 to 5, 8 to 12 and 9 to 14 at RT, all rates similar to 2 to 3. Hence, the sextets IV and V must be from Fe_5Si_3 .

In other words, this means that Fe_5Si_3 , which is the high-temperature phase at equilibrium, can be formed by ball milling at RT.

From figures 2(e) and 2(f), we know that there is also some Fe_3Si in these samples. As the phase diagram shows, Fe_3Si exists in a large composition range (about 10–25 at.% Si). It is known that Fe_3Si is ferromagnetic at RT (the Curie point is 550°C), and the ordering structure of ideal Fe_3Si is of Fe_3Al type, which can be described as the systematic

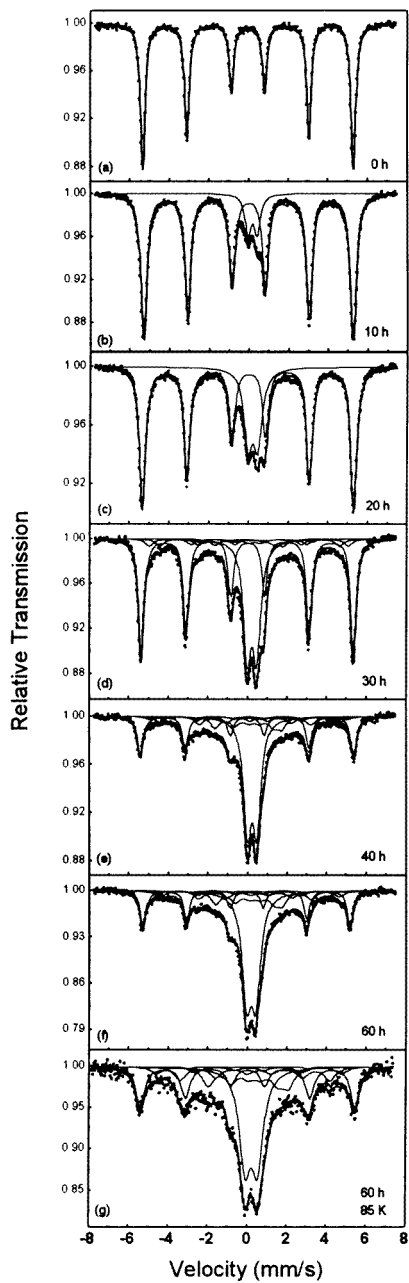


Figure 4. Mössbauer spectra of $Fe_{0.6}Si_{0.4}$ milled for different times: (a)–(f) obtained at RT; (g) obtained at 85 K.

replacement of half the body-centred atoms in α -Fe by Si in such a way that a corner Fe sees four Fe and four Si as nearest-neighbour atoms, each in a tetrahedral coordination. Therefore, the site of Fe(I) has eight Fe(II) as nearest neighbours, while the Fe(II) site has

Table 1. Fitting parameters of the RT Mössbauer spectra of $\text{Fe}_{0.6}\text{Si}_{0.4}$ for different milling times: IS, isomer shift, relative to $\alpha\text{-Fe}$; QS, quadruple splitting; H, hyperfine magnetic field; HW, half-width at half-height; A, area.

t (h)	Sextet I					Doublet			
	IS (mm s^{-1})	QS (mm s^{-1})	H (kOe)	HW (mm s^{-1})	A (%)	IS (mm s^{-1})	QS (mm s^{-1})	HW (mm s^{-1})	A (%)
0	0.00	0.00	331	0.14	100				
10	0.00	0.00	328	0.18	90	0.19	0.46	0.19	10
20	0.00	0.00	331	0.19	77	0.22	0.48	0.26	23
30	0.00	0.00	333	0.16	52	0.22	0.48	0.24	30
40	0.00	0.00	335	0.18	27	0.24	0.47	0.24	42
60	0.00	0.00	326	0.17	23	0.23	0.46	0.28	45
60 ^a	0.03	0.00	337	0.27	27	0.24	0.62	0.35	35

t (h)	Sextet II					Sextet III				
	IS (mm s^{-1})	QS (mm s^{-1})	H (kOe)	HW (mm s^{-1})	A (%)	IS (mm s^{-1})	QS (mm s^{-1})	H (kOe)	HW (mm s^{-1})	A (%)
0										
10										
20										
30	0.04	0.00	312	0.27	5	0.08	0.02	282	0.27	5
40	0.05	0.00	309	0.29	4	0.09	0.03	282	0.29	6
60	0.03	0.00	312	0.31	2	0.09	0.03	280	0.31	7
60 ^a	0.04	0.00	325	0.37	2	0.08	0.02	290	0.37	7

t (h)	Sextet IV					Sextet V				
	IS (mm s^{-1})	QS (mm s^{-1})	H (kOe)	HW (mm s^{-1})	A (%)	IS (mm s^{-1})	QS (mm s^{-1})	H (kOe)	HW (mm s^{-1})	A (%)
0										
10										
20										
30	0.46	-0.16	177	0.26	3	0.19	-0.28	108	0.26	5
40	0.47	-0.18	175	0.27	8	0.18	-0.27	105	0.27	12
60	0.49	-0.22	176	0.30	9	0.21	-0.29	105	0.30	14
60 ^a	0.49	-0.20	235	0.36	12	0.20	-0.31	126	0.36	17

^a The fitting result of the spectrum taken at 85 K.

four Fe(I) and four Si. Comparing the parameters in [9, 10, 12] with sextets II and III, it can be concluded that these two sextets are from Fe_3Si .

Here we explain the difference between the Mössbauer spectra and the x-ray diffraction in this experiment. Comparing the results of x-ray diffraction and the Mössbauer spectra, it can be found that these compounds always appear first in the Mössbauer spectrum. The reason is surely that the Mössbauer spectrum is more sensitive to the change in the surroundings around the Fe atoms.

Figure 5 shows the Raman scattering spectra of the sample milled for 0, 20 and 40 h, which describes the states of Si in these samples. In the figure, as the milling time increases, the Raman scattering peak changes from 517.0 cm^{-1} , a typical crystalline Si peak, to 514.0 and 510.5 cm^{-1} . This means that there is no amorphous Si in these samples because the peak of amorphous Si is at about 480 cm^{-1} . From the x-ray diffraction patterns, we know

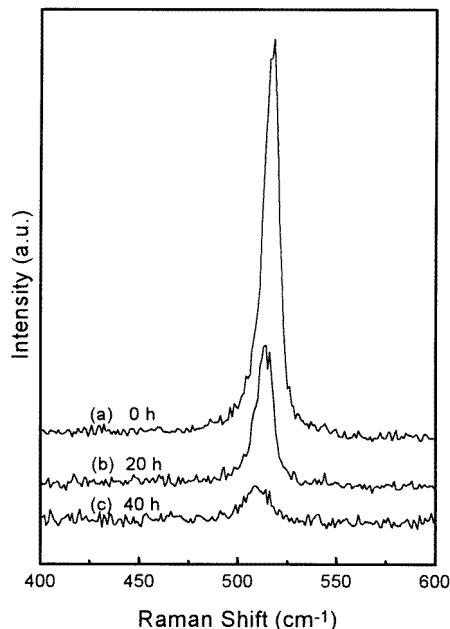


Figure 5. Raman scattering spectra of the $Fe_{0.6}Si_{0.4}$ milled for different times (a.u., arbitrary units).

that the compounds are formed and crystalline Si no longer exists in the sample milled for 40 h. Hence, the weak peak at 510.5 cm^{-1} should be from the compounds. The peak of the sample milled for 20 h is just the addition of the decreasing crystalline Si and the increasing compound peak.

It is known that, in ball milling, the crystal size of the phases will decrease markedly with increasing milling time; after a long milling time, it will become of the order of about 10 nm [5, 6]. As is well known, when the size of a ferromagnetic material decreases to its limit, it will become a super-paramagnet. In table 1, it can be seen that the proportion of FeSi decreases while those of Fe and Fe_5Si_3 increase when the sample milled for 60 h was cooled from RT to 85 K. When it was heated back to RT, the Mössbauer spectrum of the sample reverted back to the previous RT spectrum. On the other hand, as pointed out above, crystalline Si no longer exists after milling for 40 h; hence, the Si in the subsequently increased Fe_5Si_3 can only be from FeSi. Thus, the proportion of FeSi should decrease when the proportion of Fe_5Si_3 increases. However, table 1 shows that the proportion of FeSi increases. This means that there must be something in the samples milled for a long time which increases the proportion of the doublet. Considering these two points, we think that there is some super-paramagnet in the samples milled for a long time. However, it is difficult to try to distinguish the super-paramagnet from FeSi in the Mössbauer spectra.

From the experiments above, it can be concluded that, not long after being milled, crystalline Fe and Si reacted to form some compounds: FeSi, Fe_3Si and Fe_5Si_3 . With the results from Mössbauer spectra and x-ray diffraction, the high-temperature phase Fe_5Si_3 was confirmed in these RT ball-milled samples. No obvious amorphous trace is found in the samples.

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References

- [1] Koch C C, Cavin O B, McKamey C G and Scarbrough J O 1983 *Appl. Phys. Lett.* **43** 1017
- [2] Schwarz R B and Koch C C 1986 *Appl. Phys. Lett.* **49** 146
- [3] Eckert J, Schultz L and Urban K 1988 *Appl. Phys. Lett.* **55** 117
- [4] Hellstern E, Fech H J, Fu Z and Johnson W L 1988 *J. Appl. Phys.* **65** 305
- [5] Yavari A R, Desre P J and Benameur T 1992 *Phys. Rev. Lett.* **68** 2235
- [6] Eckert J, Holzer J C, Krill C E III and Johnson W L 1993 *J. Appl. Phys.* **73** 2794
- [7] Escorial A G, Adeva P, Cristina M C, Martin A, Carmona F, Cebollada F, Martin V E, Leonato M and Gonzalez J M 1991 *Mater. Sci. Eng. A* **134** 1394
- [8] Umemoto M 1995 *Mater. Trans. Japan Inst. Mat.* **36** 373
- [9] Stearns M B 1963 *Phys. Rev. B* **129** 1136
- [10] Shinjo T, Nakamura Y and Shikazono N 1963 *J. Phys. Soc. Japan* **18** 797
- [11] Warlimont H 1968 *Z. Metallk.* **59** 595
- [12] Haggstrom L, Granas L, Wappling R and Devanarayanan S 1973 *Phys. Scr.* **7** 125
- [13] Sidorenko F A, Gel'd P V, El'ner V Ya and Ryzhenko B V 1982 *J. Phys. Chem. Solids* **43** 297
- [14] El'sukov E P, Konygin G N, Barinov V A and Voronina E V 1992 *J. Phys.: Condens. Matter* **4** 7597
- [15] Yu Z 1984 *Acta Petrol. Mineral. Annl.* **3** 23
- [16] Pauling L and Soldate A M 1948 *Acta Crystallogr.* **1** 212