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Low-Temperature Synthesis of β-FeSi$_2$ Powder Using a Sodium Melt

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β-FeSi$_2$ powder was prepared by heating a mixture of Fe and Si powders with Fe/Si molar ratios of 1:2.25–2.50 in a Na melt at 773–1073 K for 1.5–24 h under an Ar atmosphere, while no β-FeSi$_2$ was obtained at 1073 K for 24 h without Na. The β-FeSi$_2$ phase was identified by powder X-ray diffraction. The primary and secondary grain sizes of β-FeSi$_2$ powder observed by transmission electron microscopy and scanning electron microscopy were 100–400 nm and 5–80 μm, respectively.

Introduction

β-FeSi$_2$ is an attractive candidate material for use as a high-temperature thermoelectric converter because of its large Seebeck coefficient.[1] It is also an environmentally friendly material because of the low toxicity of its constituent elements, Fe and Si, which are abundant on earth. According to the Fe–Si binary phase diagram,[2] β-FeSi$_2$ decomposes into ϵ-FeSi and α-FeSi$_2$ at temperatures over 1255 K. The conventional preparation process of β-FeSi$_2$ for thermoelectric devices is based on the classical powder metallurgical melting technique.[3] A mixture of Fe and Si powders is compacted and sintered at a temperature above 1373 K to be a mixture of ϵ-FeSi and α-FeSi$_2$ phases. The mixture is annealed for over 100 h at a temperature where β-FeSi$_2$ is stable.

Several interesting methods for low-temperature and/or short-processing time synthesis of β-FeSi$_2$ have been investigated. For example, Umemoto et al.[3] studied mechanical-alloying processes in the Si-rich Fe–Si system from elemental powders by ball milling. Only weak and broad X-ray diffraction peaks of β-FeSi$_2$ were observed in the X-ray diffraction pattern of the powder prepared from the elemental powders with a composition of Fe$_{30}$Si$_{70}$ by milling for 500 h. Nagai[4] prepared starting materials by mechanical alloying of elemental powders or mechanical grinding from the powders ϵ-FeSi and α-FeSi$_2$ and synthesized β-FeSi$_2$ by hot-pressing of starting materials at 1173 K for 30 min and 25 MPa.

Oikawa et al.[5] reported the direct formation of β-FeSi$_2$ from Fe and Si powders at 1203 K for 20 h in an evacuated fused silica tube. They found that Si vapor saturated in the sealed tube reacted with solid Fe and formed ϵ-FeSi, which initiated the reaction with solid Si to form the β-FeSi$_2$. Maeno et al.[6] prepared β-FeSi$_2$ powder by heating a compacted powder mixture of Fe and Si with a catalyst of 5 wt % KCl at 1127 K for 5 h in an Ar atmosphere.

Recently, we reported the synthesis of β-SiC at 900–1000 K using a mixture of silicon and carbon powders with a Na melt or Na vapor.[7,8] The formation of β-SiC usually requires a high temperature of 1300–1800 K.[9,10] No Na–Si binary phase diagram is available, but the solubility of 10–20% Si in Na melt at 1073 K was reported by MacCaldin et al.[11] Si dissolved in Na is reactive to carbon at a low temperature, and Na acts as a kind of flux, which promotes the fusion of Si and/or as a medium for reaction enhancement. We thought that a similar low-temperature reaction between silicon and other elements could also be realized using a Na melt.

In the present study, we report the synthesis of β-FeSi$_2$ powder by heating Fe and Si powder mixtures with a Na melt under an Ar atmosphere at 773–1073 K. The effects of Fe–Si compositions in the starting mixtures as well as heating temperature and time on the products were investigated.

Experimental Section

A total of 50 mg (0.9 mmol) of Fe powder (Wako, 99.9%, <45 μm) and 50–63 mg (1.8–2.2 mmol) of Si powder (Koujundo Kagaku, 99.999%, <75 μm) were weighed to have a molar ratio of Fe/Si of 1:$x_{\mathrm{Si/Fe}}$ ($x_{\mathrm{Si/Fe}} = 2.00$–$2.50$) and stirred with a small spatula in a glass container (5 mL). The mixed powder was loaded into a sintered BN crucible ($\varphi 6 \times 13$ mm in inner volume, Showa Denko, 99.5%) with 510 mg (9 mmol) of Na metal in an Ar gas-filled glovebox (MBraun, O$_2$, H$_2$O < 1 ppm).

The crucible was set in a stainless-steel tube (SUS316, inner diameter of 11 mm, inner length of 80 mm), as shown in Figure 1. The tube was sealed with stainless-steel caps in an Ar atmosphere. The sample was heated up to prescribed temperatures (773–1073

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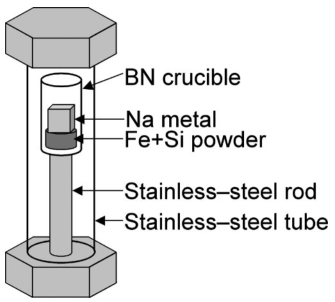

Figure 1. Schematic drawing of the container for β-$FeSi_2$ powder synthesis.

K) for 2 h, with temperatures being maintained for 1.5–24 h with an electric furnace. After heating, the sample was cooled in the furnace by shutting off the electric power to the furnace. The SUS tube was cut in the glovebox, and the sample was taken out of the tube. Single crystals included in the as-prepared sample were sealed in glass capillaries under an Ar atmosphere. X-ray diffraction data of the single crystals were obtained at room temperature using an X-ray diffractometer (Rigaku, RAPID-II) with graphite monochromatized Mo Kα radiation (λ = 0.7107 Å). Data collections and cell refinement were performed with RAPID-AUTO (Rigaku, RAPID-AUTO, Rigaku Corporation, Tokyo, Japan).

The Na and NaSi in the sample were first removed by the reaction with 2-propanol and ethanol and then with distilled water. After several washings with distilled water, the sample was dried at 353 K in air. The phases of the obtained samples were identified by powder X-ray diffraction (XRD) with pyrolitic graphite monochromatized Cu Kα radiation (λ = 1.5418 Å) at a scanning rate of 0.02°/s in the 2θ range from 20° to 70°. The lattice parameters were refined by the Le Bail method for the powder XRD patterns using the software RIETAN-FP.[12] The calibration of the diffraction angle was performed using a standard reference material, silicon (NIST SRM 640c a = 5.431 195 Å). Data for this refinement were collected at room temperature over a 2θ range from 20° to 140° at a 0.02° step, each for 7 s. The morphology of the β-$FeSi_2$ powder was observed with a scanning electron microscope (SEM; Philips, ESEM XL30) and with a transmission electron microscope (TEM, JEOL, JEM-2000EX). Specimens for TEM observation were prepared by dispersing the powder samples on holey carbon films. The compositions of Fe, Si, and Na in the sample were determined with an energy-dispersive X-ray analyzer (EDX; EDAX) attached to the SEM by the ZAF (element number, absorption, and fluorescence corrections) quantification method.

Results and Discussion

The as-prepared samples in the crucible were covered with Na metal. Thin platelet single crystals, 0.5–2.0 mm long, 0.1–0.3 mm wide, and 0.1 mm thick, with silver metallic luster were observed in and at the surface of the solidified Na melt. The single-crystal X-ray diffraction measurement revealed that the crystals have monoclinic symmetry with unit-cell dimensions, i.e., a = 1.2165(1) nm, b = 0.6547(1) nm, c = 1.1139(1) nm, and β = 118.89(1)°, which were in good agreement with those of NaSi reported by Witte et al.[13] (space group: $C2/c$, a = 1.219 nm, b = 0.655 nm, c = 1.118 nm, and β = 119.90°). The black powder of the Fe–Si compounds contained on the inner bottom of the crucible remained after removal of the Na metal and NaSi crystals from the as-prepared sample by washing with alcohol and water.

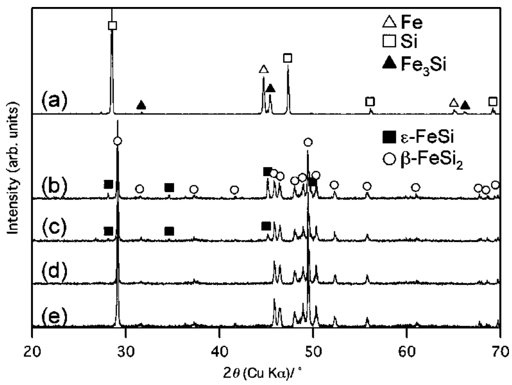

Figure 2. Powder XRD patterns of the samples prepared at 1073 K for 24 h without Na at $x_{Si/Fe}$ = 2.00 (a) and with Na at $x_{Si/Fe}$ = 2.00 (b), 2.15 (c), 2.25 (d), and 2.50 (e), where $x_{Si/Fe}$ is the Si/Fe molar ratio of the starting mixture.

Figure 2 shows XRD patterns of the powder samples prepared from Fe–Si powder mixtures of $x_{Si/Fe}$ = 2.00–2.50 with and without Na by heating at 1073 K for 24 h, followed by washing with alcohol and water. Diffraction peaks corresponding to Fe, Si, and Fe_3Si were observed in the XRD pattern of the sample prepared without Na (Figure 2a). On the other hand, diffraction peaks of β-$FeSi_2$ and a few small peaks of ϵ-FeSi were observed in the XRD patterns of the samples prepared from the mixtures of $x_{Si/Fe}$ = 2.00 and 2.15 with Na (parts b and c of Figure 2). The peak intensity of ϵ-FeSi decreased with an increasing $x_{Si/Fe}$, and all diffraction peaks of the samples obtained from the Fe–Si mixtures of $x_{Si/Fe}$ = 2.25 and 2.50 with Na were indexed with the unit cell of β-$FeSi_2$ (parts d and e of Figure 2).

Table 1 lists observed 2θ, d spacings, and intensities of the sample prepared with the Fe–Si powder mixture of $x_{Si/Fe}$ = 2.25 and Na for 24 h at 873 K, compared to the d spacings and intensities calculated with RIETAN using the crystal structure data of β-$FeSi_2$ by Dusausoy et al. [space group: $Cmca$, a = 0.9863(7) nm, b = 0.7791(6) nm, and c = 0.7833 (6) nm].[14] The unit-cell parameters of the sample refined by the Le Bail method were a = 0.98765(2) nm, b = 0.78111(2) nm, and c = 0.78250(2) nm, which were consistent with the reported ones.

Although relative intensities of most diffraction peaks were close to those of calculated intensities, the intensities of some peaks, in particular, for 2 2 1 and 3 1 2 diffractions were extremely weaker than the calculated ones. These discrepancies could not be explained with the preferred orientation of grains. Similar diffraction patterns with small intensities of these peaks were often seen in the XRD patterns presented in the reports of β-$FeSi_2$ synthesis, for example, by mechanical alloying,[3,4] low-temperature synthesis using a catalyst of KCl at 1127 K,[6] and spark-plasma sintering.[15] We are now studying the discrepancies between the observed and calculated intensities. Our preliminary results suggest that

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Table 1. 2θ, d Spacings, and Intensities of the XRD Pattern Observed for the Sample Prepared with the Si–Fe Powder Mixture of $x_{\mathrm{Si/Fe}} = 2.25$ and Na for 24 h at 873 K and Those Calculated with the Structure Data of β-FeSi$_2$ Reported by Dusausoy et al. [Space Group: *Cmca*, $a = 0.9863(7)$ nm, $b = 0.7791(6)$ nm, and $c = 0.7833(6)$ nm][14]

h	k	l	$2\theta_{\mathrm{obs}}$ (Å)	d_{obs} (Å)	I_{obs}	d_{calcd} (Å)	I_{calcd}
1	1	1	18.377	4.8239	3	4.8195	4
0	2	0	22.750	3.9056	1	3.8955	1
1	1	2	27.019	3.2975	7	3.2978	8
2	0	2	29.095	3.0667	85	3.0670	79
2	2	0	29.128	3.0633	69	3.0568	82
2	2	1	31.333	2.8525	2	2.8477	20
3	1	1	31.605	2.8286	5	2.8252	3
0	2	2	32.363	2.7641	1	2.7619	1
4	0	0	36.356	2.4691	2	2.4658	2
2	2	2	37.249	2.4120	9	2.4097	4
1	1	3	37.443	2.3999	2	2.4012	0
3	1	2	37.483	2.3974	8	2.3960	35
0	2	3	41.602	2.1691	2	2.1689	3
1	3	2	42.671	2.1172	1	2.1141	1
4	2	0	43.319	2.0870	1	2.0835	0
4	2	1	44.914	2.0165	7	2.0134	20
3	1	3	45.843	1.9778	23	1.9777	24
3	3	1	45.887	1.9760	25	1.9722	25
0	0	4	46.378	1.9562	20	1.9583	17
0	4	0	46.465	1.9528	27	1.9478	22
0	4	1	47.978	1.8947	21	1.8902	29
1	1	4	48.831	1.8636	15	1.8649	41
5	1	1	48.927	1.8601	22	1.8577	21
4	2	2	49.457	1.8414	100	1.8394	100
2	0	4	50.116	1.8187	7	1.8200	6
2	4	0	50.198	1.8160	6	1.8116	5
1	3	3	50.331	1.8115	28	1.8100	26
3	3	2	50.362	1.8104	3	1.8078	10
2	4	1	51.629	1.7690	3	1.7650	9
0	2	4	52.258	1.7491	14	1.7496	12
0	4	2	52.318	1.7472	9	1.7440	8
5	1	2	53.210	1.7200	2	1.7184	11
2	2	4	55.706	1.6487	7	1.6489	7
2	4	2	55.763	1.6472	10	1.6442	9
6	0	0	55.804	1.6461	2	1.6438	2
4	2	3	56.419	1.6296	3	1.6285	9
3	3	3	57.246	1.6080	1	1.6065	0
0	4	3	59.045	1.5632	3	1.5612	2
5	1	3	59.869	1.5436	2	1.5428	1
5	3	1	59.906	1.5428	1	1.5402	1
4	4	0	60.386	1.5317	2	1.5284	1
6	0	2	61.020	1.5173	3	1.6438	3
6	2	0	61.038	1.5169	3	1.5157	3
4	4	1	61.656	1.5031	1	1.5001	1
6	2	1	62.299	1.4891	1	1.4870	2
5	3	2	63.687	1.4600	1	1.4579	4
4	4	2	65.378	1.4263	1	1.4238	0
0	4	4	67.747	1.3821	7	1.3810	6
7	1	1	68.590	1.3671	6	1.3653	6
5	3	3	69.734	1.3474	7	1.3460	8

the disorder arrangements in the crystal structure may be related to the weakness. The details of the structure analysis will be reported in another paper.[16]

When the Fe–Si mixture of $x_{\mathrm{Si/Fe}} = 2.25$ and Na were heated at 673 K for 24 h and washed with alcohol and water after heating, no peak from silicides was recognized by powder XRD (Figure 3a). Single crystals of NaSi were not contained in the as-prepared sample. The diffraction peaks of β-FeSi$_2$ and a few small peaks of ϵ-FeSi were observed in the XRD patterns of the sample prepared at 773 K (Figure 3b). The powder of the β-FeSi$_2$ was also obtained by heating at 873 K, followed by washing with alcohol and water (Figure 3c). NaSi single crystals were accompanied by the formation of β-FeSi$_2$ in these as-prepared samples.

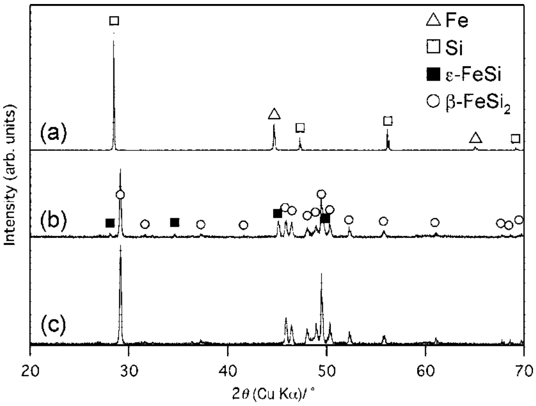

Figure 3. Powder XRD patterns of the samples prepared with the Si–Fe powder mixture of $x_{\mathrm{Si/Fe}} = 2.25$ and Na at 673 (a), 773 (b), and 873 K (c) for 24 h.

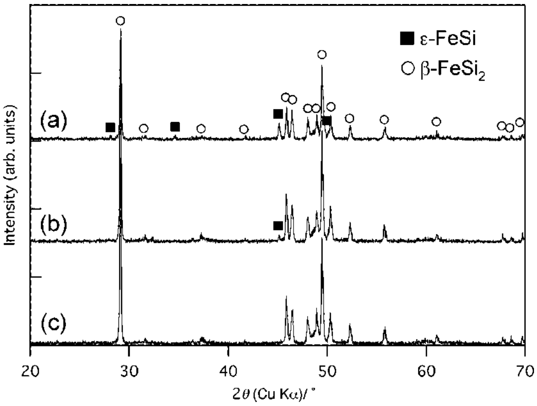

Figure 4. Powder XRD patterns of the samples prepared with the Si–Fe powder mixture of $x_{\mathrm{Si/Fe}} = 2.25$ and Na at 873 K for 1.5 (a), 3 (b), and 6 h (c).

As shown in Figure 4a, β-FeSi$_2$ was the main phase in the sample prepared by heating the Fe–Si powder mixture of $x_{\mathrm{Si/Fe}} = 2.25$ and Na at 873 K for only 1.5 h. Diffraction peaks of ϵ-FeSi were also observed in the XRD patterns of the sample heated for 1.5 and 3 h (parts a and b of Figure 4). The diffraction peak intensities of ϵ-FeSi decreased with an increasing heating time, and the peaks of ϵ-FeSi disappeared when heated for 6 h (Figure 4c).

Figure 5 shows SEM micrographs of the Fe and Si powders used as source materials and β-FeSi$_2$ powder prepared by heating the Fe–Si mixture of $x_{\mathrm{Si/Fe}} = 2.25$ at 873 and 1073 K for 24 h with Na. The grain sizes of Fe and Si were 5–80 μm. The surface of the grains was undulate but smooth (parts a and b of Figure 5). Pinched grains of 5–80 μm with cracks on the surface were seen in the obtained samples (parts c and e of Figure 5). A high-magnification SEM image revealed that the grains were composed of a few hundred nanometer-sized particles. The average size and standard deviation of the particles in the grains prepared at 873 K were 150 and 50 nm and smaller than 300 and 110 nm at 1073 K (parts d and f of Figure 5). The particle sizes and deviations were determined by the average of the sizes observed for 100 particles in areas of the SEM images.

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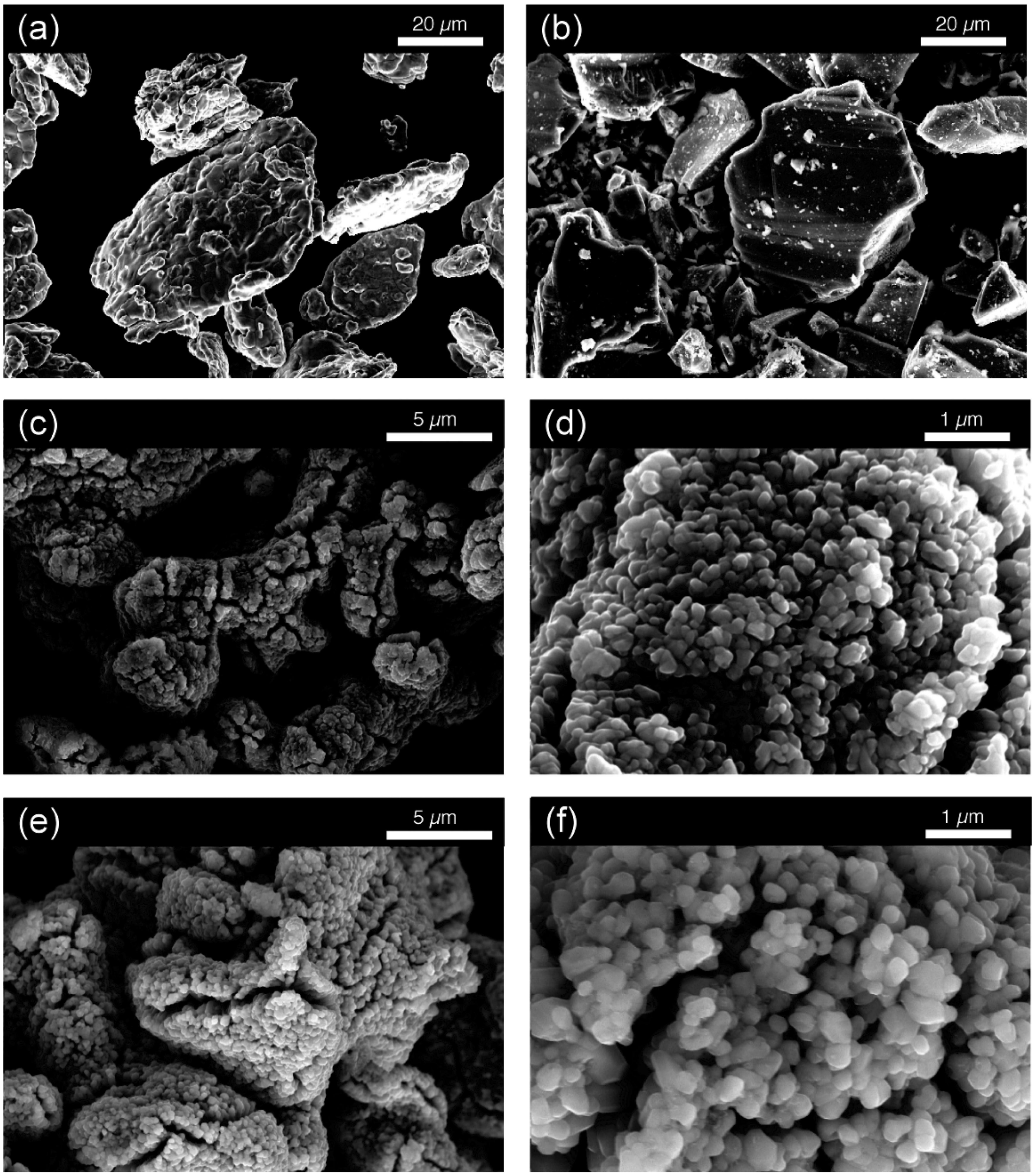

Figure 5. SEM images of Fe (a) and Si (b) powders used as source materials and the β-FeSi$_2$ powder prepared with the Si–Fe powder mixture of $x_{\mathrm{Si/Fe}} = 2.25$ and Na at 873 (c and d) and 1073 K (e and f) for 24 h.

The samples prepared at 873 and 1073 K for 24 h with Na were also observed by TEM (Figure 6). The grain sizes observed in the TEM image were consistent with the size of the particles observed in the SEM images. Spot patterns of the electron diffraction indicated that each grain was a single crystal of β-FeSi$_2$, and the particles with a size of several hundred nanometers observed in the SEM were primary grains of β-FeSi$_2$.

Si K (1.76 keV) and Fe K (6.46 and 7.10 keV) and L (0.70 keV) peaks were observed, while Na K peaks (1.03 keV) were not observed in the EDX spectrum of the sample prepared by heating the Fe–Si mixture of $x_{\mathrm{Si/Fe}} = 2.25$ at 1073 K for 24 h with Na (Figure 7). The Fe/Si molar ratio of the particles analyzed by the ZAF correction method was 1:2.04, which agreed with the stoichiometric composition of β-FeSi$_2$ within a standard deviation of 3%. The Na content in the powder was below the detection limit of the EDX analysis (0.5 wt %).

A small amount of Fe$_3$Si was obtained by the solid-state reaction of Fe and Si powders at 1073 K for 24 h (Figure 2a). According to the binary phase diagram of Fe and Si,[2] it should also be possible to prepare β-FeSi$_2$ at this temperature. However, β-FeSi$_2$ could not be prepared experimentally by the reaction of Fe and Si powders at and below 1073 K. It was reported that Fe$_3$Si was formed at the interface of contacted Si single crystal and Fe sheet after annealing at 973 K for 7 h, which suggested that the formation of Fe$_3$Si is faster than that of β-FeSi$_2$.[17] The formation of Fe$_3$Si shown in Figure 2a was also caused by the same way, at the contact face of Si and Fe grains.

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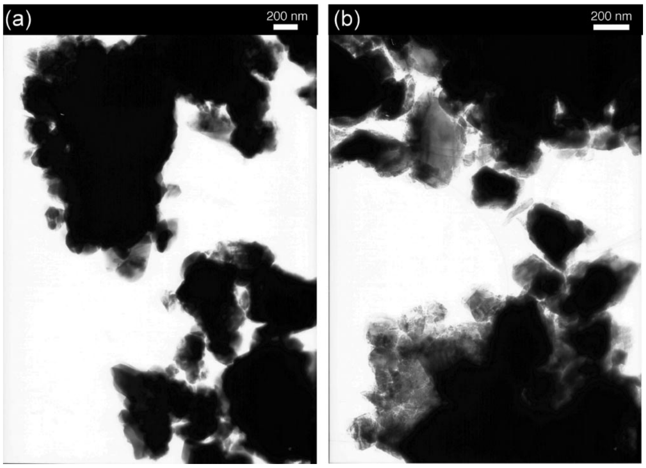

Figure 6. TEM images of the β-FeSi$_2$ powder prepared with the Si–Fe powder mixture of $x_{\mathrm{Si/Fe}} = 2.25$ and Na for 24 h at 873 (a) and 1073 K (b).

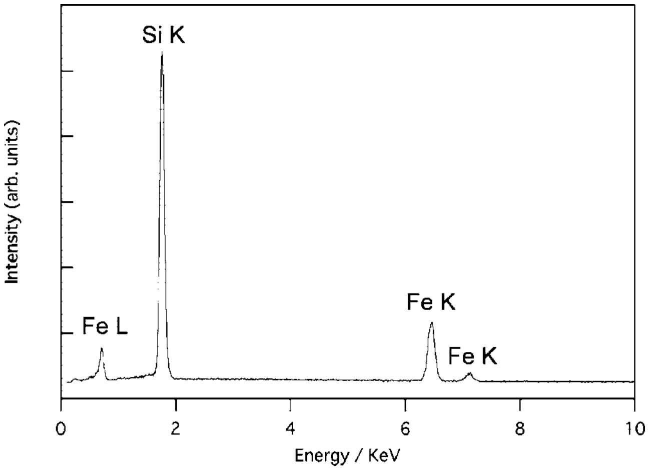

Figure 7. Energy-dispersive X-ray spectrum of β-FeSi$_2$ powder prepared with the Fe–Si powder mixture of $x_{\mathrm{Si/Fe}} = 2.25$ and Na at 1073 K for 24 h.

The low-temperature formation of β-FeSi$_2$ reported in the previous studies was carried out by heating a compact Fe–Si powder mixture at 1127 K with catalysis of 5 wt % KCl, which melts at 1049 K.[6] In the present study, we were able to prepare β-FeSi$_2$ with Na (melting point of 371 K) even at 773 K, which was about 350 K lower than the temperature of the previous study. To our knowledge, no phase diagram of the Na–Si binary system is available, but the solubility of Si in liquid Na at 1073 K was estimated to be between 10 and 20 atomic %.[11] On the other hand, the solubility of Fe in liquid Na at 773–1073 K was in the range of 10^{-2}–100 ppm,[18] which greatly depends upon the oxygen content of liquid Na, but about 2 orders of magnitude smaller than the solubility of Si in Na.[11] Therefore, Si in the starting powder mixture dissolved into the Na melt first even at 773 K, and then, Fe–Si binary compounds were formed by the reaction between Si in the melt and Fe powder grains. The results of the reaction time dependence shown in Figure 4 suggested the diffusion of Si into the Fe grains because ϵ-FeSi detected in the sample prepared by heating for 1.5 h changed into β-FeSi$_2$ by heating for 3 h. Because the molar volumes of Fe and β-FeSi$_2$ are 7.09 and 22.7 cm^3, respectively, source Fe grains probably broke into fragments. The cracks observed on the surface of grains observed in the SEM images of Figure 5e may also be caused by the volume change.

A small amount of NaSi crystallized whenever β-FeSi$_2$ was prepared with a Na melt. NaSi as well as solidified Na can be removed by washing with alcohol and water. β-FeSi$_2$ is the silicide with the highest Si content in the Fe–Si binary system. An excess amount of Si from the stoichiometric composition of β-FeSi$_2$ in the starting mixture was needed to obtain the β-FeSi$_2$ powder after washing. At the composition of $x_{\mathrm{Si/Fe}} = 2.00$ and 2.15, ϵ-FeSi coexisted in the samples. These results suggest that β-FeSi$_2$ is in equilibrium with a Na–Si melt at 773–1073 K. The method with a Na melt is expected to be useful not only for low-temperature preparation of iron silicides but also for the preparation of other silicide compounds.

Conclusions

Low-temperature synthesis of β-FeSi$_2$ powder was achieved at 773–1073 K for 1.5–24 h by heating a mixture of Fe and Si powders with a Na melt in an Ar atmosphere. The powder grains consisted of β-FeSi$_2$ particles with a size of a few hundred nanometers. β-FeSi$_2$ powder was prepared from the Fe–Si powder mixtures with molar ratios of Fe/Si = 1:2.25 and 2.50. NaSi single crystals were included in the as-prepared samples after heating and were removed from the samples with Na by washing with alcohol and water. Excess silicon in the starting mixtures was dissolved in the Na melt at the heating temperatures, and single crystals of NaSi probably grew during cooling.

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