Phase relations in the system Fe-FeSi at 21 GPa

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ABSTRACT

High-pressure experiments were conducted to investigate the phase relations in the binary system Fe-FeSi at a pressure of 21 GPa and temperatures between 1350 and 2200 °C by using a multi-anvil apparatus. The system has a eutectic point at 26 wt% Si and 1820 °C, which is 400 °C lower than the melting point of pure Fe. On the Fe-rich side of the eutectic point, the temperature difference between the solidus and liquidus curves is less than 50 °C and the compositional difference is small between the coexisting solid and liquid. At subsolidus temperatures, homogeneous Fe-Si alloys were quenched with compositions up to 21.7 wt% Si. The more Si-enriched composition, Fe(+25.1 wt% Si), was found to coexist to with CsCl-type FeSi. These results suggest that a large amount of Si could have dissolved into liquid Fe at high pressures during core formation if it occurred under reducing conditions. However, the difference in Si content between the outer core and the inner core would be very small, if the solubility of Si in solid Fe remains large at inner core pressures.

INTRODUCTION

The Earth's outer core is believed to consist of liquid Fe with one or more light alloying elements (e.g., Birch 1952; Poirier 1994). Experimental and theoretical studies showed that the solid inner core also might contain a certain amount of light element(s) (e.g., Jephcoat and Olson 1987; Anderson and Ahrens 1994; Stixrude et al. 1997). Silicon has been suggested as a light element possibly incorporated into the core from geophysical and geochemical arguments (e.g., Birch 1952; Ringwood 1959; Wänke 1981; Allegre et al. 1995; Zhang and Guyot 1999a). Barlchan and Cowan (1966) performed shock-wave experiments on Fe-Si alloys up to 270 GPa and their results showed that the outer core may contain 14–20 wt% Si. Allegre et al. (1995) calculated the bulk composition of the Earth and the composition of the mantle and core, and found that the core may include up to 7.3 wt% Si. If Si is actually an important light element in the core, high-pressure phase relations in the system Fe-Si are key to understanding the physicochemical processes of both core formation and inner-core crystallization.

Subsolidus and melting phase relations in the system Fe-Si at ambient pressure have been well established because of its metallurgical importance. Body-centered cubic (bcc) Fe can contain up to about 18 wt% Si in solid solution, but the solubility of Si in face-centered cubic (fcc) Fe is limited to about 2 wt%. The eutectic points are located at 1200 °C and 19.1 wt% Si and at 1203 °C and 22.0 wt% Si (Kubaschewski 1982). Order-disorder transitions also have been reported. However, high-pressure phase relations are not yet known precisely. High-pressure experimental studies on Fe-rich Fe-Si alloys with in-situ X-ray diffraction (XRD) measurements have not given consistent results on the subsolidus phase relations and the maximum solubility of Si in solid Fe (Zhang and Guyot 1999b; Lin et al. 2002; Dubrovinsky et al. 2003). A phase transformation from ε-FeSi to CsCl-type FeSi at 24 GPa also has been reported (Dobson et al. 2002).

In the present study, we report the subsolidus and melting phase relations in the system Fe-FeSi at 21 GPa based on multi-anvil quenching experiments. The results have important implications for the dissolution of Si into the liquid core in the accreting Earth and possibly for the crystallization of the inner core.

EXPERIMENTAL PROCEDURE

Phase-equilibrium experiments were performed at a pressure of 21 GPa and temperatures between 1350 and 2200 °C using 1000 ton Kawai-type high-pressure device (SEDI-1000) installed at the Magma Factory, Tokyo Institute of Technology. The 8/3 assembly (8 mm octahedron edge length and 3 mm truncated edge length of tungsten carbide), similar to that originally described by Bertka and Fei (1997), was used. The details of pressure calibrations were reported elsewhere (Hirose 2002). Starting materials were mechanical mixtures of powdered Fe and either FeSi or Si, with total Si ranging from 3 to 28 wt%. The mixtures were loaded into an Al_2O_3 capsule and heated by a Re heater. In several runs, we loaded two different starting materials separated by Al_2O_3 powder. The total sample length was 100 to 700 μm. Sample temperature was measured and controlled with a W5%Re-W26%Re thermocouple. The temperature gradient has been estimated to be less than 30 °C over 200 μm at 2000 °C (Hirose and Fei 2002). Run duration was typically greater than 10 min for subsolidus conditions below 2000 °C, and 2–5 min at temperatures above 2000 °C or for melting experiments (Table 1).

Recovered samples were polished and examined by using a JEOL JXA-8800 electron microprobe. We used an ~1 μm beam spot for analyses of solid phases and a larger beam spot (5 to 10 μm in diameter) for quenched liquid. FeSi was used as the standard. The samples were also analyzed by a microbeam X-ray diffractometer in reflection geometry (RIGAKU RINT-2500). Operating condition was 40 kV accelerating potential and 300 mA beam current. We used a monochromatic X-ray beam with a size of 50 μm and a wavelength of 2.290 Å for angular dispersive XRD.

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TABLE 1. Experimental conditions and run products

Run no.	Starting composition (wt% Si)	T (°C)	Time (min.)	Phases	Composition (wt% Si)*
Partial system of Fe and Fe(+25.1 wt% Si)					
c297a	3	1950	10	Fe(+Si)	2.90(11)
c291a	3	2050	3	Fe(+Si)	3.01(11)
c345	7	1850	10	Fe(+Si)	7.45(03)
c293	10	1700	5	Fe(+Si)	9.84(08)
c296	10	1800	10	Fe(+Si)	9.22(04)
c297b	10	1950	10	Fe(+Si)	9.48(16)
c291b	10	2050	3	Fe(+Si)	9.32(05)
c344	10	2150	3	liquid	†
c354	16	1850	15	Fe(+Si)	16.23(08)
c352	16	1950	5	Fe(+Si)	16.26(09)
				liquid	not determined
c351	16	2000	5	liquid	16.10(10)
c350	16	2100	5	liquid	15.91(23)
c332	20	2200	3	liquid	20.21(27)
c339	22	1850	3	Fe(+Si)	21.74(10)
c333	22	1980	3	liquid	21.52(20)
c331	24	1875	10	liquid	23.80(23)
Partial system of Fe(+25.1 wt% Si) and FeSi					
c322	26.5	1800	3	Fe(+Si)	25.02(22)
				FeSi	33.68(03)
c335	26.5	1840	3	FeSi	33.73(25)
				liquid	26.27(10)
c289	28	1350	180	Fe(+Si)	25.12(09)
				FeSi	33.27(16)
c292	28	1650	5	Fe(+Si)	24.97(15)
				FeSi	33.48(17)
c305	28	1750	15	Fe(+Si)	25.03(03)
				FeSi	33.36(21)
c323	28	2000	2	liquid	†
c306	28	2200	2	liquid	†

* The numbers in parentheses represent one standard deviation in the last digits.
† Samples were contaminated by about 20 wt% Re.

FIGURE 1. Phase diagram of the system Fe-FeSi at 21 GPa. Squares and crosses show the compositions of solid and liquid phases, respectively. Iron exhibits a high solubility of Si, up to 25.1 wt%, at subsolidus conditions. In more Si-enriched compositions, an Fe (+25.1 wt% Si) phase coexists with FeSi. The system has a eutectic point at 1820 °C and 26 wt% Si.

FIGURE 2. Silicon X-ray map of sample c292 quenched from 1650 °C. The solid Fe (+25.1 wt% Si) phase (dark gray) coexisted with the solid FeSi (bright gray).

RESULTS AND DISCUSSION

The microprobe observations on the recovered samples revealed that each solid and liquid phase is chemically homogeneous and showed no evidence for the incomplete reaction. The microprobe analyses and the XRD measurements suggest that no reaction between the Al$_2$O$_3$ capsule and the Fe(+Si) sample. This finding is in agreement with the earlier study by Ringwood and Hibberson (1991) that showed very limited solubility of Al$_2$O$_3$ in molten Fe. However, in a few cases trace amounts of silica grains were detected with the microprobe, but no peaks of stishovite and other silica phases were observed in the XRD patterns.

A phase diagram for the Fe-FeSi system at 21 GPa is illustrated in Figure 1 on the basis of our multi-anvil experiments (Table 1). Fe-Si alloys were formed under subsolidus conditions, with compositions up to 22 wt% Si. The quenched alloys are homogeneous solid phases, observed using the microprobe. XRD patterns showed that these quenched samples consist of a single phase with a bcc structure. The unit-cell parameter of the bcc-structured Fe-Si alloy decreases linearly with increasing Si content from 2.866 Å for pure Fe to 2.795 Å for Fe (+25.1 wt% Si).

In experiments with the Si-enriched compositions (>25.1 wt% Si), the Fe (+25.1 wt% Si) phase was found to coexist with the FeSi phase below the melting temperature (Fig. 2). XRD measurements revealed that these recovered samples contain a bcc Fe (+25.1 wt% Si) phase and a CsCl-type FeSi phase together
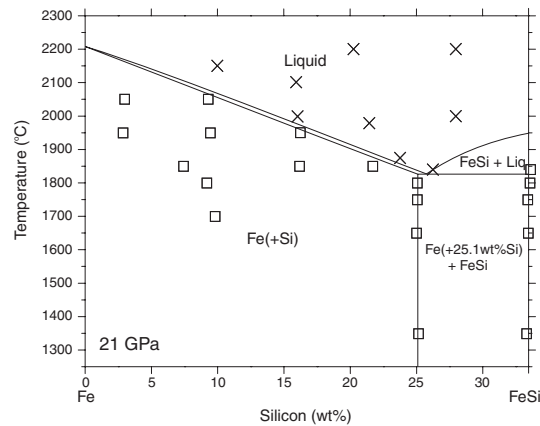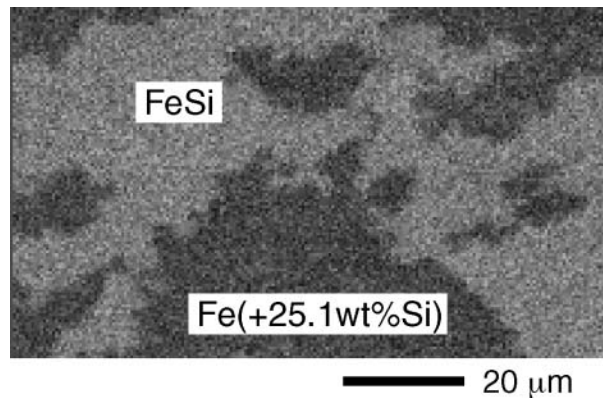
with ε-FeSi. This ε-FeSi phase was most likely converted from the CsCl-type phase during polishing, as discussed extensively by Dobson et al. (2002).

Melting was interpreted on the basis of quenching textures. Figure 3 shows a sequence of quenching textures from solid to quenched liquid. The Fe(+10 wt% Si), Fe(+16.1 wt% Si), and Fe(+23.8 wt% Si) samples (run no. c344, c351, and c331) melted at 2150, 2000, and 1875 °C, respectively. A solid Fe (+16.3 wt% Si) phase coexisted with a small fraction of liquid at 1950 °C (run no. c352). On the other hand, the Fe (+9.3 wt% Si) and Fe (+21.7 wt% Si) samples were unmelted, respectively, at 2050 and 1850 °C (run no. c291b and c339). These results tightly constrain the location of the liquidus-solidus loop (Fig. 1). The width of the liquidus-solidus loop must be small (<50 °C at 16 wt% Si). The geometry of these melting curves suggests a melting point of pure Fe around 2200 °C at 21 GPa, which is marginally consistent with that determined by the laser-heated diamond-anvil cell experiments (Shen et al. 1998).
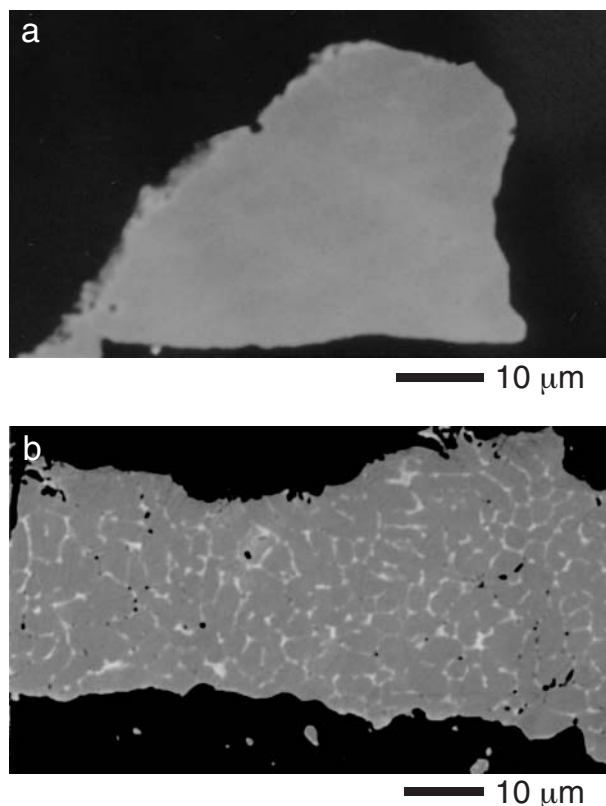
FIGURE 3. Change of quenched textures with increasing temperature for the sample with 16 wt% Si. (**a**) Back-scattered electron image of sample c354 quenched from 1850 °C. Single homogeneous Fe-Si alloy was formed under subsolidus condition. (**b**) Back-scattered electron image of sample c350 quenched from 2100 °C showing a quenched melt texture. The same melt textures were observed to 2200 °C

In the Si-rich region between Fe (+25.1 wt% Si) and FeSi, a quenched liquid with 26.3 wt% Si coexisted with solid FeSi at 1840 °C (run no. c335). A subsolidus phase assemblage of Fe (+25.1 wt% Si) and FeSi was observed at 1800 °C. These observations suggest that the system has a eutectic point that is located near 1820 °C and 26 wt% Si.

The homogeneous Fe-Si alloys quenched between Fe and Fe (+25.1 wt% Si) suggest that Fe-Si may form a continuous solid solution up to 25.1 wt% Si at high pressure and high temperature. The structure of the solid-solution phases is uncertain because of the lack of in-situ XRD data. It is possible that the Fe-Si alloys adopt the fcc strcutre at high pressure and temperature, and converted to the bcc structure during quench to ambient conditions. This hypothesis is also supported by the existence of the miscibility gap between Fe (+25.1 wt% Si) and CsCl-type FeSi, which is an isostructure with the bcc structure.

The high solubility of Si, up to 25.1 wt%, in fcc-structured Fe at temperatures above 1700 °C at 21 GPa is consistent with the results of Zhang and Guyot (1999b), but conflicts with those of Lin et al. (2002). Zhang and Guyot (1999b) conducted multi-anvil experiments using in-situ XRD measurements on Fe (+9 wt% Si) and Fe (+17 wt% Si) to 8.9 GPa and 1100 °C and

demonstrated that 9 wt% Si was incorporated in fcc-Fe at 6 GPa. They also suggested that the maximum solubility of Si in the fcc phase increased with pressure. The dissolution of 25.1 wt% Si into the fcc-Fe phase at 21 GPa is in good agreement with their observation at lower pressures that the maximum solubility can be represented by Si (wt%) = 1.95 + 1.3(±0.2) * P (GPa).

Lin et al. (2002) conducted in-situ XRD measurements using a laser-heated diamond-anvil cell to investigate the subsolidus phase relations in the Fe-rich portion of the Fe-Si system. They showed the coexistence of an Si-depleted fcc phase and an Si-enriched bcc phase in the Fe (+7.9 wt% Si) composition at 16–40 GPa, indicating that the solubility of Si in fcc-Fe is limited (less than 7.9 wt%) at high temperatures in this pressure range. They proposed a solid miscibility gap in the Fe-rich portion of the system Fe-FeSi. Further in-situ measurements are required to resolve the discrepancies.

Our study shows that Si forms an eutectic with Fe and lowers melting temperatures by 400 °C at the eutectic point relative to the melting point of pure Fe at 21 GPa. The eutectic melt contains 26 wt% Si, which is more Si-rich than that at ambient pressure. Silicon, therefore, may have been sufficiently soluble into the liquid Fe core, if the core formation occurred under reducing conditions (Kilburn and Wood 1997; Gessmann et al. 2001). The phase diagram of the iron-rich portion of the Fe-Si alloys at 21 GPa also indicates that a large amount of Si can be dissolved into solid Fe. The compositional difference is very small between the coexisting Fe-Si alloying liquid and solid (<2 wt% Si). If these trends persist to inner core pressures, the Si content in the solid inner core would be similar to that in the liquid outer core. The partitioning of Si between the liquid outer core and the solid inner core may not be consistent with the observed density deficit in the outer and inner cores, arguing Si being the only light element in the core.

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