Phase Diagrams of Fe-Si Alloys under High Pressures

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Introduction

Iron is the most abundant element in the Earth's core. However, the density of the outer core is about 10% lower than the density of iron at the pressure and temperature conditions of the outer core, indicating the presence of a low-atomic-weight component (such as H, C, O, Si, or S) in the core [1]. There is also evidence that the inner core may be less dense than pure iron and that the amount of light elements in the inner core may be about 0-3 wt% [2-4]. Silicon may be an important alloying element in the outer core, on the basis of its cosmochemical abundance and its measured thermoelastic properties [5, 6]. Silicon was excluded as the primary alloying element in the outer core on the basis of the equation of state (EOS) of the intermediate compound ε-FeSi [7]. However, studying the iron-rich portion of the Fe-Si system is more appropriate for understanding the possible effect of silicon on the EOS and crystal structure of iron under core conditions. The phase diagram of iron has been extensively studied. Body-centered cubic (bcc) iron transforms to the hexagonal close-packed (hcp) phase under high pressures, and the bcc phase transforms to the face-centered cubic (fcc) phase under high temperatures [8]. *In situ* x-ray diffraction studies to 161 GPa and 3000K demonstrate that hcp-Fe has a wide stability field extending from the deep mantle to core conditions [9]. We studied the iron-rich portion of the Fe-Si alloys in a large volume press (LVP) in order to understand the possible crystal structures and the phase diagram relevant to the Earth's core.

Methods and Materials

The starting materials, Fe4.0wt%Si and Fe7.9wt%Si alloys in the bcc structure, were obtained from Goodfellow Corporation and W. Bassett at Cornell University and were analyzed with an electron microprobe.

In situ x-ray experiments on the Fe-Si alloys were conducted in a 250-ton LVP installed at the GeoSoilEnviro Consortium for Advanced Radiation Sources (GSECARS) 13-BMD beamline at APS. The T-cup multi-anvil apparatus, consisting of eight cube-shaped anvils (10-mm edge length) made of tungsten carbide with a truncated edge length of 2 mm, was used in this study [10]. Both the starting materials (Fe4.0wt%Si or Fe7.9wt%Si alloy) and the pressure calibrant (Au) [11] were mixed with MgO powder to prevent grain growth.

The sample and the pressure calibrant were packed in separate layers in the sample chamber, which was made of a mixture of amorphous boron and epoxy resin. A $W_{0.94}Re_{0.06}$-$W_{0.75}Re_{0.25}$ thermocouple was located at the center of the sample chamber for measuring the temperature. A mixture of TiC and diamond powder (1:1 by weight) was used as the internal heater, and $LaCrO_3$ semi-sintered plates were used as thermal insulation to prevent heat loss. A white beam was used as the x-ray source, and the diffracted x-rays were collimated to 100×300 µm by slits and collected by a germanium detector at a fixed angle (2θ) of about $6°$. X-ray diffraction patterns were taken for phase identification while the sample was under high-pressure and high-temperature (high P-T) conditions. Quenched samples were carefully recovered, polished, carbon-coated, and then analyzed with a scanning electron microprobe (SEM). No reaction between MgO and the Fe-Si alloys was observed in x-ray diffraction experiments and in a SEM.

Results

We have conducted *in situ* x-ray experiments, along with chemical analyses of the quenched samples, on Fe4.0wt%Si and Fe7.9wt%Si in a LVP at about 16 GPa (Fig. 1). The bcc-Fe7.9wt%Si phase transformed to the bcc+hcp phases at ~16 GPa and 300K. When Fe7.9wt%Si was heated at ~16 GPa, the bcc+hcp phases transformed to a mixture of bcc+fcc phases. The hcp-Fe4.0wt%Si phase transformed to fcc+hcp phases under high temperatures, and, upon further heating, the fcc+hcp phases transformed to fcc-Fe4.0wt%Si only (Fig. 1). Upon pressure quench, the sample reverted to the bcc phase.

The quenched samples were then analyzed with an SEM, and the results indicate that the starting material decomposed into two chemical compositions at high P-T; the bcc phase was presumably enriched in silicon, and the coexisting hcp or fcc phase was depleted in silicon relative to the starting composition (Fig. 2).

Discussion

Compared to the phase diagram of pure iron [8, 9], it is evident that the stability field of the bcc phase can be extended to higher pressures and temperatures with the addition of silicon (Fig. 1). Three regions of the two-phase equilibria are observed: bcc+hcp, bcc+fcc, and hcp+fcc. As shown, adding silicon into iron can change
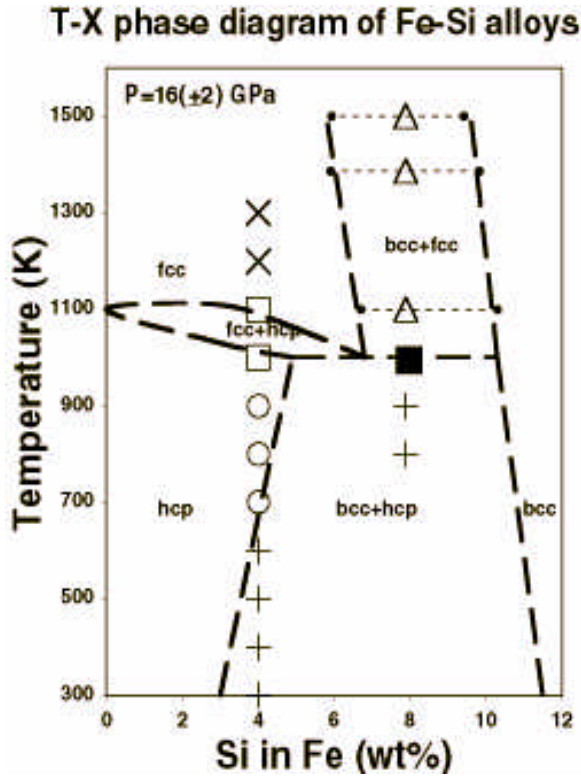
T-X phase diagram of Fe-Si alloys

FIG. 1. Schematic temperature-composition (T-X) phase diagram (black dashed lines) of iron-rich Fe-Si alloys at about 16±2 GPa. Crosses indicate bcc+hcp; open circles indicate hcp only; open squares indicate fcc+hcp; X's indicate fcc only; solid squares indicate bcc+fcc+hcp; open triangles indicate bcc+fcc; and tie lines indicate coexisting compositions in quenched samples that were analyzed by SEM. The experiments for Fe4.0wt%Si and Fe7.9wt%Si in an LVP were conducted at about 18 GPa and 14 GPa, respectively. For Fe7.9wt%Si alloy, two laser-heated diamond anvil cell experiments at 1387 and 1501K help establish the trend of the bcc+fcc phase region.

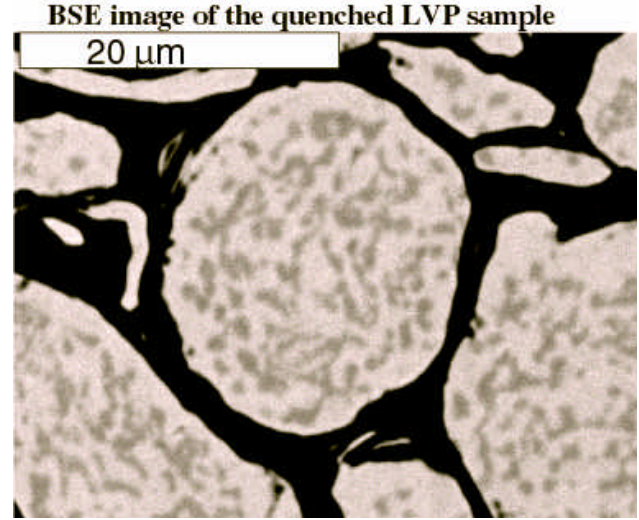## BSE image of the quenched LVP sample

FIG. 2. Back-scattered electron (BSE) image of the quenched LVP sample from 14.1 GPa and 1100K. The Si contents of the bcc and fcc phases were presumably preserved by turning off the power supply at high pressure. Chemical analyses of the sample indicate that the bcc phase contains 10.3 ±0.1 wt% silicon in dark areas and the fcc phase contains 6.7 ±0.1 wt% silicon in bright areas. Black areas are the MgO matrix. As shown, no reaction between the sample and the MgO matrix was observed in a SEM. The white bar on the picture is 20 μm.

the phase diagram of iron; the hcp to fcc phase transformation at lower silicon contents becomes a more complicated phase transition sequence at higher silicon contents (Fig. 1). The maximum solubility of silicon in the fcc phase at zero pressure is only 1.9 wt% [12], but the effect of pressure increases the solubility of silicon in the fcc phase to over 6 wt% at 16 GPa [13].

Our results show that a light element alloyed with iron can change the topology of the subsolidus phase diagram of iron under high P-T conditions. Adding silicon into iron stabilizes the bcc phase to much higher pressures and temperatures. However, only 2-4 wt% silicon is not enough to change the phase diagram of iron (Fig. 1). Therefore, if the inner core contains only 2-4 wt% silicon,

it is likely to have the hcp structure. It is also conceivable that the inner core could be a mixture of a silicon-rich bcc phase and a silicon-poor hcp phase. The existence of two phases with different compositions may influence interpretation of the observed seismic anisotropy of the inner core [14, 15].

As demonstrated in the Fe-Si alloy experiments reported on here, a small alloying component can have a large effect on the phase diagram. Since the physical properties of the liquid often mimic the properties of the corresponding solids, it is likewise possible that adding a small alloying component to liquid iron may also have a significant effect on the liquid structure of iron [16].

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