Iron-Nickel Alloy in the Earth's Core

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Introduction

Iron-nickel (Fe-Ni) alloy is the most abundant component in the Earth's core [1]. The amount of Ni in the core is about 5.5 wt%, on the basis of geochemical models [2]. The phase diagram and physical properties of Fe have been extensively studied [3]. Iron crystallizes in the bcc structure under ambient conditions, and it transforms to the hcp structure under high pressures and the fcc structure under high temperatures [4]. hcp-Fe has a wide stability field, extending to inner core conditions.

The phase diagrams of Fe-Ni alloys were previously investigated by using an externally heated diamond anvil cell (EHDAC) by Huang et al. [5, 6]. Their results suggested that fcc and hcp phases may coexist under inner core conditions [5]. If this is correct, it would be important to our understanding of the formation and properties of the inner core. However, the experiments of Huang et al. [5] were limited to the relative low pressure and temperature (P-T) range (25 GPa and 873K) of an EHDAC. Application to core conditions was made difficult by the large extrapolation in higher P-T and by the sluggishness of the hcp-fcc transition at low temperature, which limited the application of Huang et al.'s study [5] to the Earth's core. Therefore, we studied an Fe10%Ni alloy (10% indicates wt%) in a laser-heated diamond anvil cell (LHDAC) and EHDAC in order to examine the alloying effect of Ni on the Fe phase diagram. The axial ratios (c/a) of hcp-Fe10%Ni and hcp-Fe7.9%Si [7] were also determined from high P-T x-ray diffraction patterns and compared to that of hcp-Fe in order to understand the effect of Ni and Si on the c/a ratio of hcp-Fe under high P-T conditions.

Methods and Materials

The starting material, Fe10%Ni ($\pm$0.5 wt% Ni) in the bcc structure, was obtained from W. Bassett at Cornell University. A thin, flat disk of the sample, approximately 10-μm thick and 50 μm in diameter, was loaded into a DAC having a stainless-steel sample chamber that was 100 μm in diameter and 25-μm thick. A sandwiched sample configuration, which used dried NaCl as the thermal insulator and pressure medium, was used in this study [8-10].

A double-sided Nd:YLF laser heating system, operating in multimode (TEM_{00} + TEM_{01}), was used to laser heat the sample from both sides of a DAC at the GeoSoilEnviro (GSE)CARS sector at the APS [10]. The laser beam diameter was about 25 μm. Graybody temperatures were determined by fitting the thermal radiation spectrum between 670 and 830 nm to the Planck radiation function [10]. The temperature uncertainty (1σ), averaged from multiple temperature measurements and temperatures from both sides of the sample across the laser-heated spots, was about 50 to 150K in most of the experiments. A white beam was used as the x-ray source for energy-dispersive x-ray diffraction (EDXRD), or a monochromatic beam was used as the source for angle-dispersive x-ray diffraction (ADXRD). The synchrotron x-ray beam was about 8 μm in diameter. The diffracted x-rays were collected by a germanium detector at a fixed angle (2θ) of about 8° in EDXRD or by a charge-coupled device (CCD) in ADXRD. Pressures were calculated from the room temperature equation of state (EOS) of NaCl [8, 9] before laser heating. No thermal pressure corrections were made to the pressures at high temperatures in LHDAC experiments. The quenched samples from the LHDAC were polished and then analyzed with a scanning electron microprobe (SEM), the JEOL 5800-LV, at The University of Chicago.

An EHDAC was also used to study the phase transitions of Fe10%Ni [11] in ADXRD experiments. The thermal EOS of NaCl in B1 structure was used as the internal pressure calibrant [12]. These experiments involve P-T conditions that were lower but better controlled than the LHDAC experiments.

Results

The phase relations of an Fe10%Ni alloy were studied in an LHDAC cell from 30 to 86 GPa and 1200 to 2382K and in an EHDAC up to 27 GPa and 1000K (Fig. 1). bcc-Fe10%Ni transformed to the hcp phase under high pressures. Upon heating, hcp-Fe10%Ni transformed to a mixture of fcc+hcp phases under high temperatures, and upon further heating, the fcc+hcp phases transformed to the fcc phase only. The volume of the hcp phase is about 1% smaller than that of the coexisting fcc at approximately 40 GPa and 1602K. SEM analyses of the quenched sample from about 42 GPa and 1438K also show that the Ni concentration in the laser-heated area varies from 8.4 to 10.6 wt%, while the Ni concentration remains at about 10.1 $\pm$0.5 wt% in the surrounding unheated area, reflecting Ni partitioning between the hcp and fcc phases. The axial ratios (c/a) of hcp-Fe10%Ni and hcp-Fe8%Si [7] at various P-Ts were determined (Fig. 2).

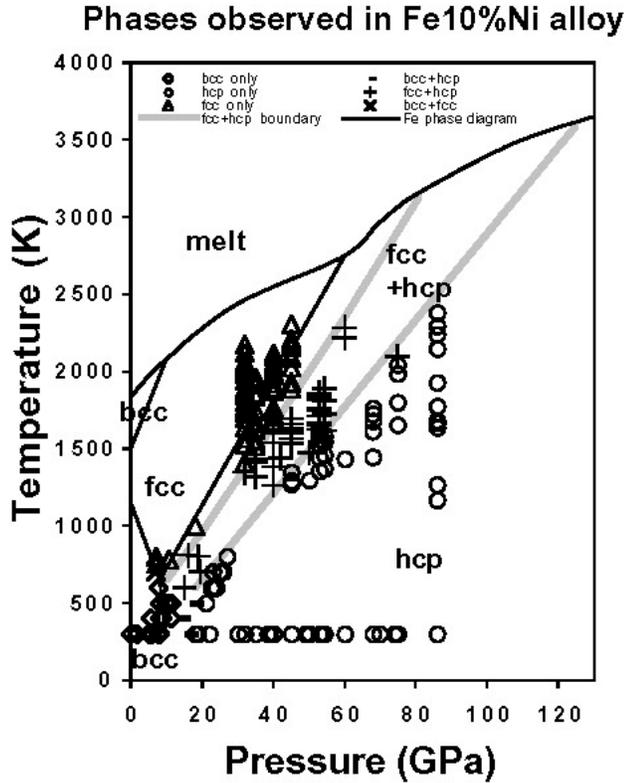## Phases observed in Fe10%Ni alloy

FIG. 1. Phases observed in LHDAC and EHDAC experiments with a starting material of Fe10%Ni. Black lines indicate the phase diagram of iron [3]; thick gray lines indicate the limits of the fcc+hcp phase region in Fe10%Ni.

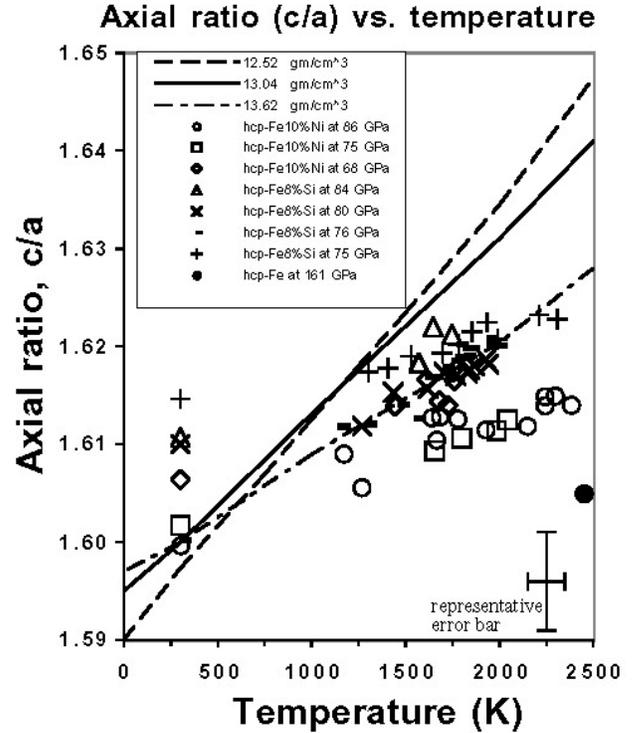## Axial ratio (c/a) vs. temperature

FIG. 2. Axial ratios (c/a) of hcp-Fe10%Ni and hcp-Fe8%Si [7] above 68 GPa as a function of temperature. Standard deviation of the c/a ratio is approximately 0.005. Estimated error bars on temperature and c/a ratio are shown in the lower right corner. Theoretical calculation for hcp-Fe at constant volume is from Ref. 14; experimental result for hcp-Fe is from Ref. 3.

Discussion

Compared to the phase diagram of pure Fe [3], it is evident that the stability field of the fcc phase can be extended to higher pressures and lower temperatures with the addition of Ni (Fig. 1). However, the effect of Ni on the phase diagram of Fe is not as dramatic as the addition of Si in Fe [7]. Nickel remains in the fcc structure under high pressures [13], and Fe transforms to the hcp structure under high pressures [3]. The difference between the phase diagrams of Ni and Fe indicates that a region of two-phase equilibrium should exist between the fcc and hcp phases of the Fe-Ni alloy under high pressures. A region of two-phase coexistence between fcc and hcp phases is observed under high P-T in this study (Fig. 1).

Extrapolating the region of two-phase coexistence to higher P-T conditions, it is seen that Fe with up to 10 wt% Ni is in the hcp structure under inner core conditions. The slope of hcp to fcc+hcp phase transformation for Fe10%Ni is steeper than that extrapolated from EHDAC experiments on Fe10%Ni [5]. The amount of Ni in the core is only about 5.5 wt% [2]. Hence, the crystal

structure of the inner core is likely to be in the hcp, if it is assumed that Ni is not strongly partitioned into the inner core and that the inner core contains only a small amount of elements other than iron [7].

The c/a ratios of hcp-Fe10%Ni and hcp-Fe8%Si decrease slightly with increasing pressure and increase substantially with increasing temperature (Fig. 2). This behavior has been recognized at relatively lower P-T conditions and was discussed previously [14]. The extrapolated c/a ratio at 5700K from a weighted least-squares linear fit of the data is approximately 1.64 for hcp-Fe10%Ni at ~86 GPa and 1.67 for hcp-Fe8%Si at ~76 GPa, lower than a theoretically predicted value of 1.7 for hcp-Fe at 5700K and inner-core pressure [14]. The c/a ratio of hcp-Fe measured experimentally at ~161 GPa and ~2450K is about 1.605, similar to that measured at lower P-T conditions [3] but inconsistent with the theoretical calculations [14]. More experiments on the c/a ratio of Fe should be conducted in order to resolve this discrepancy. The x-ray intensity of the hcp (002) diffraction decreases with increasing pressure in ADXRD experiments, indicating that the hcp crystals display preferred

orientation (or texture) at high pressures, with the c axes parallel to the loading axis of the DAC [15]. Nevertheless, according to the data of Wenk et al. [15], nonhydrostatic effects on the c/a ratio of hcp-Fe are small even under the extreme conditions of 220 GPa and 300K. The changes in the elastic constants of hcp-Fe as a consequence of an increasing c/a ratio [14] have been used to explain the seismological observations of the inner core anisotropy [16]. A lower c/a ratio would reduce the anisotropy of the hcp phase [14], which may influence the interpretation of the seismologically observed anisotropy of the inner core.

Acknowledgments

References

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