Fe-Ru and Fe-Os Phase Diagrams at High Pressures and Temperatures

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Introduction

The Earth's inner core is composed of an Fe-rich alloy. At the relevant pressure-temperature (P-T) conditions of >330 GPa and >4500K, it is widely believed that Fe exists in the hexagonal close-packed (hcp) structure [1, 2]. Many important geochemical properties of hcp-Fe, such as the solubility of light elements or metal/melt partitioning coefficients, must be established experimentally under high-temperature conditions. Unfortunately, hcp-Fe exists only at high pressure (>15 GPa) conditions, and even at moderately high pressures (15-60 GPa), the temperature range of stability of the hcp phase is limited by the stability of face-centered cubic (fcc)-Fe at higher temperatures [2]. For example, metal-sulfide melt chemistry, which is vital to our understanding of the core, cannot be studied directly by using current experimental (i.e., multianvil press) techniques, because the accessible P-T range does not overlap the conditions under which hcp-Fe coexists with a melt. Therefore, another means for experimentally constraining the high-P-T chemistry of Fe-rich hcp-metal is being sought.

We speculated that alloying Fe with other metals that prefer the hcp phase should expand the hcp stability field of the alloy relative to that of pure Fe. It has been shown that Ni, an fcc metal, enhances the stability of the fcc phase in Fe-Ni alloys, and that Si, a bcc metal, does likewise for the bcc phase in Fe-Si alloys [3, 4]. In this work, Fe-Ru and Fe-Os were chosen for study because (1) Ru and Os are hcp metals under all P-T conditions in which they have been investigated; (2) they are highly siderophile elements that will easily form alloys with Fe; and (3) Ru and Os are in the same period as Fe in the periodic table, so some continuity of their chemical properties is to be expected.

Methods and Materials

Iron powder (grain size, purity, source) was mixed with Ru black or Os powder to compositions of $Fe_{83}Ru_{17}$ and $Fe_{71}Os_{29}$. The mixtures were further blended with Al_2O_3 (50 vol %) to prevent annealing under high-P,T conditions [5].

These sample mixtures were loaded into an octahedral cell assembly for the multianvil high-pressure apparatus at beamline station 13-BM-D at the APS. The cell assembly has been described in Ref. 5. Metal powder mixtures were loaded into one of two sample chambers, each about 150-μm thick. The other chamber, positioned symmetrically on the other side of the W-Re thermocouple, contained MgO and Au to be used as an internal pressure calibrant [6]. Both the sample and the pressure calibrant were heated by using a TiC + diamond resistance heater. Pressure was administered by the 250-ton press [7] installed at the GSECARS beamline at the APS, by using a T-cup multi-anvil apparatus [8], which consisted of eight cubes of sintered tungsten carbide (WC) having truncated corners with 2.0-mm edge lengths.

X-ray diffraction experiments were performed under high-P-T conditions to establish the Fe-Ru and Fe-Os phase diagrams by monitoring the crystal structure of the samples. X-ray access to the sample was made through the gaps between the WC cubes. Energy-dispersive x-ray spectra were collected over the energy range of 25 to 130 keV by using a Ge solid-state detector. The diffraction angle was fixed at either 5.4° or 6.0° for each experiment. Alignment of the x-rays with the sample was facilitated by a transmitted x-ray imaging system [5].

At the beginning of each experimental run, the metal sample mixture was alloyed under high-P-T conditions. The Fe powder could be seen to transform from the bcc structure to the hcp structure as the pressure was increased to the desired level [5]. The sample was then heated until alloying was observed between Fe and Ru or Os; this was manifest in a pronounced increase in the observed lattice parameters of the Fe-rich hcp alloy and a decrease in the intensity of hcp Os metal (pure Ru metal was not observed because the starting material was amorphous). Typically, temperatures of 1100°C or greater were necessary for suitably rapid alloy formation.

When the alloying was complete, the phase diagram determinations began. Temperatures were ordinarily changed in steps of 50 or 10°C. At each new temperature, an x-ray diffraction spectrum of 300-second duration, was collected from the sample and from the Au pressure calibrant. Then a series of consecutive 300-second diffraction spectra were collected from the sample to determine whether or not a phase change or reequilibration was in progress. At the onset of a phase change, or during reequilibration at a new temperature in the two-phase hcp + fcc field, the sluggish kinetics of these metal systems were clearly evident in the time evolution of the diffraction spectra. Specifically, the diffraction peak intensities were observed to vary as the relative proportions of the two phases changed, and the lattice parameters were also observed to slowly migrate

according to the changing composition of the coexisting fcc and hcp phases. Efforts were made to equilibrate the sample to every extent practical during the experiments, in order to monitor the progress of the reactions in the diffraction spectra. The phase transition kinetics were most sluggish at low temperatures, and at temperatures below ~1000°C, the samples were sometimes held under fixed P-T conditions for an hour or more. In some cases, an intermediate phase having a B1-related crystal structure appeared temporarily during phase transitions; however, this phase generally vanished with continued equilibration.

Each experimental run consisted of a series of heating/cooling cycles at a few different pressures, in an effort to obtain sufficient coverage in P-T space to establish the hcp/hcp + fcc and hcp + fcc/fcc phase boundaries. At the end of each run, the sample was brought to a P-T point of interest in the two-phase region, held there to allow equilibration, and then quenched and decompressed. The recovered samples were mounted and polished for examination by optical and electron microscopy and microanalysis by energy-dispersive x-ray spectroscopy.

Results

The phase diagram of $Fe_{83}Ru_{17}$ was determined up to 16 GPa and 1150°C. These results are shown in Fig. 1. In this composition, the hcp/hcp + fcc phase boundary is nearly parallel to the hcp/fcc transition boundary in the pure Fe phase diagram, but it is uniformly 225°C higher. Likewise, the hcp + fcc/fcc boundary in $Fe_{83}Ru_{17}$ is also parallel to the Fe hcp/fcc boundary, but it is 400°C higher.

The phase diagram of $Fe_{71}Os_{29}$ was determined up to 15 GPa and 1300°C. These results are shown in Fig. 2. In this composition, the hcp/hcp + fcc phase boundary is subparallel to the hcp/fcc transition boundary in the pure Fe phase diagram, but it is higher in temperature by 700°C. The hcp + fcc/fcc boundary in $Fe_{71}Os_{29}$ occurs at temperatures higher than those attained in this set of experiments.

Discussion

The demonstrated expansion of the hcp field in Fe-rich alloys (Figs. 1 and 2) is sufficient to permit experimental investigations of a wide range of physical and chemical properties that are relevant to studies of the Earth's core. For example, the eutectic temperature of the Fe-FeS system is in the hcp-only field of the $Fe_{83}Ru_{17}$ phase diagram for pressures greater than ~14 GPa, and it is in the hcp-only field of $Fe_{71}Os_{29}$ above ~5 GPa. This will allow metal/melt partitioning experiments between the hcp alloy and the coexisting melt for the first time. The solubility of candidate alloying light elements in the core, such as S, O, C, and Si, can also be determined in the hcp
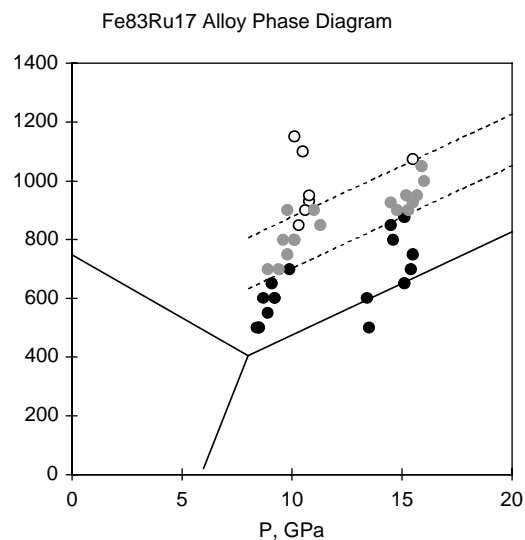

FIG. 1. Phase diagram of $Fe_{83}Ru_{17}$ alloy determined by synchrotron x-ray diffraction under in situ high-P-T conditions. The addition of 17 at. % Ru increased the temperature at which the fcc phase appears by approximately 225°C, and the hcp phase persists in a two-phase region up to 400°C higher than its limit in the pure Fe system. Open circles = fcc phase only; closed circles = hcp phase only; gray circles = both fcc and hcp phases observed; solid lines = Fe phase diagram [5]; dashed lines = estimated alloy phase boundaries.

phase. Other relevant material properties that would be geophysically interesting to measure in Fe-rich hcp alloys might include thermal conductivities, chemical diffusivities, and elastic parameters.

For more general application of the Fe-Ru and Fe-Os phase diagrams to geochemical investigations of Fe-rich hcp alloys, it will be necessary to better constrain the compositional dependence of the phase boundaries by further studies that employ different alloy compositions. For example, $Fe_{71}Os_{29}$ has a broader hcp-stable region than $Fe_{83}Ru_{17}$ (Figs. 1 and 2), but it has not yet been established whether this reflects an inherently stronger effect with Os as opposed to Ru or it simply reflects the greater concentration of the alloying component. Extension of the diagrams to higher pressures, and particularly to higher temperatures, would also expand their applicability.

Acknowledgments

Fe71Os29 Alloy Phase Diagram

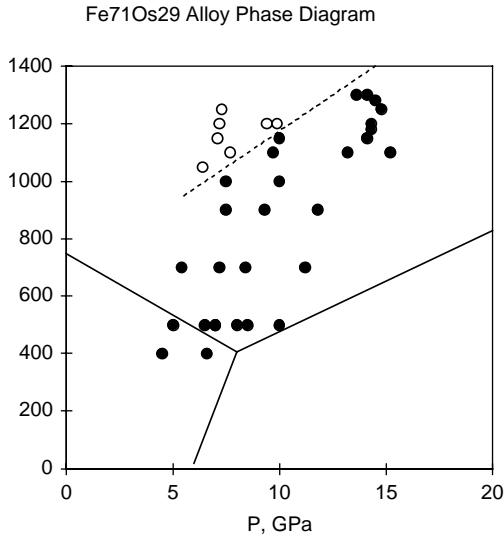*FIG. 2. Phase diagram of Fe$_{71}$Os$_{29}$ alloy determined by synchrotron x-ray diffraction under in situ high-P-T conditions. The addition of 29 at. % Os increased the temperature at which the fcc phase appears by approximately 700°C, and the hcp phase persists in a two-phase region beyond that. Open circles = fcc phase only; closed circles = hcp phase only; gray circles = both fcc and hcp phases observed; solid lines = Fe phase diagram [5]; dashed lines = estimated alloy phase boundaries.*

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