

Fe-Os and Fe-Ru 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 conditions of >330 GPa and >4500 K, 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 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 using current experimental (i.e., multi-anvil press) techniques, because the accessible P,T range does not overlap the conditions under which hcp-Fe coexists with a melt. Therefore another means is sought by which the high-P,T chemistry of Fe-rich hcp-metal can be experimentally constrained.

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 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 Material

Iron powder was mixed with Ru or Os powder to the desired binary alloy compositions. The mixtures were further blended with Al₂O₃ (50% by volume) to prevent annealing under high-P,T conditions [5].

These sample mixtures were loaded into an octahedral cell assembly for the multi-anvil high pressure apparatus at the Advanced Photon Source beamline 13-BM-D. The cell assembly has been described by [5]. Metal powder mixtures were loaded into one of two sample chambers, each about 150 μ m 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 sample and pressure calibrant were heated using a TiC+diamond resistance heater. Pressure was administered by the 250 ton press [7] installed at the GSECARS beamline at the APS, using a T cup multi-anvil apparatus [8], which consisted of 8 cubes of sintered 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 25-130 keV 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 100 °C. At each new temperature an x-ray diffraction spectrum, of 300 s duration, was collected from the sample and from the Au pressure calibrant. Then a series of consecutive 300 s diffraction spectra were collected from the sample to determine whether or not a phase change or re-equilibration was in progress. At the onset of a phase change, or during re-equilibration 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, monitoring the progress of the reactions in the diffraction spectra. Of course 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 $\text{Fe}_{90}\text{Os}_{10}$ was determined up to 15 GPa and 1300 °C, and these results are shown in Fig. 1. In this composition the hcp+fcc/fcc phase boundary is subparallel to the hcp/fcc transition boundary in the pure Fe phase diagram, but is higher in temperature by ~550 °C. The cooling cycle in these experiments occurred too rapidly to permit accurate determination of the hcp-in temperature during cooling. This sluggishness of the fcc-to-hcp transition has been observed previously [2,5]. The hcp/hcp+fcc boundary in $\text{Fe}_{90}\text{Os}_{10}$ occurs at temperatures too low to be accurately determined in this set of experiments.

Discussion

These results, combined with those reported earlier [9], demonstrate that the addition of Ru or Os to Fe stabilizes the hcp structure of Fe-rich alloys to lower pressures and higher temperatures. The expansion of the hcp field in Fe-rich alloys (Figs. 1) is sufficient to permit experimental investigations into 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 $\text{Fe}_{83}\text{Ru}_{17}$ phase diagram for pressures greater than ~14 GPa, and in the hcp-only field of $\text{Fe}_{71}\text{Os}_{29}$ above ~5 GPa; this will allow metal/melt partitioning experiments between hcp alloy and 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 phase. Other relevant material properties that would be geophysically interesting to measure in Fe-rich hcp alloys might include thermal conductivity, chemical diffusivities, and elastic parameters. Preliminary work applying these results have been reported [10].

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References

- [1] R. Boehler, *Nature* **363**, 534-536 (1993).
- [2] G. Shen, H.-K. Mao, R. J. Hemley, T. S. Duffy, M. L. Rivers, *Geophys. Res. Lett.* **25**, 373-376 (1998).
- [3] J.-F. Lin, D. L. Heinz, A. J. Campbell, J. M. Devine, G. Shen, *Science* **295**, 313-315 (2002).
- [4] J.-F. Lin, D. L. Heinz, A. J. Campbell, J. M. Devine, W. Mao, G. Shen, *Geophys. Res. Lett.* **29**, 10.1029/2002GL015089 (2002).
- [5] T. Uchida, Y. Wang, M. L. Rivers, S. R. Sutton, *J. Geophys. Res.* **106**, 21799-21810 (2001).
- [6] S.-H. Shim, T. S. Duffy, T. Kenichi, *Earth Planet. Sci. Lett.* **203**, 729-739 (2002).
- [7] Y. Wang, M. Rivers, S. Sutton, P.Eng, G. Shen, I. Getting, *Rev. High Pressure Sci. Technol.* **7**, 1490-1495 (1998).
- [8] M. T. Vaughan, D. J. Weidner, Y. Wang, J. Chen, C. Koleda, I. Getting, *Rev. High Pressure Sci. Technol.* **7**, 1520-1522.
- [9] A. J. Campbell, Y. Uchida, J. M. Devine, Y. Wang, APS Activity Report 2002.
- [10] A. J. Campbell, M. Moses, Y. Fei, *Amer. Geophys. Union Fall Meeting* (2004).

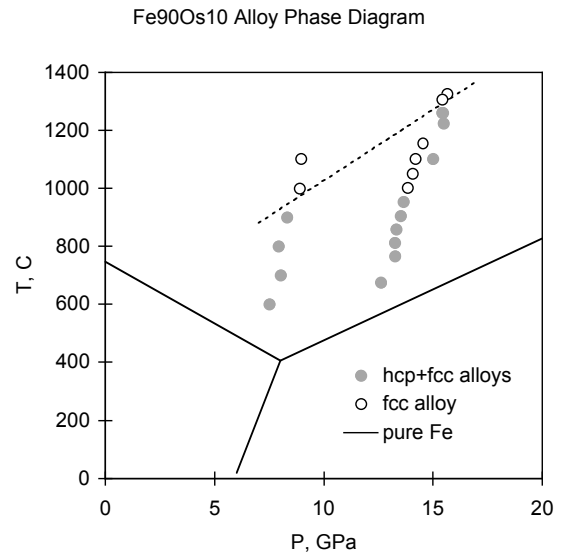


Fig. 1 Phase diagram of $\text{Fe}_{90}\text{Os}_{10}$ alloy determined by synchrotron x-ray diffraction under in situ high pressure-temperature conditions. The addition of 10 at% Os increased the temperature to which the hcp phase persists by approximately 550 °C relative the pure Fe system. Open circles: fcc phase only; gray circles: both fcc and hcp phases observed; solid lines: Fe phase diagram [5]; dashed lines: estimated alloy phase boundaries. The cooling cycle at 14 GPa was too rapid for accurate determination of the hcp-in temperature.