

PHASE DIAGRAM OF THE SYSTEM Fe-FeO AT HIGH PRESSURE

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Fe-FeO at atmospheric pressure The 1 atm. phase diagram of Fe-FeO contains a large liquid immiscibility region (LIR). The solubility of molten FeO in Fe has been studied experimentally as a function of temperature and the high quality of the data permits a reasonable extrapolation to higher temperatures (1). Such extrapolation indicates a solubility in excess of 20 wt% FeO in molten iron at 3200K and atmospheric pressure. This is over half the amount calculated to be present in the earth's outer core, if oxygen is considered to be the sole light element (2). The complete miscibility of Fe and FeO at high temperature is also a reasonable supposition based on the behaviour of other first-row transition metal oxide systems (1).

Fe-FeO at high pressure No direct experimental determination has been made of the phase diagram of Fe-FeO at elevated pressure, but a schematic phase diagram can be constructed by consideration of the effect of pressure upon end-member melting points, upon the extent of the LIR and upon eutectic temperatures and compositions.

The experimental measurements of the effect of pressure on the melting points of Fe and FeO can be extrapolated to higher pressure using various melting laws. It is found that the melting point of FeO lies above that of Fe for all pressures above approximately 4 GPa, and the effect of a high pressure phase transformation in FeO (3,4) is to further increase the discrepancy between the melting temperatures of Fe and FeO. Although extrapolations involve substantial absolute uncertainty, the more refractory character of FeO relative to Fe at high pressure is not in doubt.

In a general sense, the immiscibility between liquid Fe and FeO reflects an incompatibility in bond character between the end-member melts, and indirectly, a similar disparity in bond type between the corresponding crystalline phases. The high-pressure phase transformation in FeO is likely to have a significant effect on the phase diagram of Fe-FeO because of the probable covalent nature of the bonding in the high-pressure phase (hpp) (4). The melt formed from FeO (hpp) is likely to become more structurally compatible with the liquid iron melt as pressure increases, resulting in a depression or even closing of the liquid miscibility gap. As a detailed quantitative analysis of the decrease of the LIR with pressure is still lacking, we shall assume only that the temperature at the top of the LIR remains constant with increasing pressure.

The variation of the eutectics in the system Fe-FeO with pressure can be assessed on the basis of thermodynamic considerations. It has been calculated that dT/dP for a binary eutectic is reduced from dT/dP of the melting points of the pure end-members by a term related to the entropy of mixing in the liquid state (5). This has been confirmed experimentally in a number of binary systems, including Fe-FeS (6).

On the basis of the above considerations, a series of schematic phase diagrams of the system Fe-FeO at high pressure has been constructed. With increasing pressure, the melting point of FeO rises above the melting point of Fe and a new phase region consisting of FeO (B1) + metallic liquid forms. The temperature of the Fe-rich eutectic increases more slowly with pressure than the melting point of Fe, which causes a more pronounced lowering of the

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melting temperature of Fe by solution of oxygen. The Fe-rich eutectic is displaced towards more oxide-rich compositions and the eutectic near pure FeO is correspondingly displaced towards less FeO-rich compositions. As pressure increases, several factors contribute to a contraction of the liquid immiscibility field:

- (1) an upward displacement of the melting points of Fe and FeO relative to the top of the liquid immiscibility region which is assumed to remain fixed,
- (2) a more rapid increase with pressure of the melting points of Fe and FeO relative to the eutectic temperatures,
- (3) a progressive displacement of the eutectic compositions towards the liquid immiscibility region.

The pressure scale for this series of schematic phase diagrams depends critically upon ΔV , the difference in FeO molar volume between the metallic and non-metallic liquids which is very poorly known. General experience concerning pressure-induced structural changes in melts suggests that the contraction of the liquid immiscibility region will occur gradually over a wide pressure interval, but perhaps at an accelerated pace once pressure is increased beyond that required for the solid-state phase transformation. With the onset of complete liquid miscibility, the Fe-FeO phase diagram becomes qualitatively similar to that for the Fe-FeS system at atmospheric pressure.

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