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Fe-O-Zn (Iron-Oxygen-Zinc)

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The early results on this ternary system were reviewed by [1989Rag], who presented a tentative isothermal section at 900 °C. Recently, Hayes and coworkers [2000Jak, 2001Deg, 2004Han, 2005Han] reinvestigated the system under different experimental conditions: (i) at metallic iron saturation, (ii) in air, and (iii) at oxygen pressures that lie between (i) and (ii).

Binary Systems

The Fe-O phase diagram [1991Wri] exhibits the following compounds. Wustite (FeO) is a metal-deficient monoxide with the *B*1, NaCl-type cubic structure. Magnetite (Fe_3O_4) has the $H1_1$, Al_2MgO_4-type cubic structure. Hematite (αFe_2O_3) is $D5_1$-type rhombohedral. Other less-common polymorphic forms of the above compounds are known [1991Wri]. In the Fe-Zn system [Massalski2], several intermediate phases are known in the zinc-rich region. In the Zn-O system, zincite (ZnO) has a hexagonal structure, space group $P6_3mc$. A cubic monoxide ZnO is stable at high pressures. ZnO_2 has the FeS_2, pyrite-type cubic structure.

Ternary Phase Equilibria

Starting with high purity powders of FeO, ZnO, and Fe (99.5 mass% purity) [1993Ito] prepared briquettes, which were sealed in evacuated quartz tubes, annealed at 827 °C for 3-7 d and quenched in water. The phases were identified with x-ray powder diffraction and the phase compositions were measured with an electron probe microanalyzer (EPMA). Using a stabilized zirconia solid electrolyte, [1993Ito] measured the partial pressures of oxygen by the emf method. The composite isothermal section at 827 °C constructed by [1993Ito] in the Fe-Fe_2O_3-ZnO-Zn region is shown in Fig. 1. The phase distribution is very similar to the tentative isothermal section at 900 °C presented by [1989Rag]. In the three-phase equilibria of (Fe), (Zn), and ZnO, (Fe) contains 38.6 at.% Zn, liquid Zn has 11 at.% Fe and ZnO dissolves 0.46 at.% Fe. Magnetite (Fe_3O_4) and zinc ferrite ($ZnFe_2O_4$) form a continuous solid solution. Hematite (Fe_2O_3) dissolves negligible amount of Zn.

At metallic iron saturation, the phase equilibria of this ternary system were investigated by [2000Jak]. With starting materials of ZnO and Fe of 99.5 mass% purity, [2000Jak] first prepared ZnO pellets by sintering ZnO powder at 1500 °C in air. The pellets were then surrounded by Fe powder and the assembly was annealed between 900 and 1200 °C in high-purity N_2. This diffusion-couple type arrangement resulted in the formation of wustite next to the outer Fe layer and zincite (ZnO with dissolved Fe) below it. The coexisting compositions at the wustite-zincite interface were measured with EPMA and listed.

The phase equilibria in air (0.21 atm of O_2 and 1 atm of total pressure) were investigated by [2001Deg] and [2004Han]. Starting with oxide powders of Fe_2O_3, ZnO and Fe of 99.5 mass% purity, [2001Deg] pelletized and equilibrated powder mixtures between 900 and 1500 °C for annealing times of 18-240 h. The samples were quenched in a flow of air or in iced water. The phase equilibria were studied with optical and scanning electron microscopy. The phase compositions were determined by EPMA. The EPMA results yield only the total Fe content, without distinguishing between ferrous and ferric ions.

In their study of the ZnO-rich region in air, [2004Han] carried out x-ray diffraction studies of the ZnO-rich phase to ascertain whether a second polymorph or an independent phase existed in this region. They concluded that there was only one ZnO phase (hexagonal symmetry, $P6_3mc$ space group). Also, to determine the ferrous and ferric ion concentrations, they carried out wet chemical analysis using the ammonium metavanadate technique. They found that iron oxide dissolved in zincite was mainly of the ferric form. The solubility of iron oxide in zincite increases rapidly above 1200 °C. Also, the morphology of the zincite crystals changes from a rounded shape to a plate-like shape above 1200-1300 °C, the latter shape being beneficial for the sinter performance during smelting.

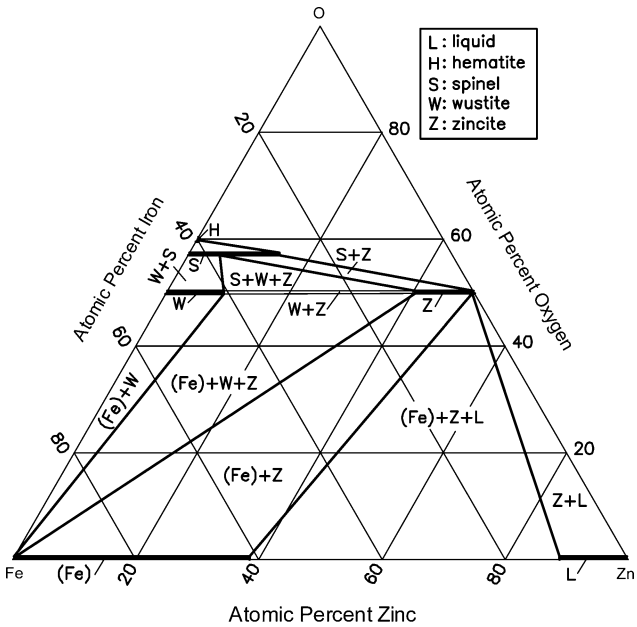

Fig. 1 Fe-O-Zn isothermal section at 827 °C [1993Ito]

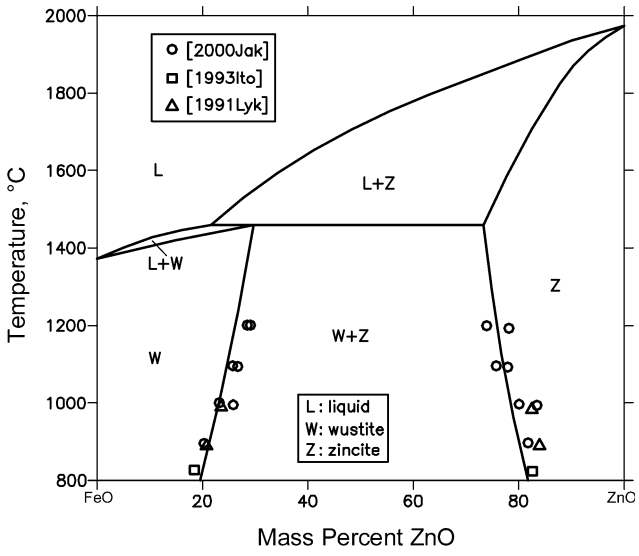

Fig. 2 FeO-ZnO computed vertical section at metallic iron saturation [2001Deg]

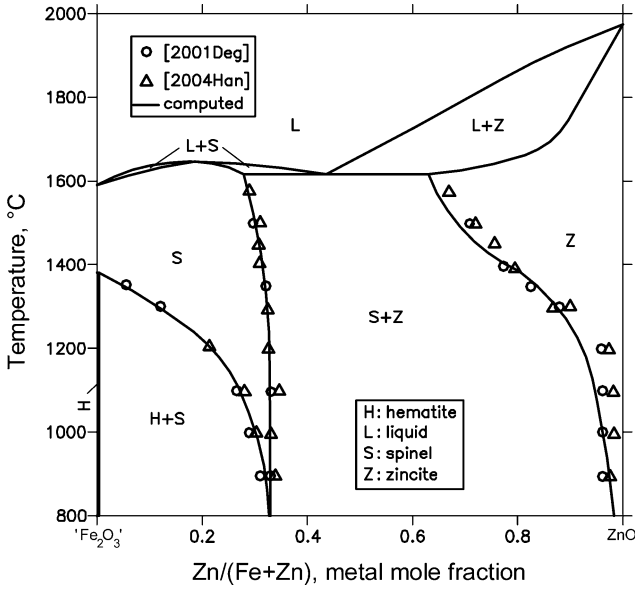

Fig. 3 Fe_2O_3-ZnO computed pseudo-binary section in air [2004Han]

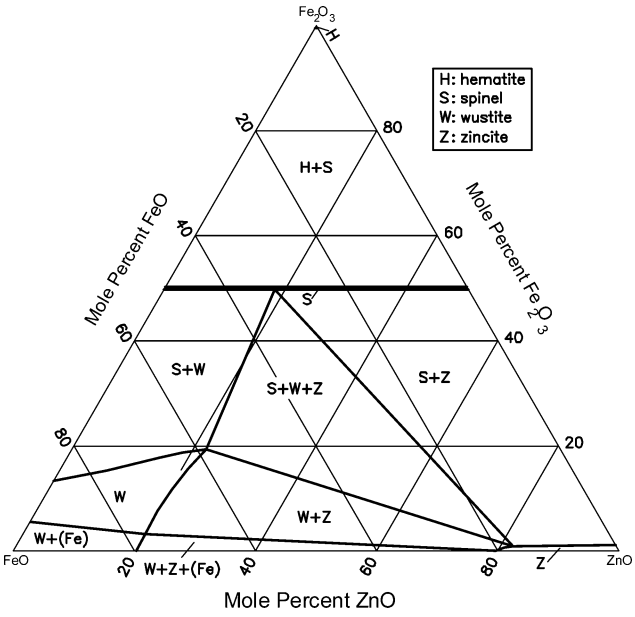

Fig. 4 Fe-O-Zn computed isothermal section at 900 °C on the FeO-Fe_2O_3-ZnO plane [2001Deg]

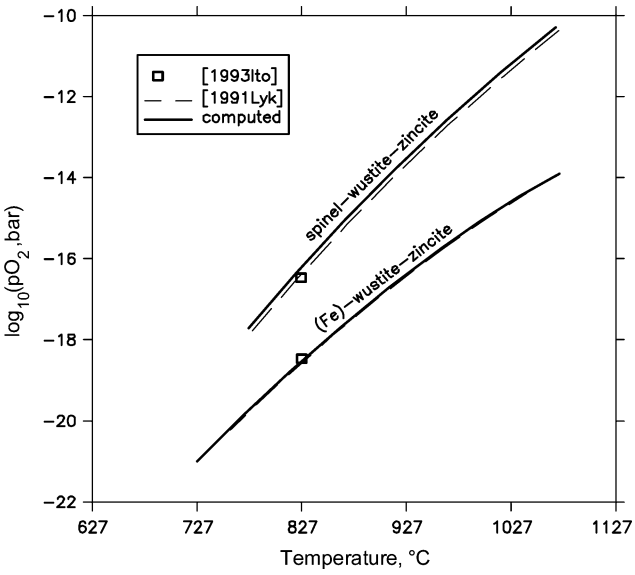

Fig. 5 Fe-O-Zn computed oxygen partial pressures for the indicated three-phase equilibria [2001Deg]

A thermodynamic description for the FeO-Fe_2O_3-ZnO region was developed by [2001Deg] for calculating the phase equilibria. A quasi-chemical model was used for the liquid oxide phase (slag). The spinel structure was described with a three sublattice model. The oxygen anions stay on the fcc sites. The two cations were assumed to be distributed on both the octahedral and the tetrahedral sites. The magnetic contribution to the Gibbs energy was taken into account. For describing the wustite and zincite solution phases, FeO, ZnO, and Fe_2O_3 were taken as the components.

The vertical section calculated by [2001Deg] along the FeO-ZnO join at iron saturation is shown in Fig. 2, along with experimental data of [2000Jak] and earlier workers. Agreement with the experimental results is good. Substantial mutual solid solubility between FeO and ZnO is seen, which increases with increasing temperature. It may be noted that Fe is an additional equilibrium phase in the phase fields in Fig. 2. Figure 3 shows the calculated pseudo-binary section along the ZnO-Fe_2O_3 join [2004Han]. The experimental data of [2001Deg] and [2004Han] show good

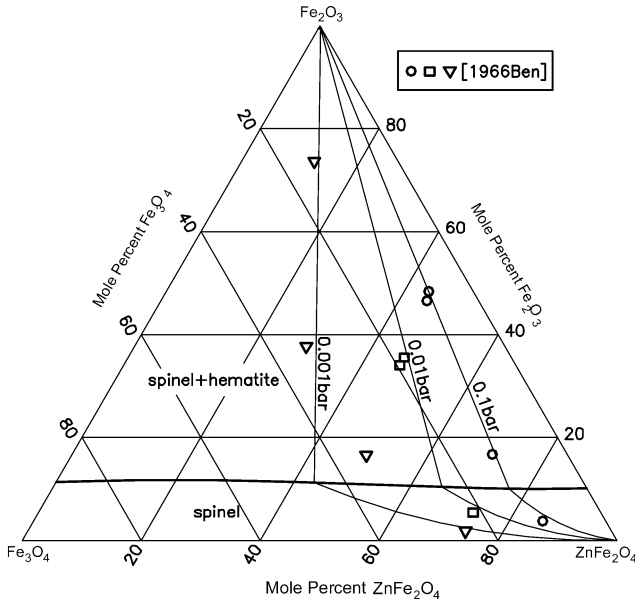

Fig. 6 Fe-O-Zn computed equilibria between spinel and hematite at 1100 °C [2001Deg]

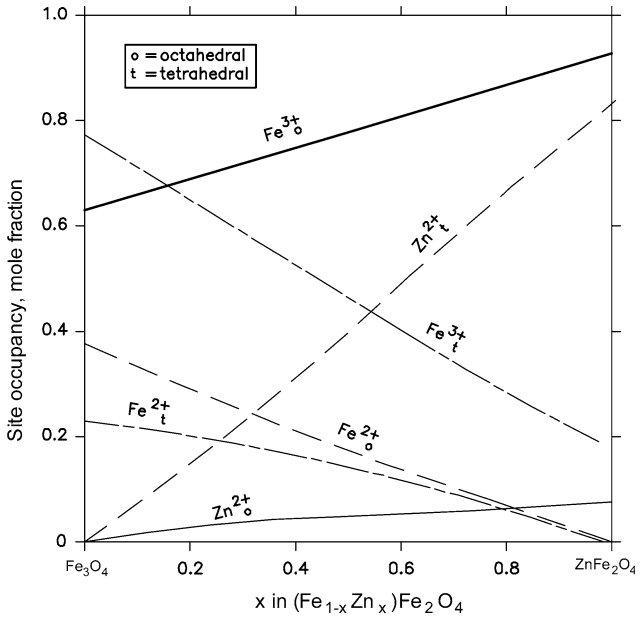

Fig. 7 Fe-O-Zn computed octahedral/tetrahedral distribution of Fe^{2+}, Fe^{3+}, and Zn^{2+} ions in spinel at 900 °C [2001Deg]

agreement with the computed phase diagram. Figure 4 is the calculated isothermal section at 900 °C on the FeO-Fe_2O_3-ZnO plane [2001Deg]. Fe_2O_3 and $ZnFe_2O_4$ form a continuous solid solution. Zincite dissolves a small amount of Fe_2O_3. Figure 5 shows the comparison between calculated and experimental oxygen partial pressures as a function of temperature for the three-phase equilibria of (spinel + wustite + zincite) and (iron + wustite + zincite). Figure 6

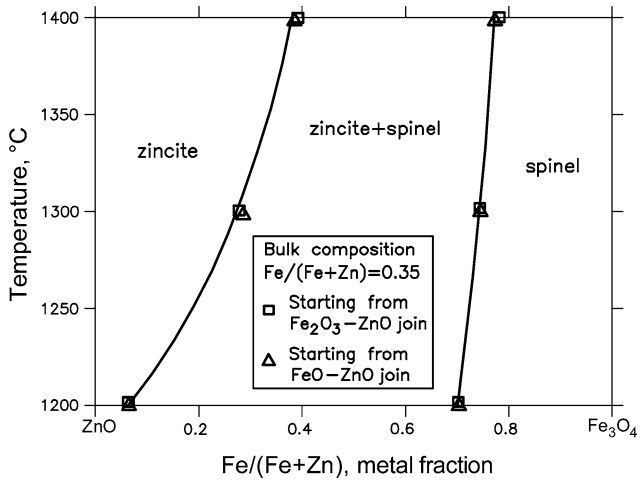

Fig. 8 Fe_3O_4-ZnO pseudo-binary section at $pO_2 = 10^{-6}$ atm [2005Han]

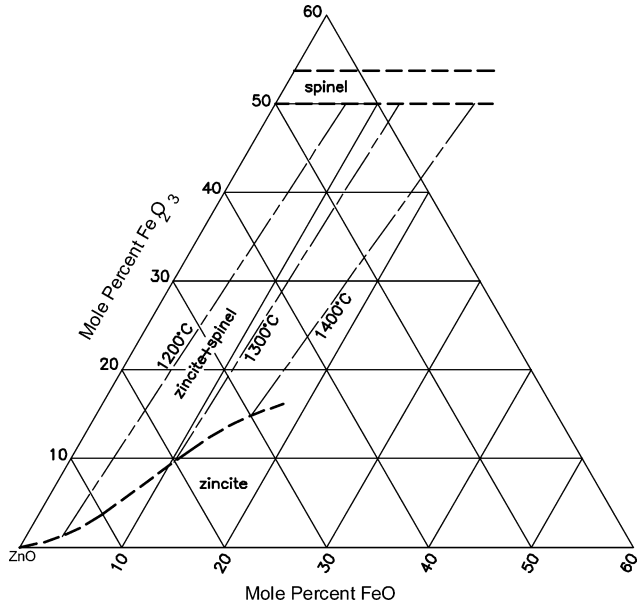

Fig. 9 Fe-O-Zn equilibria between zincite and spinel at $pO_2 = 10^{-6}$ atm and at the indicated temperatures [2005Han]

is an isothermal section at 1100 °C depicting the calculated equilibria between spinel and hematite. The comparison with the experimental data shows good agreement. The predicted octahedral/tetrahedral distribution of Fe^{2+}, Fe^{3+}, and Zn^{2+} ions in spinel at 900 °C is shown in Fig. 7.

For oxygen partial pressures that lie between iron-saturation and air, [2005Han] determined the phase equilibria between 1200 and 1400 °C and between $pO_2 = 10^{-4}$ and 10^{-10} atm. The fixed O_2 pressures were maintained during annealing by flowing known gas mixtures of $H_2/N_2/CO_2$ or CO/CO_2. The phase equilibria were studied with optical microscopy and electron probe microanalysis. The ferrous/ferric ion concentrations were obtained from wet

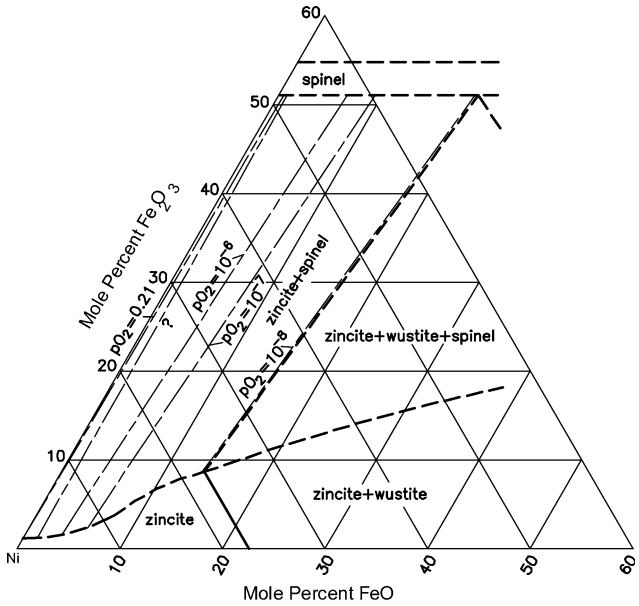

Fig. 10 Fe-O-Zn isothermal section at 1200 °C, showing the pO_2 isobars (atm) [2005Han]

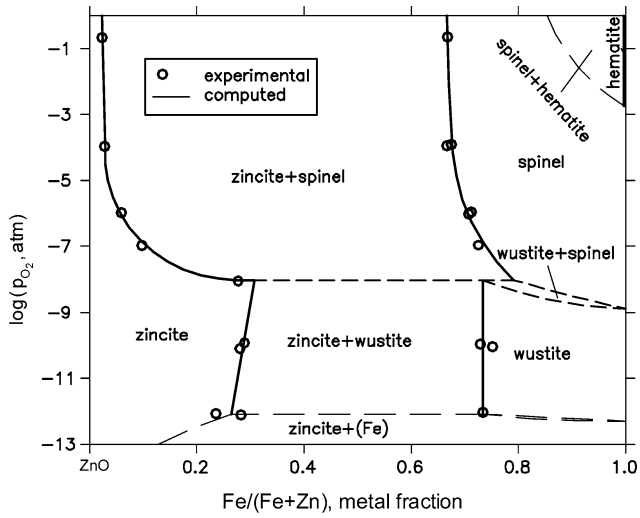

Fig. 11 Fe-O-Zn computed isothermal section at 1200 °C as a function of pO_2 (atm) [2005Han].

chemical analysis. The pseudo-binary section along the ZnO-Fe_3O_4 join constructed by [2005Han] at $pO_2 = 10^{-6}$ atm is shown in Fig. 8. Figure 9 is an isobaric section at $pO_2 = 10^{-6}$ atm, with the experimental tie-lines between zincite and spinel at 1200, 1300, and 1400 °C. Both ferrous and ferric ion concentrations in zincite increase with increasing temperature. Figure 10 depicts the isothermal section at 1200 °C, showing the experimental pO_2 isobars. The isobar of 10^{-8} atm lies close to the three-phase region of (wustite + zincite + spinel). A full calculated isothermal section at 1200 °C is shown in Fig. 11 as a function of pO_2 (atm) (total pressure = 1 atm) [2005Han].

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