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Fe-Ni-O (Iron-Nickel-Oxygen)

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The early results on this ternary system were reviewed by [1989Rag], who presented partial isothermal sections at 1540 and 1000 °C, a schematic liquidus projection and a reaction scheme. Subsequently, [1990Sch] investigated this system, using high-temperature *in situ* coulometric titration with solid oxygen ion electrolyte. At 1000 °C, they determined the boundaries of the wustite and spinel fields, as well as the nonstoichiometry of the monoxide $(Ni,Fe)_{1-\delta}O$. [1995Luo] carried out a thermodynamic analysis of the system and presented computed full isothermal sections at 1540 and 1000 °C. Recently, [2008Rha] studied the subsolidus region of this system.

Binary Systems

In the Fe-Ni phase diagram, a continuous face-centered cubic (fcc) solid solution (denoted γ) forms between γFe and Ni and is stable over a wide range of temperature. The Fe-O phase diagram [1991Wri] exhibits the following compounds. Wustite (FeO) is a metal-deficient monoxide with the $B1$, 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 Ni-O system [1984Neu], a eutectic reaction occurs at 1440 °C, which yields (Ni) and NiO ($B1$, NaCl-type cubic, called bunsenite).

Ternary Phase Equilibria

[1990Sch] employed a solid state galvanic cell for coulometric titration in a stream of N_2/air or CO/CO_2 gas mixtures. The boundaries of the single-phase fields of wustite and spinel and the defect concentration in (Fe,Ni)O were determined in the temperature range of 1030-900 °C and an oxygen potential range of $-12.5 \le \log aO_2 \le -0.67$. Using their experimental results, [1990Sch] constructed an isothermal plot of metal mole fraction versus oxygen potential at 1000 °C. The solubility limit of iron ions in bunsenite was also determined by [1990Sch] between 1000 and 1380 °C from annealing experiments on powder mixtures.

[1995Luo] used the binary descriptions from the literature in their thermodynamic analysis. For the ternary liquid phase, an ionic liquid model with two sublattices (one for the cations and the other for the oxygen anions and vacancies) was used. The oxide phases were described by the compound energy formalism. The spinel phase was described with three sublattices to account for the deviation from stoichiometry. Wustite and hematite were modeled with two and three sublattices, respectively. The experimental data on the solubility of oxygen in solid nickel and on the thermodynamic properties of the compound phases were used as inputs. The optimized parameters were listed. The isothermal section at 1540 °C computed by [1995Luo] is shown in Fig. 1. The calculated compositions of the phases and the partial pressure of O_2 in the three-phase equilibria between 800 and 1100 °C agreed well with the evaluated data of [1989Rag]. The computed invariant reactions and their temperatures again showed good agreement with those given by [1989Rag].

With starting powders of 99.98% Fe_2O_3, 99.99% NiO, 99.99% Fe, and 99.8% Ni (all mass%), [2008Rha] prepared pellets under pressure. Two methods of equilibration were used: (i) gas/oxide equilibrated in open systems at fixed oxygen partial pressures, which were obtained by flowing known proportions of CO/CO_2 gas mixtures through the tube furnace, and (ii) oxide/alloy mixtures equilibrated in closed systems (in evacuated and sealed tubes). The equilibrium state was checked by using extended annealing times as well as by approaching equilibrium from opposite directions. Microstructures were examined with optical and scanning electron microscopes. The phase compositions were measured by an electron probe microanalyzer and listed. Factsage software was used to calculate the phase equilibria for comparison with the experimental results.

The pseudo-binary section in air along the Fe_2O_3-NiO join constructed by [2008Rha] is shown in Fig. 2.

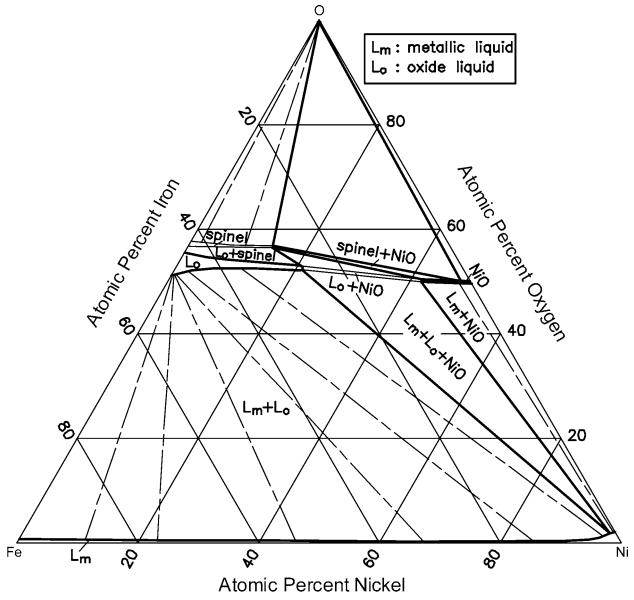

Fig. 1 Fe-Ni-O computed isothermal section at 1540 °C [1995Luo]

The calculated diagram is also shown. One of the main features in Fig. 2 is the larger solubility of Fe in (Ni,Fe)O (bunsenite) found by [2008Rha]. At 1200 °C, the solubility is 16.1 and 4.2 metal mole percent in the results of [2008Rha] and [1990Sch], respectively and 5.8 mol.% by calculation. [2008Rha] attributed the larger solubility in their studies to the improved experimental techniques used by them and a closer approach to equilibrium.

Three isothermal sections constructed by [2008Rha] at 1200, 1100, and 1000 °C are shown in Fig. 3, 4, and 5. They are plots of metal mole fraction versus the partial pressure of oxygen. In Fig. 3, the upper and lower horizontals correspond to the invariant equilibrium: (Ni,Fe)O ↔ (Fe,Ni)$_3$O$_4$ + (Ni,Fe) and (Fe,Ni)$_3$O$_4$ + (Ni,Fe) ↔ (Fe,Ni)O, respectively. As indicated above, the solubility of Fe in (Ni,Fe)O (bunsenite) measured by [2008Rha] is higher than solubilities found in earlier investigations and the calculations. The metal mole percent of Ni in alloy, spinel, and bunsenite at the upper invariant horizontal was found to be, respectively, 95.6, 25.3, and 74.2 at 1000 °C; 95.3, 23.8, and 56.4 at 1100 °C; and 92.8, 14.9, and 33.8 at 1200 °C.

In the oxide region, isothermal sections at 1200, 1100, and 1000 °C were constructed by [2008Rha] on the FeO-NiO-Fe$_2$O$_3$ plane. These are shown in Fig. 6, 7, and 8. The bunsenite and wustite phase fields expand with increasing

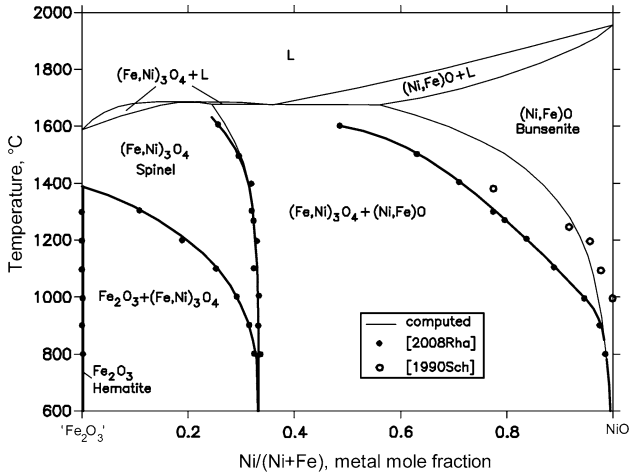

Fig. 2 Fe-Ni-O pseudo-binary section in air along the Fe_2O_3-NiO join [2008Rha]

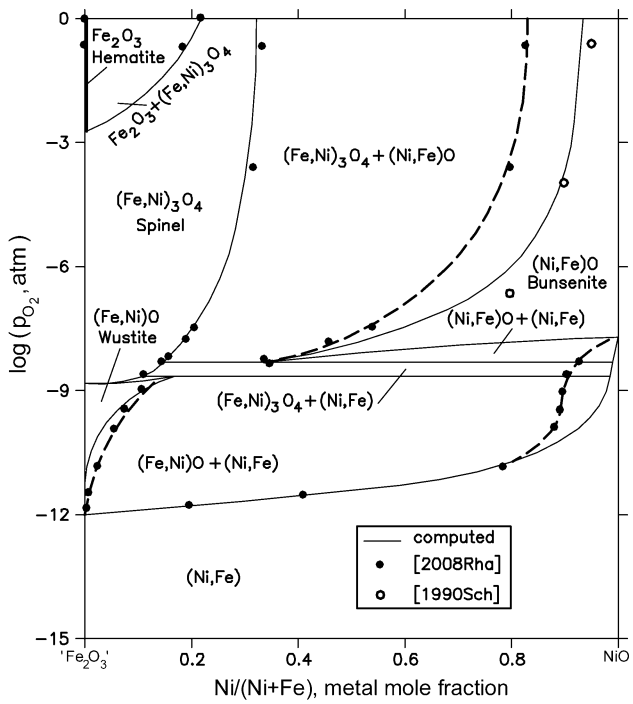

Fig. 3 Fe-Ni-O metal mole fraction vs. oxygen partial pressure at 1200 °C [2008Rha]

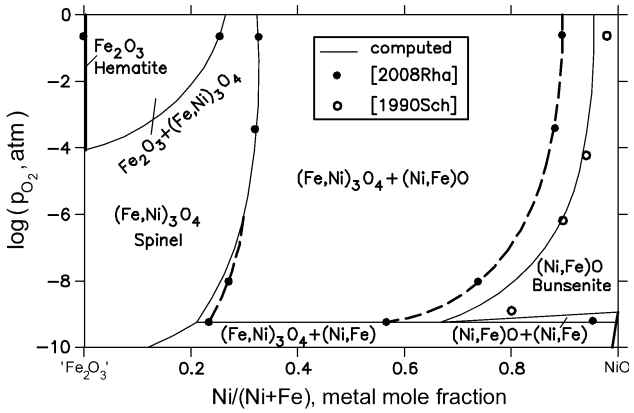

Fig. 4 Fe-Ni-O metal mole fraction vs. oxygen partial pressure at 1100 °C [2008Rha]

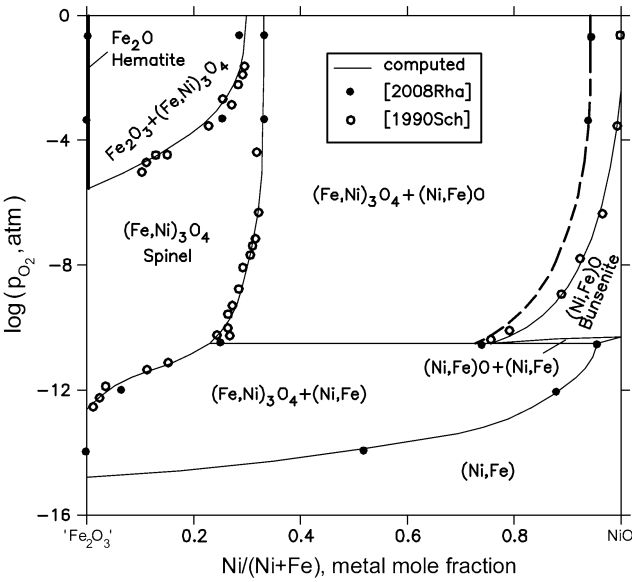

Fig. 5 Fe-Ni-O metal mole fraction vs. oxygen partial pressure at 1000 °C [2008Rha]

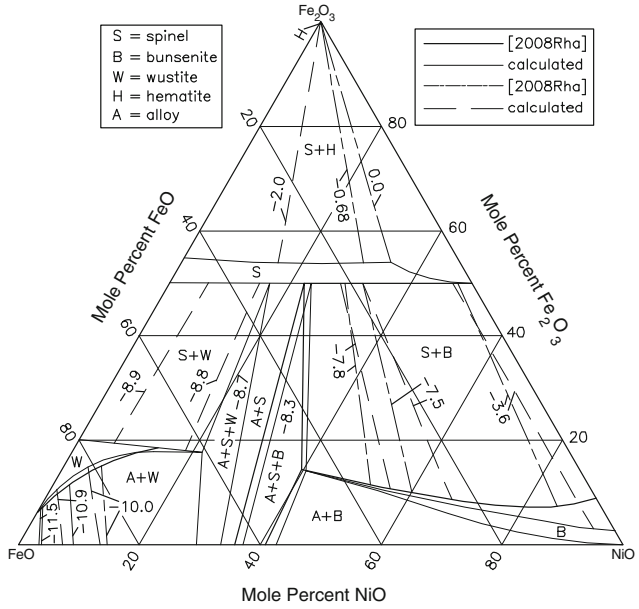

Fig. 6 Fe-Ni-O isothermal section at 1200 °C on the FeO-Fe_2O_3-NiO plane [2008Rha]. The numbers on tie-lines and tie-triangles are values of log pO_2(atm)

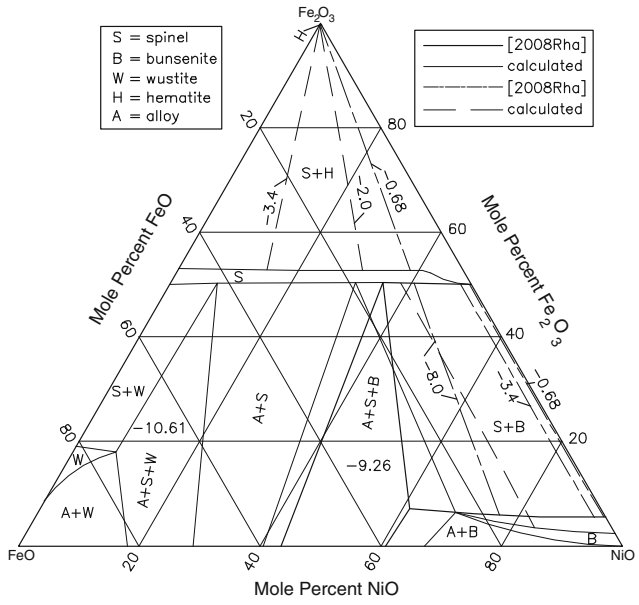

Fig. 7 Fe-Ni-O isothermal section at 1100 °C on the FeO-Fe_2O_3-NiO plane [2008Rha]. The numbers on tie-lines and tie-triangles are values of log pO_2(atm)

temperature. The non-stoichiometry of the spinel phase increases with temperature. The tie-lines (constant oxygen partial pressure lines) are shown in two-phase regions. The oxygen partial pressures corresponding to the alloy-spinel-wustite three-phase equilibrium at 1200, 1100, and

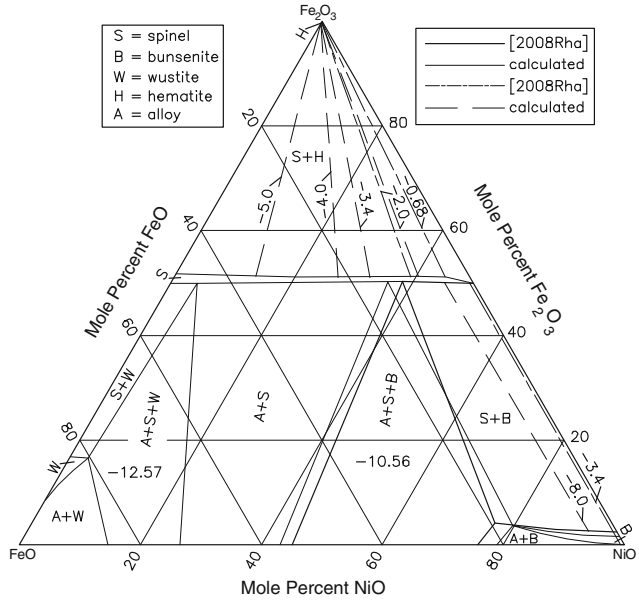

Fig. 8 Fe-Ni-O isothermal section at 1000 °C on the FeO-Fe_2O_3-NiO plane [2008Rha]. The numbers on tie-lines and tie-triangles are values of log pO_2(atm)

1000 °C are $10^{-8.7}$, $10^{-10.61}$, and $10^{-12.57}$ atm, respectively. The corresponding partial pressures for the alloy-spinel-bunsenite equilibrium are $10^{-8.33}$, $10^{-9.26}$, and $10^{-10.56}$ atm.

The calculations were done by [2008Rha], using the previously published solution database for the oxides and assuming an ideal solution between metallic Fe and Ni. A revised optimization of the solution database using the new results is desirable to validate the conclusions of [2008Rha]. Also, new experimental information on the oxidation states of Fe in the presence of nickel ions will be useful [2008Rha].

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