Fe-Ir-S (Iron-Iridium-Sulfur)

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The previous review of this system [1988Rag] reported no phase diagram information but mentioned the existence of a ternary compound $FeIr_2S_4$ with the cubic spinel structure. Recently, [1999Mak] determined three isothermal sections at 1100, 1000, and 800 °C. The above ternary compound is present at the two higher temperatures with a non-stoichiometric composition range.

Binary Systems

In the tentative Fe-Ir phase diagram [1993Swa], the Fe-based fcc phase and fcc Ir form a continuous solid solution γ, which is stable over a wide temperature range. The γ face-centered cubic (fcc) $\rightarrow$ body-centered cubic (bcc) transformation in Fe is lowered by Ir. At ~625 °C, hexagonal close-packed (hcp) ε forms congruently from γ at ~38 at.% Ir. There are two intermediate phases in the Fe-S system [1982Kub]. The monosulfide pyrrhotite $Fe_{1-x}S$ (hexagonal NiAs type) is stable at Fe-deficient (S-rich) compositions with a range of 50-55 at.% S. $Fe_{1-x}S$ with 52 at.% S melts congruently at 1188 °C. In the Fe-FeS region, the solidification is through a eutectic reaction at 988 °C. In the FeS-S region, a monotectic reaction at 1082 °C yields $Fe_{1-x}S$ of 54.2 at.% S and a sulfur-rich liquid $(S)_l$. At 743 °C, cubic FeS_2 (pyrite) forms peritectically and undergoes a transition to orthorhombic FeS_2 (marcasite) at 425 °C. The phase relations below 350 °C in the pyrrhotite region are complex with the occurrence of several ordered forms. In the Ir-S system, there are three intermediate phases: Ir_2S_3 (Rh_2S_3 type orthorhombic), IrS (complex orthorhombic) and $IrS_{~3}$ (Rh_3Se_8 type hexagonal) [Pearson3]. A eutectic reaction $L \leftrightarrow$ (Ir) + Ir_2S_3 has been reported at 45 at.% S and at 2000 ± 100 °C [1992Fis].

Ternary Isothermal Sections

Using starting materials of Fe (15-20 ppm of metallic impurities), 99.995% Ir and 99.999% S, [1999Mak] melted 113 alloy compositions in evacuated tubes, which were annealed for 2-5 weeks and quenched. The phase equilibria were studied by microscopy and electron probe microanalysis. Three isothermal sections at 1100, 1000, and 800 °C were determined. These sections are redrawn in Fig. 1-3. At 1100 °C (Fig. 1), the ternary phase with the cubic spinel structure (denoted τ here) is present. It is non-stoichiometric and has a composition range of $Fe_{22.3}Ir_{20.5}S_{57.2}$-$Fe_{18.9}Ir_{23.1}S_{58.0}$. Pyrrhotite ($Fe_{1-x}S$) dissolves up to 5.8 at.% Ir. The solubility of Fe in the Ir-S compounds is small, less
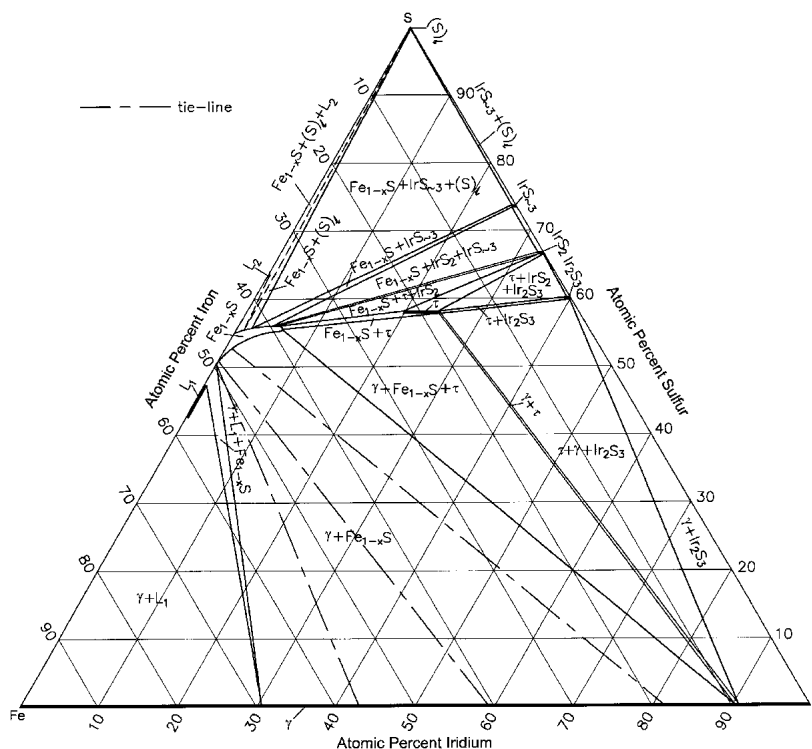

Fig. 1 Fe-Ir-S isothermal section at 1100 °C [1999Mak]
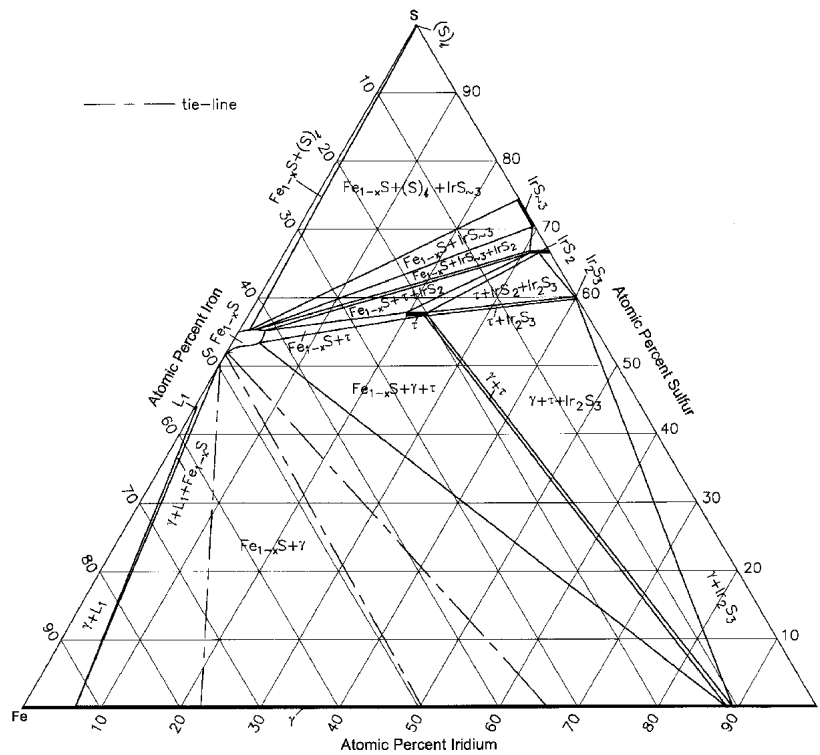
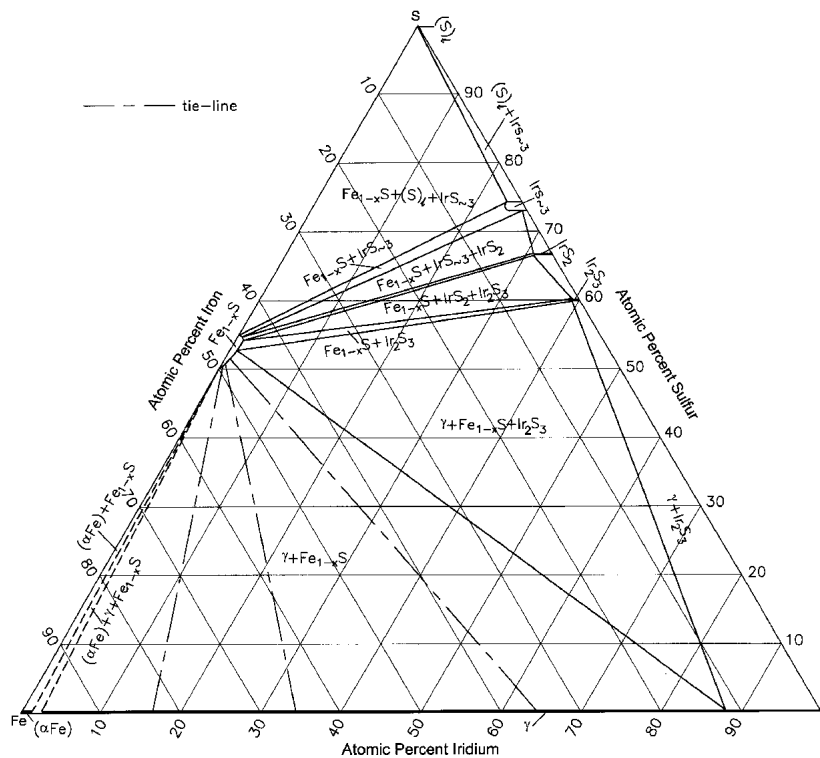**Fig. 2** Fe-Ir-S isothermal section at 1000 °C [1999Mak]

Fig. 3 Fe-Ir-S isothermal section at 800 °C [1999Mak]

than 1 at.%. The γ phase with Ir range of 30.6-90.3 at.% forms tie lines with $Fe_{1-x}S$ with Ir range of ~0-5.8 at.%, with a concomitant S range of 50-55 at.%. Selected tie lines are shown in Fig. 1. The ternary phase τ forms tie lines with all the binary compounds (except IrS_{-3}).

In the isothermal section at 1000 °C (Fig. 2), the trian-

gulation is the same as at 1100 °C (Fig. 1), except for the absence of the liquid phase L_2. The three-phase equilibrium of the Fe-rich sulfide liquid L_1, $Fe_{1-x}S$ (50 at.% S) and γ (6.7 at.% Ir) occurs closer to the Fe corner than at 1100 °C. A dominant two-phase field of $Fe_{1-x}S$ and γ is present. Selected tie lines are shown in this field in Fig. 2 [1999Mak]. $Fe_{1-x}S$ (pyrrhotite) dissolves 3.4 at.% Ir, when in equilibrium with τ and γ (88.7 at.% Ir) and also with τ and IrS_2. $Fe_{1-x}S$ dissolves 2.6 at.% Ir, when in equilibrium with IrS_2 and IrS_{-3} [1999Mak].

In the isothermal section at 800 °C (Fig. 3), the ternary phase τ is not stable. $Fe_{1-x}S$ in equilibrium with γ (88 at.% Ir) and Ir_2S_3 (1 at.% Fe) dissolves 0.87 at.% Ir. The solubility of Ir in $Fe_{1-x}S$ in the three-phase equilibria of ($Fe_{1-x}S$ + Ir_2S_3 + IrS_2), ($Fe_{1-x}S$ + IrS_2 + IrS_{-3}) and [$Fe_{1-x}S$ + $IrS_{\sim3}$ + $(S)_l$] are 0.9, 1.0 and 0.2 at.% respectively. The inadequate equilibrium in experiments performed at 500 °C by [1999Mak] precluded the construction of a reliable section. However, the results at this temperature indicated that FeS_2 (pyrite) dominates the equilibria at medium-to-high S contents. Another binary phase $Ir_{17}S_{15}$ is present along with Ir_2S_3 and IrS_2. $Fe_{1-x}S$ contains only traces of Ir at 500 °C.

[1997Bry] investigated the Ir-$Fe_{1-x}S$ and $Fe_{1-x}S$-Ir_2S_3 sections by differential thermal analysis, x-ray spectral microanalysis and optical microscopy. They found that the Ir solubility in $Fe_{1-x}S$ increases from 0.1 at.% at 50 at.% S to ~2.4 at.% at 54 at.% S in samples subjected to differential thermal analysis. Along the $Fe_{1-x}S$-Ir_2S_3 join, "a sulfide solid solution" (presumably the ternary phase τ with a homogeneity range) decomposes eutectoidally on cooling to $Fe_{1-x}S$ and Ir_2S_3.

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