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

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The phase relations of this quaternary system were partially characterized at 1100 and 1000 °C by [2000Mak].

Binary Systems

For brief descriptions of the Fe-Ir, Fe-S, and Ir-S systems, see the Fe-Ir-S review in this issue. The Fe-Pt and Pt-S phase diagrams are briefly covered under Fe-Pt-S. Ir and Pt [both face-centered-cubic (fcc)] form a continuous solid solution over a wide temperature range. A miscibility gap appears at lower temperatures, where two fcc phases (Ir-rich and Pt-rich) are present [Massalski2].

Ternary Systems

Updates on the Fe-Ir-S and Fe-Pt-S systems appear in this issue. The Fe-Ir-Pt and Ir-Pt-S systems do not appear to have been investigated.

Quaternary Phase Equilibria

With starting materials of Fe (15-20 ppm metallic impurities), 99.98% Pt, 99.995% Ir and 99.999% S, [2000Mak] melted 112 samples in evacuated glass tubes with annealing times of 4-5 weeks. Compositions in the S rich region were not investigated. The quenched samples were examined by optical microscopy and electron probe microanalysis. The partial phase relations at 1100 and 1000 °C were presented in two ways. Ternary alloy compositions, in equilibrium with the various sulfide phases ($Fe_{1-x}S$, PtS, Ir_2S_3, the ternary phase τ originating from the Fe-Ir-S system and the two sulfide melts L_1 and L_2 from the Fe-S system), were plotted on the Fe-Ir-Pt plane. Projections were also made on this plane of the coexisting compositions for two-phase and three-phase equilibria and of the tie-tetrahedra for four-phase equilibria. No new ternary or quaternary phase was found.

The ternary alloy phases in equilibrium with the sulfide phases at 1100 and 1000 °C are shown Fig. 1 and 2. At 1100 °C (Fig. 1), a major part of the field is occupied by the fcc solid solution γ, with a miscibility gap at the Pt end between γ and (Pt). The composition ranges (in at.% Pt) of the phases along the Fe-Pt side are γ (0-43), FePt (45.8-58), $FePt_3$ (60-77), and (Pt) (80-100), with little or no solubility of S. The maximum solubilities of Ir in FePt, $FePt_3$ and (Pt) are 24.0, 29.3 and 5.1 at.% respectively. The approximate projections of the sulfide phase fields on the Fe-Ir-Pt plane are indicated in Fig. 1 [2000Mak].

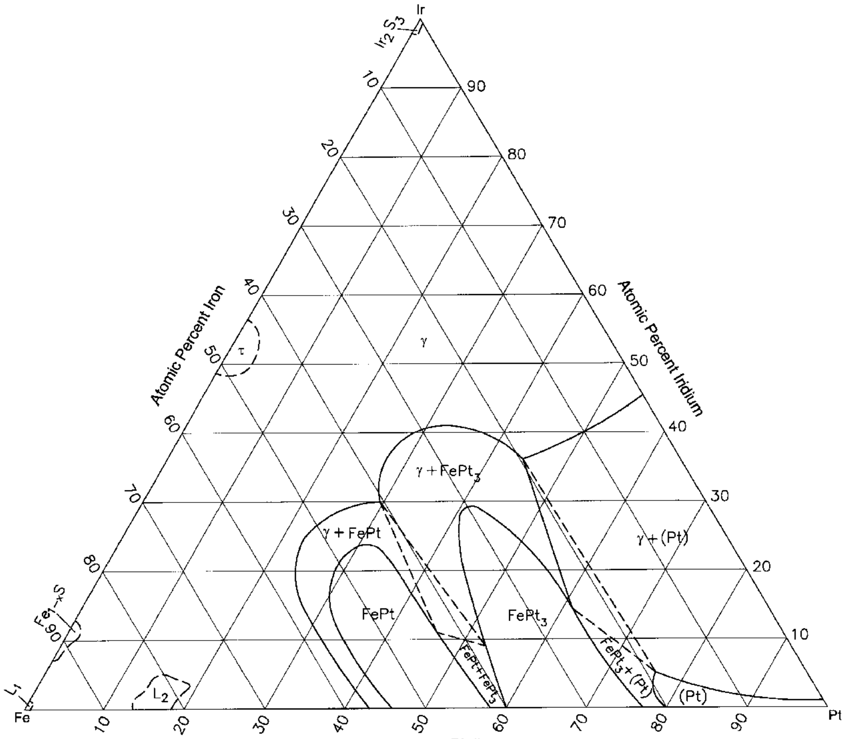

Fig. 1 Fe-Ir-Pt-S composition of alloy phases in equilibrium with sulfide phases at 1100 °C [2000Mak]

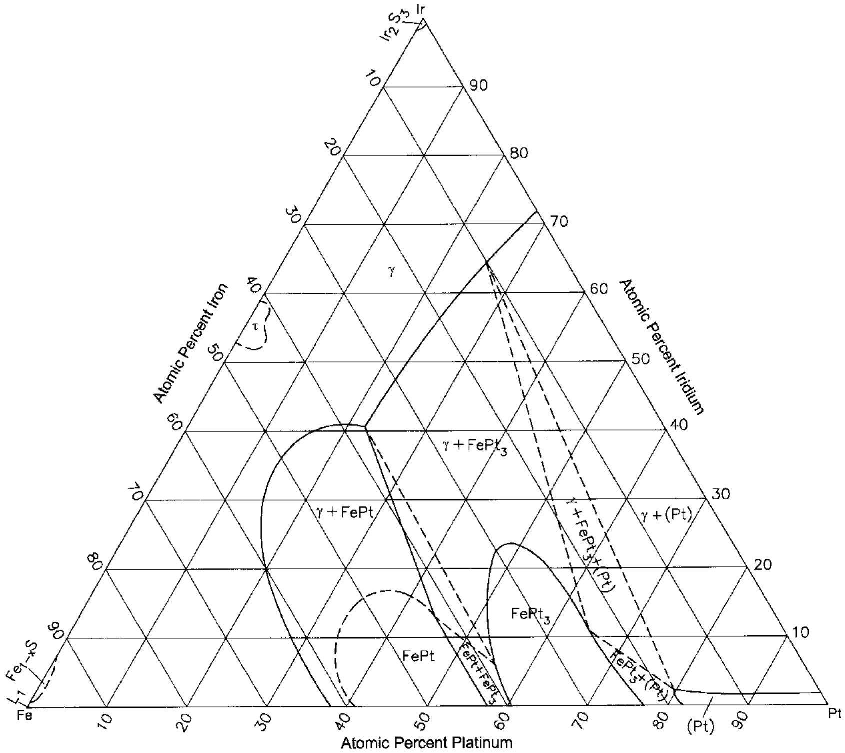

Fig. 2 Fe-Ir-Pt-S composition of alloy phases in equilibrium with sulfide phases at 1000 °C [2000Mak]

At 1000 °C (Fig. 2), the area occupied by the fcc solid solution γ reduces significantly as compared with that at 1100 °C in Fig. 1. The composition ranges (in at.% Pt) of the phases along the Fe-Pt side are γ (0-38), FePt (41-57.5), $FePt_3$ (60.5-77), and (Pt) (82-100). The maximum solubilities of Ir in FePt, $FePt_3$, and (Pt) are ~17, 23.6, and 2.2 at.% respectively. The approximate projections of the sulfide phase fields on the Fe-Ir-Pt plane are indicated in Fig. 2 [2000Mak].

The solubility of Ir and Pt in the Fe-rich sulfide melt (L_1) is very low, less than 0.1 at.%. At 1100 °C, the maximum solubility of Ir and Pt in $Fe_{1-x}S$ is 5.8 and 0.6-0.9 at.%, respectively. At 1000 °C, the maximum solubility in $Fe_{1-x}S$ is 3.4 at.% Ir (at 54.1 at.% S) and 0.1-0.2 at.% Pt, respectively. As in the ternary systems, the solubility of these metals increases with increasing S content of $Fe_{1-x}S$. The maximum solubility occurs when $Fe_{1-x}S$ is in equilibrium with other sulfide phases (and not with the alloys). The solubility at 1100 °C of Ir and Pt in the S-rich sulfide melt (L_2) reaches up to 2.5 and 14.3 at.% respectively. The high solubility of Pt and the low solubility of Ir in the S-rich sulfide melt is the opposite of what is seen in $Fe_{1-x}S$. PtS and Ir_2S_3 dissolve only small amounts of the other metals. The composition ranges of the ternary phase τ in the quaternary system are $Fe_{15.9\text{-}21.6}Ir_{18.9\text{-}23.9}Pt_{0.7\text{-}2.2}S_{56.8\text{-}58.1}$ at 1100 °C and $Fe_{16.9\text{-}19.4}Ir_{22.3\text{-}24.7}Pt_{0.4\text{-}1.1}S_{57.3\text{-}58.3}$ at 1000 °C [2000Mak].

The projections made by [2000Mak] on the Fe-Ir-Pt plane of two-phase equilibria give two points on phase-boundary surfaces corresponding to the two ends of the tie-line. Projections of three-phase equilibria yield three points on the phase boundaries. These data are inadequate to delineate the phase boundaries fully. The description of the equilibria by [2000Mak] is summarized briefly below. At 1100 °C, alloys with a high Fe content (>69 at.%) for both Pt-poor, Ir-rich and Pt-rich, Ir-poor compositions are in equilibrium with the Fe-rich sulfide liquid L_1. The melt L_1 dissolves only traces of Pt or Ir. The two-phase equilibria of $Fe_{1-x}S$-γ extend to Fe contents in the lower range: ~10 at.% Fe in Pt-free alloys and ~20 at.% Fe in alloys containing both Ir and Pt.. In Pt-rich alloys, the three-phase equilibria of $Fe_{1-x}S$-γ-ordered phase occur at ~27.5 at.% Fe. Beyond this limit, the S-rich sulfide melt and the ternary phase τ enter the equilibrium successively. [2000Mak] indicated a tie-tetrahedron of $Fe_{1-x}S$-γ-$FePt_3$-τ with narrow composition ranges for the four phases. As the compositions must remain fixed in the four-phase equilibrium, their values are assumed here to be the average: $Fe_{1-x}S$ (40.5Fe, 5.35Ir, 0.3Pt, 53.85S), γ (16Fe, 60.5Ir, 23.5Pt), $FePt_3$ (26.8Fe, 4.8Ir, 68.4Pt), and τ (20Fe, 22.5Ir, 0.7Pt, 56.8S). A second tie-tetrahedron of Ir_2S_3-γ-$FePt_3$-τ occurs at the composition Ir_2S_3 (0.37Fe, 39.48Ir, 0.15Pt, 60S), γ (18Fe, 44.5Ir, 37.5Pt), $FePt_3$ (26.5Fe, 1.5Ir, 72Pt), τ (18.9Fe, 22.9Ir, 1.1Pt, 57.1S). Figure 3 shows the location of the $Fe_{1-x}S$-γ-$FePt_3$-τ and Ir_2S_3-γ-$FePt_3$-τ tie-tetrahedra at 1100 °C in a perspective view.

At 1000 °C, only alloys with Fe content greater than 87.5-93.3 at.% are in equilibrium with the Fe-rich sulfide melt L_1. The three phase assemblage of $Fe_{1-x}S$ + L_1 + alloy was found at the alloy compositions 87.5Fe-3.0Ir-9.5Pt and 93.3Fe-6.7Ir. The Ir and Pt contents in L_1 and $Fe_{1-x}S$ are very small. The $Fe_{1-x}S$-alloy(s) equilibrium continues, until

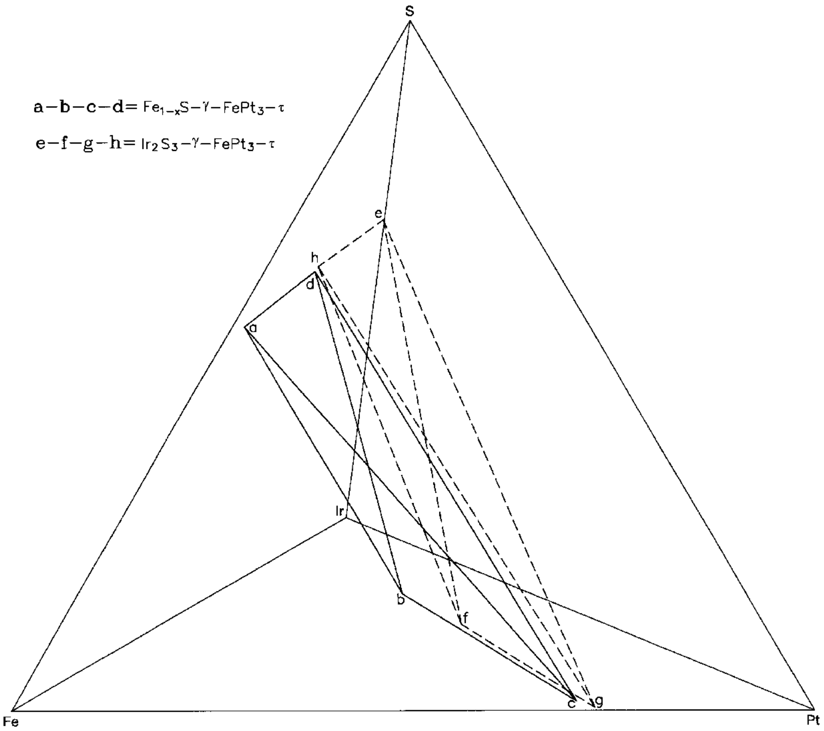

Fig. 3 Fe-Ir-Pt-S location of the tie-tetrahedra at 1100 °C [2000Mak]

the four-phase equilibrium of $Fe_{1-x}S$-γ-$FePt_3$-τ is reached, with the compositions of the participating phases as $Fe_{1-x}S$ (42.4Fe, 3.4Ir, 0.15Pt, 54.05S), γ (14Fe, 72.5 Ir, 13.5Pt), $FePt_3$ (26.5Fe, 9Ir, 64.5Pt), and τ (19.3Fe, 23.0 Ir, 0.4Pt, 57.3 S). A second tie-tetrahedron of Ir_2S_3-γ-$FePt_3$-τ has the following compositions of the participating phases: Ir_2S_3 (0.3Fe, 39.6Ir, 0.1Pt, 60S), γ (~15Fe, ~66.5Ir, ~18.5Pt); $FePt_3$ (27Fe, 5Ir, 68Pt); τ (17.7Fe, 24.1Ir, 0.5Pt, 57.7S). The other equilibria found are Ir_2S_3-$FePt_3$, γ-(Pt)-PtS, Ir_2S_3-γ-PtS, $Fe_{1-x}S$-$FePt_3$-PtS, τ-$FePt_3$-PtS, $Fe_{1-x}S$-τ-$FePt_3$, and τ-Ir_2S_3-$FePt_3$. The S-rich sulfide liquid L_2 is not present at 1000 °C.

Reference

2000Mak: E. Makovicky and S. Karup-Moller: "Phase Relations in the Metal-Rich Portions of the Phase System Pt-Ir-Fe-S at 1000°C and 1100°C," *Mineralogical Mag.,* 2000, *64,* pp. 1047-56.