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As-Fe-Pt-S (Arsenic-Iron-Platinum-Sulfur)

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The phase equilibria of this quaternary system was investigated by [1992Mak] at 850 and 470 °C.

Binary Systems

The As-Fe phase diagram [1993Oka] depicts three stoichiometric compounds: Cu_2Sb type tetragonal Fe_2As, MnP type orthorhombic FeAs (westerveldite), and FeS_2 (marcasite) type orthorhombic $FeAs_2$ (loellingite). The partial As-Pt diagram [Massalski2] exhibits one compound $PtAs_2$ with the FeS_2 (pyrite) type cubic structure. In the As-S phase diagram [Massalski2], a liquid miscibility gap is present with a monotectic reaction at 780 °C. Several intermediate compounds are found at temperatures below 320 °C. The update on the Fe-Pt-S system in this issue gives brief descriptions of the Fe-Pt, Fe-S, and Pt-S binary systems.

Ternary Systems

The As-Fe-Pt system does not have any ternary compounds. At 850 °C, the liquid near the eutectic composition of 24 at.% As in the As-Fe system dissolves an appreciable amount of Pt [1992Mak]. The review of the As-Fe-S system by [1988Rag] presented a schematic liquidus projection, a reaction scheme, and four isothermal sections at 825, 690, 491, and 320 °C, based mainly on the work of [1960Cla] and [1969Bar]. A ternary compound FeAsS (arsenopyrite) is known. It forms peritectically at 702 °C and has a homogeneity range of about 8 at.% at constant Fe content. A *P-T* diagram in the region of arsenopyrite was constructed for the As-Fe-S system by [1990Pas]. The As-Pt-S system was investigated by [1976Ski], who presented an isothermal section at 1000 °C. An update of the Fe-Pt-S system appears in this issue.

The Quaternary Phase Equilibria

Makovicky et al. [1992Mak] melted about 80 quaternary compositions in sealed silica tubes, which were given a final anneal at 850 or 470 °C for periods up to 80 days. The phase equilibria were studied by reflected-light microscopy and electron probe microanalysis. At 850 °C, the arsenopyrite ternary compound is not stable; the only phases present are the components and the binary phases with their extensions into the quaternary region. The maximum observed solubility in these phases is listed in Table 1. Four melts are present along the binary edges. Of these, $(Pt,As)_l$ and $(S,As)_l$ show little solubility for components other than their basic components. The $(Fe,As)_l$ melt, however, dissolves 23.7 at.% Pt and 2.6 at.% S. Among the binary phases, $PtAs_2$ (sperrylite) (denoted sp) dominates the system, dissolving up to 25.3 at.% S [1992Mak]. This solubility limit corresponds to $PtAs_{1.24}S_{0.76}$ and does not include the composition PtAsS (mineral name: platarsite). Both $PtAs_2$ and PtAsS have the cubic structure of FeS_2 (pyrite) and hence platarsite may be considered as a solid solution based on $PtAs_2$. In contrast, [1976Ski] showed no solubility of S in $PtAs_2$ at 1000 °C. Three-phase assemblages determined by [1992Mak] represent co-existing compositions rather than phase boundaries. The edges of the tie-tetrahedra (four-phase assemblages) are phase boundaries. The compositions (in at.%) of the participating phases in the four-phase equilibria are:

Table 1 Compositions (in at.%) of Phases in the As-Fe-Pt-S System [1992Mak]

Phase	850 °C	470 °C
$(Pt,As)_l$	0.6-0.8 Fe, ~0 S	…
$(S,As)_l$	0.05 Pt, <0.1 Fe	Traces
$(Fe,As)_l$	2.6 S, 31.7 As, 23.7 Pt	…
$Pt(As,S)_2$	≤25.3 S, 0.8-1.2 Fe	≤23 S
PtS	~2.7 As, 0.9 Fe	~2-2.5 As, 0.1 Fe
PtS_2	0.7 As, 0.3-0.7 Fe	…
$Fe_{1-x}S$	~0.24 As at 50 S and 0.4 As, 0.5 Pt at 56.2 S	0.5-1.6 As(51.2→54.3 S), 0-0.1 Pt
FeS_2	…	0.8-1.5 As, 0-≤0.04 Pt
Fe_2As	?	0.02-3.6 As, 0.02-3.5 Pt
FeAs	0.3-2.0 S, 0.2-0.6 Pt	0.2-1.2 S, 0-0.01 Pt
$FeAs_2$	0.8-1.2 Pt	1.2 S, 0.03-0.1 Pt
FeAsS	…	0-0.17 Pt
(αFe)	8.7 As	7.2 As, 0.05 Pt
FePt	0.4-1.0 As, 43.7-49.5 Pt	~0.2-1.1 As, 49.7-50.2 Pt
$FePt_3$	~0.7 As, 64-68.1 Pt	~1.3 As, 72.7-75.9 Pt
(Pt)	1.8 As, ~18 Fe	2.2 As, ~17 Fe
(As)	0.3 Fe, 0.1 Pt	…

In the Pt rich region, sp (2.6 S)-FePt (~45 Pt, 0.5 As)-PtS (0.8 As)-$(Pt,As)_l$ (0.6 Fe, ~31.6 As);

In the central region of the composition tetrahedron, sp (1.7S)-PtS (0.9Fe,1.2 As)-FePt (46.5Pt, 1.1As)-$Fe_{1-x}S$ (52.7S,0.1Pt, 0.1As);

In the S rich region, there are two tie-tetrahedra: sp (~26 S,1.2 Fe)-PtS (~0.6As)-$Fe_{1-x}S$ (0.4 As,0.5 Pt)-PtS_2 (0.6Fe,0.3 As); and sp (24.5 S,1.25 Fe)-PtS_2 (~0.7 Fe, ~0.6 As)-$Fe_{1-x}S$ (55.5 S, 0.1 As, 0.5 Pt)-$(S,As)_l$ (~17.7 As, ~0.05 Fe).

In the Fe-As enriched region, $(Fe,As)_l$ (~56.4 Fe, 31.3 As, 1.9 S, 10.4 Pt)-sp-FePt (43.6 Pt, 0.7 As)-$Fe_{1-x}S$ (51.1 S, 0.05 Pt, 0.2 As).

Two other four-phase equilibria in this region $(Fe,As)_l$-FeAs-sp-$Fe_{1-x}S$ and FeAs-$FeAs_2$-sp-$Fe_{1-x}S$ were not investigated in detail. The binary phases Fe_2As and $FePt_3$ are stable at 850 °C but do not appear in the equilibria described by [1992Mak]. The ternary regions separating the tetrahedra are of very limited volume in most cases. Figure 1 is a

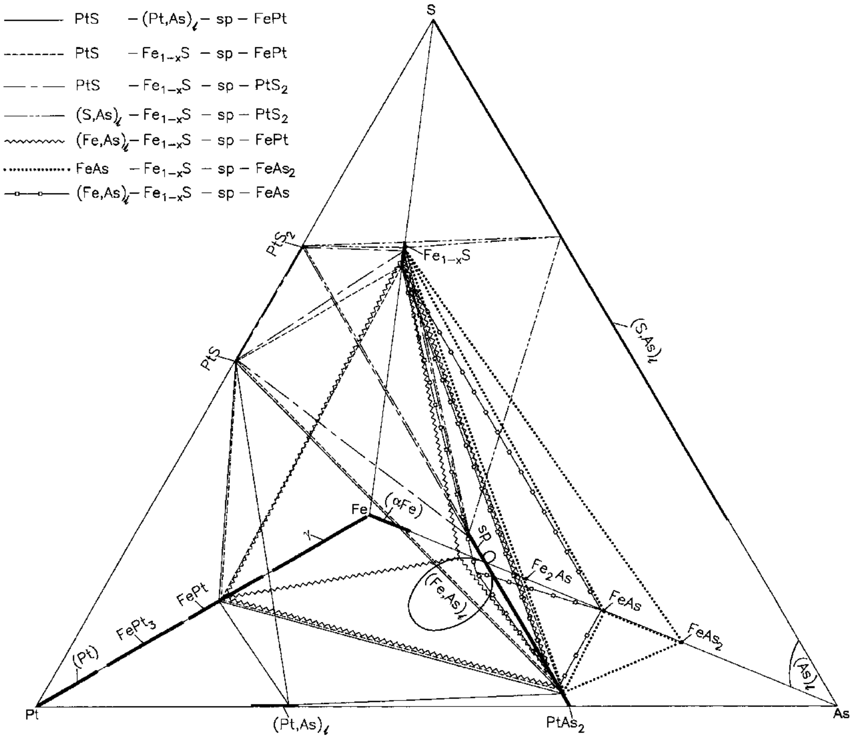

Fig. 1 As-Fe-Pt-S showing the location of the tie-tetrahedra within the composition tetrahedron at 850 °C

perspective view of the location of the above tie-tetrahedra at 850 °C. It is an incomplete presentation of the phase relationships within the composition tetrahedron.

At 470 °C, only one melt (S,As)$_l$ is stable. In Fe rich alloys, the body-centered cubic (bcc) α-phase and Fe$_3$Pt are stable. The As-Fe-S ternary phase FeAsS (denoted asp) is present. As at 850 °C, FeAs$_2$ dissolves a large amount of S, up to 20-23 at.%. The important four-phase assemblages identified by [1992Mak] are (compositions in at.%): sp(1.7S, 0.3Fe)-PtS(0.3As, 0.7Fe)-Fe$_{1-x}$S(0.15Pt,0.2As, 52.7S)- FePt$_3$ (~0.7 As); sp (0.05 S)-FePt$_3$ (0.4 As)-FeAs (1.2 S, 0 Pt)-Fe$_{1-x}$S (51.1 S, 0.3 As, 0.16 Pt); FeAs-Fe$_2$As-FePt-Fe$_{1-x}$S; γ-(αFe)-Fe$_2$As-Fe$_{1-x}$S (50 S); asp-FeAs-sp-Fe$_{1-x}$S; asp-FeAs$_2$-sp-Fe$_{1-x}$S; asp-FeAs$_2$-sp-(As); sp-PtS-Fe$_{1-x}$S-FeS$_2$; and sp-Fe$_{1-x}$S-FeS$_2$-asp.

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