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As-Cu-Fe-S (Arsenic-Copper-Iron-Sulfur)

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Arsenic and other Group VA elements have a detrimental effect on the mechanical and electrical properties of copper. The phase relationships in this system are relevant to an understanding of the problem of removal of As during Cu smelting. [2001Men] studied the influence of As on the liquid miscibility gap in the Cu-Fe-S system at 1200 °C.

Binary Systems

The As-Cu phase diagram [1988Sub] depicts three intermediate phases: Cu_6As (mineral name: algodonite, *alg*), Cu_3As (domeykite, *dom*), and Cu_5As_2 (koutekite, *kt*). Cu_6As, with a homogeneity range that includes the composition Cu_8As, is a low-temperature phase, forming peritectoidally from (Cu) and Cu_3As at 325 °C. Both Cu_3As and Cu_5As_2 have high- and low-temperature modifications [1988Sub]. The As-Fe phase diagram [Massalski2] depicts three stoichiometric compounds: Fe_2As (Cu_2Sb type tetragonal), FeAs (MnP type orthorhombic), and $FeAs_2$ (FeS_2-marcasite type orthorhombic; mineral name: loellingite, *lo*). The As-S system [Massalski2] has three intermediate phases: As_4S_3 (dimorphite, *dm*), AsS (realgar, *rl*), and As_2S_3 (orpiment, *orp*). There are no intermediate phases in the Cu-Fe system. A metastable liquid miscibility gap is known [Massalski2]. The Cu-S system [1983Cha] is characterized by the presence of two liquid miscibility gaps. The gap at Cu-rich compositions has a monotectic temperature of 1105 °C. $Cu_{1.76\text{-}1.79}S$ [CaF_2 type face-centered cubic (fcc); mineral name: digenite, *dg*] forms congruently at 1130 °C. Cu_2S (chalcosite, *cc*) is monoclinic at low temperatures and has the $B8_2$ type hexagonal structure between 103 and 435 °C. Above 435 °C, it has the CaF_2 type cubic structure and is continuous with digenite. CuS ($B18$ type hexagonal; mineral name: covellite, *cv*) forms peritectoidally at 507 °C. There are two intermediate phases in the Fe-S system: the metal-deficient monosulfide $Fe_{1-x}S$ (NiAs type hexagonal; mineral name: pyrrhotite, *po*) and FeS_2 (cubic pyrite, *py* or orthorhombic marcasite).

Ternary Systems

The As-Cu-Fe reviewed by [1992Rag] presented a schematic liquidus surface, a reaction scheme, and an isothermal

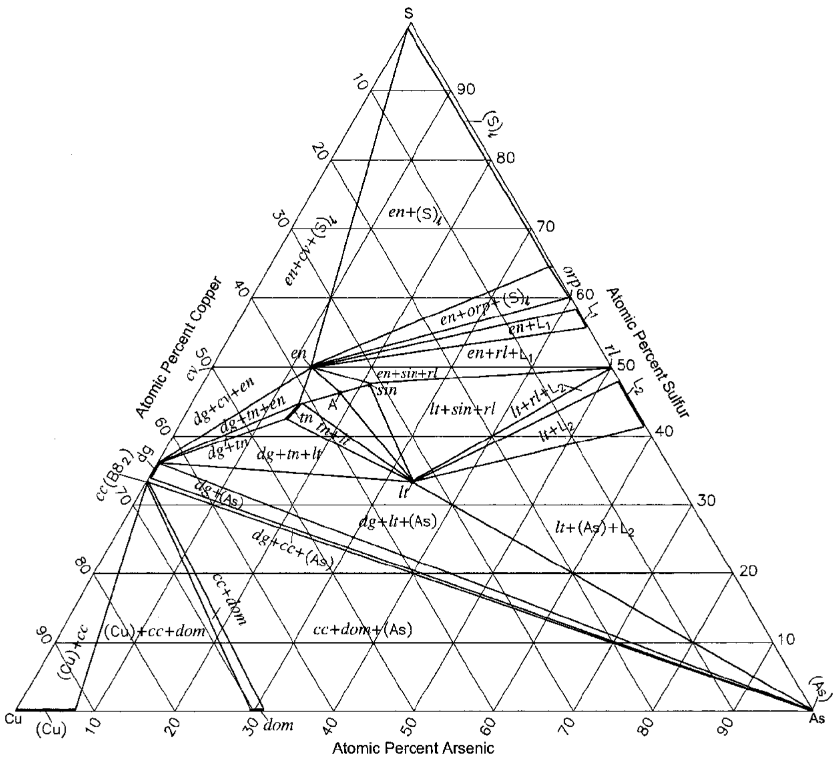

Fig. 1 As-Cu-S isothermal section at 300 °C [1971Mas]; narrow two-phase regions are omitted

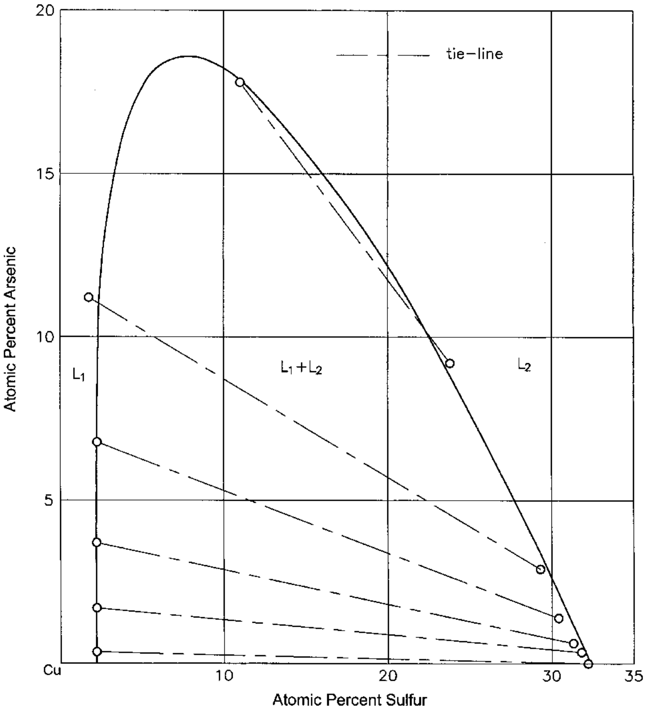

Fig. 2 As-Cu-S liquid miscibility gap near Cu corner at 1200 °C [1968Asa]

section at ~25 °C. There are no ternary compounds in this system. Four isothermal sections at 600, 500, 400, and 300 °C were determined for the As-Cu-S system by [1971Mas]. Six ternary compounds have been reported. Cu_3AsS_4 has two crystal forms. The high-temperature form (enargite, *en*) is orthorhombic, and the low-temperature form, luzonite, *lz,* is tetragonal. The transition temperature is between 275 and 300 °C. $Cu_{12}As_4S_{13}$ (tennantite, *tn*) is body-centered cubic (bcc) with 58 atoms in the unit cell and is isomorphous with $Cu_{12}Sb_4S_{13}$ (tetrahedrite, *td*). It has a small homogeneity range as given by $Cu_{12+x}As_{4+y}S_{13}$ ($0 \leq x \leq 1.72$; $0 \leq y \leq 0.08$). $Cu_6As_4S_9$ (sinnerite, *sin*) is triclinic. CuAsS (lautite, *lt*) has orthorhombic symmetry. An unknown compound $Cu_{24}As_{12}S_{31}$ (labeled *A* by [1971Mas]) is probably related structurally to sinnerite and tennantite. See [1971Mas] and [Pearson3] for more structural details of these ternary compounds. As an illustrative example, the isothermal section at 300 °C determined by [1971Mas] for the As-Cu-S system is redrawn in Fig. 1. At all temperatures between 600 and 300 °C, tie-lines exist between (As) and digenite (or chalcocite). The liquid miscibility gap determined by [1968Asa] at 1200 °C near the copper corner of the As-Cu-S system is shown in Fig. 2.

The As-Fe-S system reviewed by [1988Rag] presents a schematic liquidus projection, a reaction scheme, and four isothermal sections at 825, 690, 491, and 320 °C. The ternary compound FeAsS (arsenopyrite, *asp*) is monoclinic and has a homogeneity range of 30-38.5 at.% As and 28-37 at.% S. An update of the Cu-Fe-S system appears in this issue.

Quaternary Phase Equilibria

Using starting materials of copper and iron sulfides, as well as copper and iron chips (purities not stated), [2001Men] prepared five alloy compositions that lie in the liquid miscibility gap of the Cu-S and Cu-Fe-S systems at 1200 °C. High-purity As up to 6 wt.% was added to the charge as required to control the composition of the quaternary alloys. The samples were equilibrated at 1200 °C for 2 h and quenched in water. The composition of the separated metal and matte parts was determined by wet chemical analysis for Fe and S and by inductively coupled plasma (ICP) spectrometry for As.

In Fig. 3, the influence of small additions of As on the liquid miscibility gap is illustrated for the As-Cu-Fe-S system. With no Fe present, at S/Cu weight ratio of 0.118 (Fig. 3a), the magnitude of the slope of the tie-lines increases with increasing As content, showing satisfactory agreement with the tie-lines determined by [1968Asa] (Fig. 2). The S content in the matte phase decreases slightly with increasing As content in the charge; it remains nearly constant at 2.0-2.6 at.% in the metallic liquid. With Fe present at weight ratios of Fe/Cu = 0.131 and S/Cu = 0.154 in the charge, the slope of the tie-lines again increases with increasing As content (Fig. 3b). The S content in the metallic phase is almost constant, while that in the matte phase decreases slightly. [2001Men] obtained similar results at different charge compositions.

The As activity was measured by [2001Men] employing the double Knudsen cell-mass spectrometric method. The Raoultian activty coefficient γ_{As} at 1200 °C is independent of the Fe content and is expressed as follows:

$$\log(\gamma_{As}) = -2.90 + 92.1\ (\text{at. fraction As})$$

for the matte phase, and

$$\log(\gamma_{As}) = -5.46 + 14.6\ (\text{at. fraction As})$$

for the metallic phase.

The calculated vapor pressure of the As, As_2, and AsS species in the gaseous phase equilibrated with the immiscible liquids is very small (<1 Pa), indicating that the elimination of As from the metal phase by volatization is hardly feasible [2001Men].

Very limited information is available on the phase relationships in this quaternary system in the temperature range of ~500-250 °C [1963McK] [1963Gus], and [1974Shc]. [1963McK] presented two possible phase assemblages of the Cu-Fe-S system: (i) at intermediate temperatures, where *py* forms tie-lines with *cp, bn, cc, dg* and *cv* (Fig. 4a); and (ii) at lower temperatures, where *py* forms tie-lines only with *cp* and *cv* (Fig. 4b). On this basis, [1963McK] sketched sections through the composition tetrahedron for the above two cases at an arbitrary As content of 3 at.%. [1963McK] did not consider the existence of solid solutions and the ternary compound $Cu_{5.5}FeS_{6.5}$ (idaite). No quantitative data on the quaternary phase relationships seem to be available.

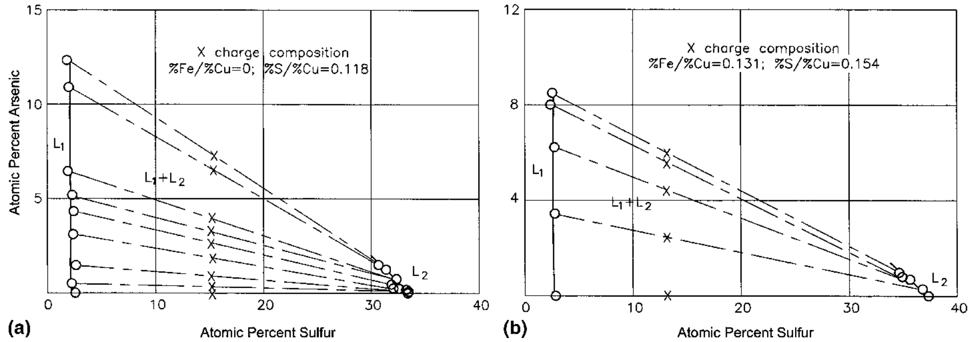

Fig. 3 As-Cu-Fe-S equilibrium between matte (L_2) and metal (L_1) at 1200 °C; charge compositions are given in wt.% [2001Men]

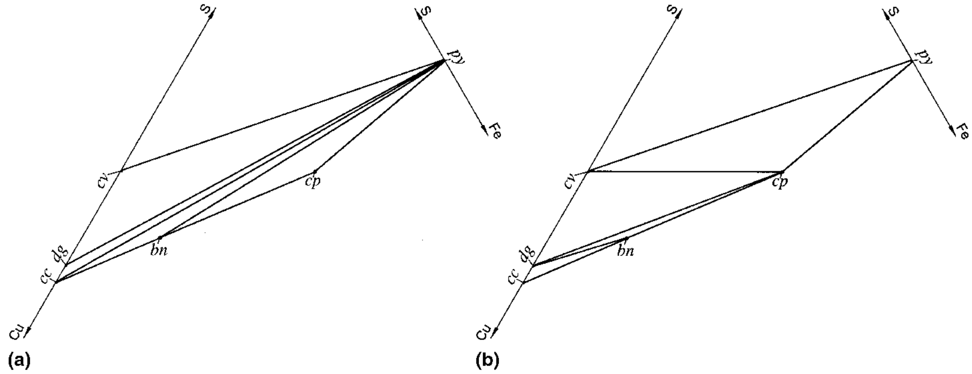

Fig. 4 Cu-Fe-S tie-lines between phases at **(a)** intermediate temperatures, and **(b)** low temperatures [1963McK]

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