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Cu-Fe-S-Sb (Copper-Iron-Sulfur-Antimony)

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Group VA elements such as As, Sb, and Bi have a deleterious effect on the mechanical and electrical properties of copper. To eliminate them during copper smelting, an understanding of their influence on the miscibility gap between the metallic melt and the matte during copper smelting is necessary. Recently, [2002Men] studied the influence of small additions of Sb on the liquid miscibility gap of the Cu-Fe-S system. [1977Tat] determined the extension at 500 °C of the tetrahedrite phase of the Cu-S-Sb ternary system into the quaternary region.

Binary Systems

For brief descriptions of the Cu-Fe, Cu-S, and Fe-S systems, see the Cu-Fe-S update in this issue. The Cu-Sb phase diagram [Massalski2] depicts a number of intermediate phases: Cu_3Sb (β), $Cu_{11}Sb_2$ (γ), Cu_4Sb (δ), Cu_3Sb (ε), $Cu_{10}Sb_3$ (ζ), and Cu_2Sb (η). The notations in parentheses are those used by [Massalski2]. Phases β and ε with the same nominal composition occur in different temperature ranges. See [Pearson3] for structural details. There are two intermediate phases in the Fe-Sb system [1993Oka]. The NiAs-type $B8_1$ phase Fe_3Sb_2 (ε) has a homogeneity range of 40-47 at.% Sb. The other intermediate phase $FeSb_2$ is stoichiometric and has the FeS_2 (marcasite)-type orthorhombic structure. The S-Sb phase diagram [1972Ski] depicts a liquid miscibility gap in the Sb-rich region and an intermediate compound Sb_2S_3 (stibnite, *stb*; $D5_8$ type orthorhombic).

Ternary Systems

An update of the Cu-Fe-S system appears in this issue. The system contains twelve ternary compounds. The known structural characteristics and stability ranges of these compounds are summarized in the update. The review of the Cu-Fe-Sb system by [1992Rag] presented a liquidus surface, a reaction scheme, and an isothermal section at 1150 °C. There are no ternary compounds in this system. The review of the Fe-S-Sb system by [1988Rag] presented a liquidus surface, a reaction scheme, and three isothermal sections at 700, 540, and 450 °C. The system contains two ternary compounds: $FeSb_2S_4$ (orthorhombic; mineral name berthierite) and FeSbS (monoclinic; mineral name gudmundite). The Cu-S-Sb system was investigated by [1968Asa], [1972Ski], and [1977Tat]. The ternary phases in this system are: Cu_3SbS_4 (famatinite, *fm*), $CuSbS_2$ (chalcostibite, *cstb*;

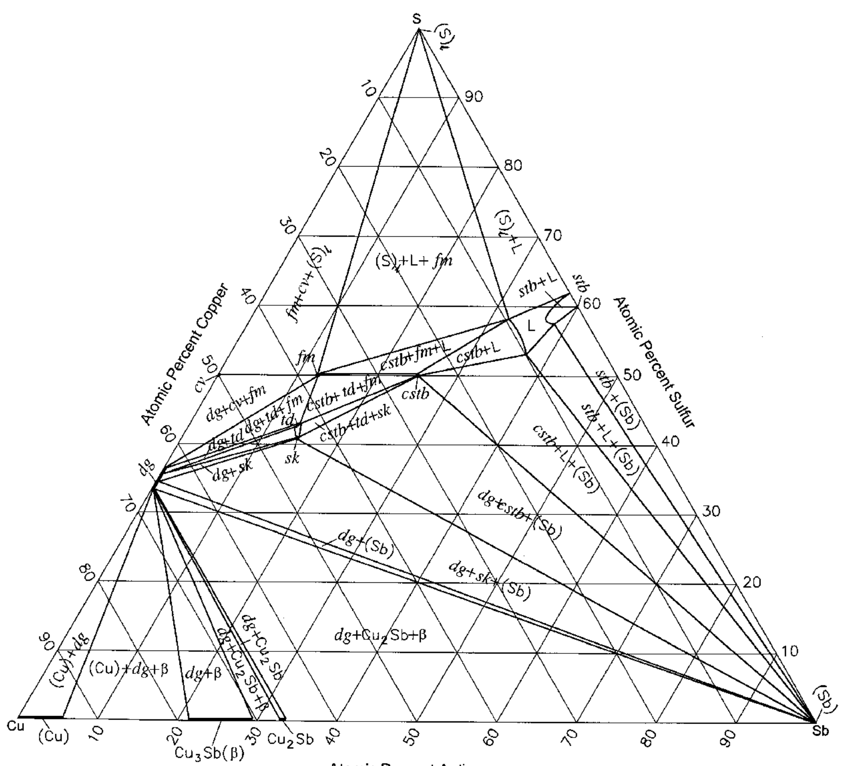

Fig. 1 Cu-S-Sb isothermal section at 500 °C [1972Ski]. Narrow two-phase regions are omitted.

orthorhombic), Cu_3SbS_3 (skinnerite *sk*, denoted *B* by [1972Ski]; orthorhombic or monoclinic) [1994Pfi] and $Cu_{12}Sb_4S_{13}$ (tetrahedrite, *td*). Tetrahedrite has a body centered cubic unit cell with 58 atoms/cell and $a = 1.03293$ nm [1997Pfi]. It is slightly off-stoichiometric and has a narrow homogeneity range of 41.8-43.4 at.% Cu and 13.4-13.9 at.% Sb, as compared with 41.4 Cu and 13.8 Sb for the stoichiometric composition [1977Tat]. The isothermal section of the Cu-S-Sb system at 500 °C from [1972Ski] is shown in Fig. 1.

Quaternary Phase Equilibria

Using starting materials of copper and iron sulfides, as well as copper and iron chips (purities not stated), [2002Men] prepared four alloy compositions that lie in the liquid miscibility gap of the Cu-S and Cu-Fe-S systems at 1200 °C. High-purity Sb up to 10 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 Sb.

The influence of small additions of Sb is illustrated for the Cu-S-Sb and Cu-Fe-S-Sb systems in Fig. 2. With no Fe present, at S/Cu weight ratio of 0.118 (Fig. 2a), the magnitude of the slope of the tie-lines increases with increasing Sb content. The S content in the matte phase decreases slightly with increasing Sb content in the charge; it remains nearly constant at 2.9-3.6 at.% in the metallic liquid. With Fe present at weight ratios of Fe/Cu = 0.072 and S/Cu = 0.122 in the charge, the slope of the tie-lines again increases with increasing Sb content, while the S content in the metallic phase is almost constant. Similar results were obtained by [2002Men] at different charge compositions.

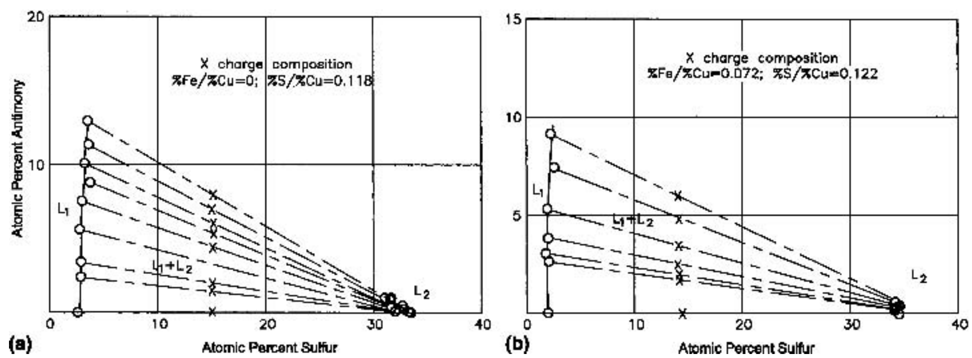

Fig. 2 Cu-Fe-S-Sb equilibrium between matte (L_2) and metal (L_1) at 1200 °C. Charge compositions are given in weight percent [2002Men]

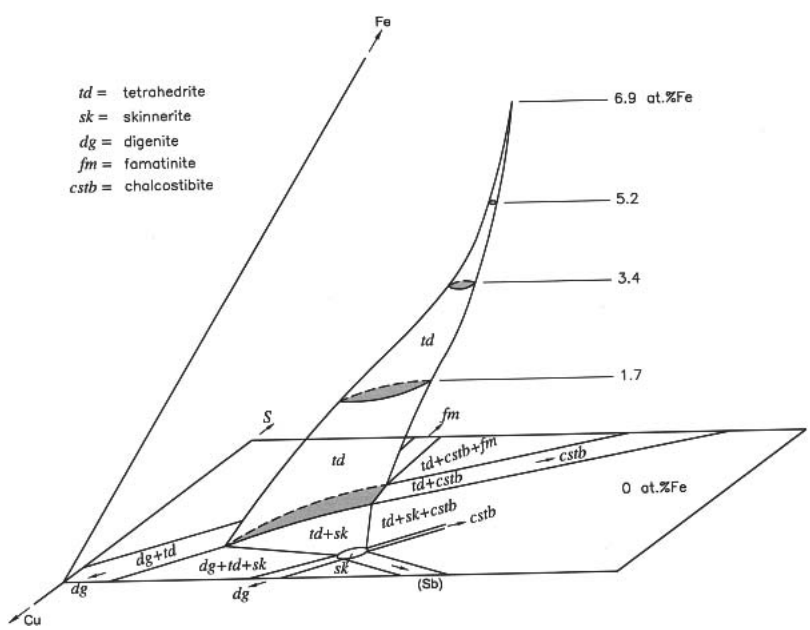

Fig. 3 Cu-Fe-S-Sb perspective view at 500 °C of the tetrahedrite solid solution [1977Tat]

The Sb activity was measured by [2002Men], employing the double Knudsen cell-mass spectrometric method. The Raoultian activty coefficient γ_{Sb} at 1200 °C is independent of the Fe content and can be expressed as follows:

$$\log(\gamma_{Sb}) = -0.596 + 43.0 \text{ (at.\% Sb)}$$

for the matte phase, and

$$\log(\gamma_{Sb}) = -1.95 + 5.84 \text{ (at.\% fraction Sb)}$$

for the metallic phase The calculated vapor pressure of the Sb, Sb_2, and SbS species in the gaseous phase equilibrated with the immiscible liquids is very small (<1 Pa), indicating that the elimination of Sb from the metal phase by volatization is hardly feasible [2002Men].

Using starting materials of 99.99% Cu, 99.99% Fe, 99.999% S, and 99.999% Sb, [1977Tat] synthesized 234 samples, around the composition range of tetrahedrite. The samples were annealed at 500 °C for 14-105 days. The phase equilibria were studied by reflected light microscopy, x-ray powder diffraction, differential thermal analysis, and microhardness measurements. Tetrahedrite, *td* ($Cu_{12}Sb_4S_{13}$) dissolves Fe up to the composition $Cu_{10}Fe_2Sb_4S_{13}$, corresponding to 6.9 at.% Fe. The extension of tetrahedrite into the composition tetrahedron in a conelike shape is shown in a perspective view in Fig. 3. This phase forms tie-lines with all binary and ternary sulfide phases except CuS. The homogeneity range of *td* decreases with increasing Fe content, the range becoming almost nil at 6.9 at.% Fe. The lattice parameter increases from 1.03260 nm at 0% Fe to 1.03835 nm at 6.9 at.% Fe. Whereas Fe-free *td* decomposes below 250 °C, *td* with 1.7 at.% Fe persists at room temperature [1977Tat].

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