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

V. Raghavan

The previous review of this system by [1979Cha] presented a list of the ternary compounds of this system, a liquidus projection, and a number of isothermal sections between 1350 and 350 °C. The update by [2004Rag] reviewed the recent thermodynamic measurements on this system. More recently, [2004Tsu] determined the phase relations at 800 °C, which differ significantly from the earlier reports.

Binary Systems

There are no intermediate phases in the Cu-Fe system. In the Cu-S system [Massalski2], $Cu_{1.76\text{-}1.79}S$ (CaF_2-type cubic; mineral name: digenite, *dg*) forms congruently at 1130 °C. Cu_2S (chalcosite, *cc*) is monoclinic below 103 °C 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 contiguous with digenite. CuS (*B*18 type hexagonal; mineral name: covellite, *cv*) forms peritectoidally at 507 °C. There are two intermediate phases in the Fe-S system: $Fe_{1-x}S$ (NiAs type hexagonal; mineral name: pyrrhotite, *po*) is stable at Fe-deficient (S-rich) compositions with a S range of 50-55 at.%. Cubic FeS_2 (pyrite, *py*) forms peritectically at 743 °C and undergoes a transition to the orthorhombic form (marcasite) at 425 °C [1982Kub].

Ternary Phases

There are a dozen intermediate phases in this system. These have been reviewed by [1979Cha] and [2004Rag]. Only two of these are of interest in the results reviewed here. Cu_5FeS_4 (mineral name: bornite, *bn*) exists in several crystal forms. Above 700 °C, the homogeneity range of bornite includes digenite, chalcocite, and Cu_5FeS_4. The ternary phase labeled intermediate solid solution (*iss*) occurs around the 50 S-50Cu line and has an Fe range of ~21-33 at.%. It has the disordered sphalerite-type cubic structure. The upper temperature limit of stability of *iss* is 960 °C. The low-temperature decomposition of *iss* is not well understood.

Ternary Isothermal Section

With starting materials of 99.99% Cu, 99.99% Fe, and 99.99% S, [2004Tsu] melted over 100 samples in evacuated

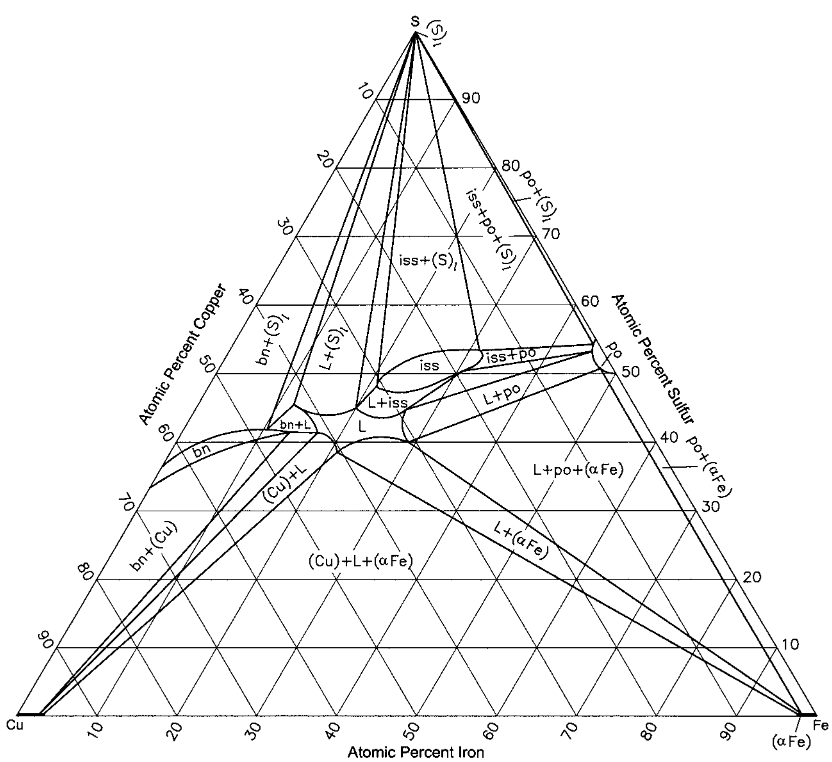

Fig. 1 Cu-Fe-S isothermal section at 800 °C [2004Tsu]

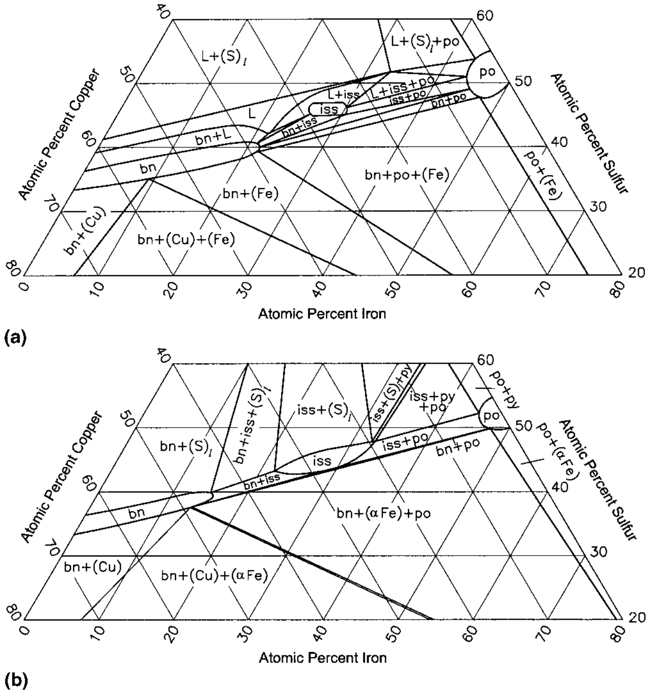

Fig. 2 Cu-Fe-S partial isothermal sections at (a) 900 °C and (b) 700 °C [1969Kul]

sealed tubes. The samples were annealed at 800 °C for 7 days and quenched in water. Polished specimens were examined under the reflected light microscope. The compositions of the phases were determined by the electron probe microanalyzer. [2004Tsu] constructed an isothermal section at 800 °C, which is redrawn in Fig. 1. For comparison, the partial diagrams at 900 and 700 °C from the results of [1969Kul] are shown in Fig. 2. In these figures, $(S)_l$ denotes the S-rich liquid. In the results of [1969Kul], the two-phase equilibria of (*bn* + *iss*) and (*bn* + *po*) are seen, whereas these are not present at 800 °C in Fig. 1 because of the intervening liquid phase. The location of the liquid field in this temperature range appears to be the important difference. In support of their results, [2004Tsu] superposed on their diagram the measured compositions of the sulfide phases obtained from recent volcanic eruptions.

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