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Cu-Fe-Se (Copper-Iron-Selenium)

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The previous review of this system by [1992Rag] presented isothermal sections at 900, 700, and 500 °C, from the results of Bernardini et al. [1979Ber, 1981Ber]. Based on the isothermal sections, a schematic liquidus projection and a reaction scheme were also included in the evaluation by [1992Rag]. Koneshova [1991Kon] determined a pseudobinary section of this system along the Cu_2Se-FeSe join.

Binary Systems

The Cu-Fe phase diagram [1993Swa] shows that there are no intermediate phases in this system. A metastable liquid miscibility gap is known in this system. The Cu-Se phase diagram [1981Cha] depicts four intermediate phases: $Cu_{2-x}Se$, Cu_3Se_2, CuSe, and $CuSe_2$. Among these, $Cu_{2-x}Se$ has two modifications (monoclinic and cubic). The high temperature cubic structure, $\beta Cu_{2-x}Se$, forms congruently at 1130 °C. The monoclinic $\alpha Cu_{2-x}Se$ forms peritectoidally at 123 °C. CuSe has three crystalline forms: α (hexagonal), β (orthorhombic), and γ (hexagonal). Cu_3Se_2 is tetragonal and $CuSe_2$ has the FeS_2 (marcasite) type orthorhombic structure. The Fe-Se phase diagram [1991Oka] depicts a number of modifications of the monoselenide around the midcomposition: $\beta Fe_{1.04}Se$, $\gamma Fe_{1-x}Se$, $\gamma' Fe_{1-x}Se$, $\delta Fe_{1-x}Se$, and $\delta' Fe_{1-x}Se$. $\beta Fe_{1.04}Se$ has the tetragonal PbO type structure. $\delta Fe_{1-x}Se$ is a NiAs-type hexagonal phase. The other phases are NiAs-related phases. $FeSe_2$ has the FeS_2 (marcasite) type orthorhombic structure. For more structural details, see [1991Oka].

Ternary Compounds

As summarized by [1992Rag], there are two ternary compounds in this system with significant homogeneity ranges. $(Cu,Fe)Se_{2-x}$, with the cubic pyrite (FeS_2) type structure, has the mineral name eskebornite. A high-pressure phase transition in eskebornite was reported by [1996Tin]. (Cu,Fe)Se occurs approximately midway between the Cu and Fe monoselenides and has the Cu_2Sb type

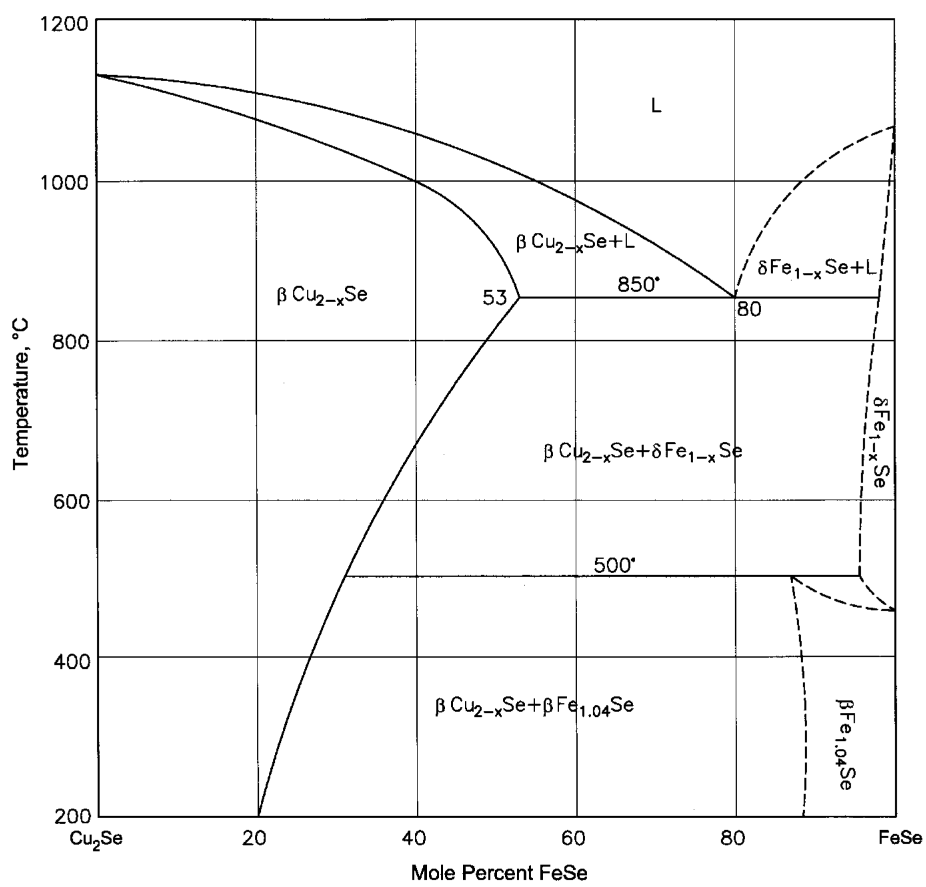

Fig. 1 Cu-Fe-Se pseudobinary section along the Cu_2Se-FeSe join [1991Kon]

tetragonal structure. Neither of these is present along the Cu_2Se-FeSe join [1991Kon].

The FeSe-Cu_2Se Pseudobinary Section

With high-purity starting materials, [1991Kon] synthesized about ten alloy compositions in evacuated quartz tubes at 950 °C, which were then annealed at 475 °C for 30 d. The phase equilibria were studied by differential thermal analysis, x-ray diffraction, metallography, and microhardness measurements. The pseudobinary section along the Cu_2Se-FeSe join constructed by [1991Kon] is redrawn in Fig. 1 to agree with accepted binary data. There is a eutectic reaction at 850 °C and at 80 mol% FeSe, which yields $\delta Fe_{1-x}Se$ and $\beta Cu_{2-x}Se$ containing up to 53 mol% FeSe. The solubility of FeSe in $\beta Cu_{2-x}Se$ decreases rapidly with decreasing temperature. A peritectoid reaction at 500 °C between $\beta Cu_{2-x}Se$ and $\delta Fe_{1-x}Se$ yields $\beta Fe_{1.04}Se$.

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