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

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The work on this important quaternary system by Craig and Kullerud and other earlier studies do not appear to have been reviewed. Three doctoral theses around 1980 [1976Lee], [1983Chu], and [1984Din], mainly on the thermodynamic properties of this system and the related subsystems, are not available in published form. This review presents the schematic phase relationships outlined by Craig and Kullerud, with additional results from more recent studies.

Binary Systems

For brief descriptions of the Cu-Fe, Cu-S, and Fe-S systems, see the Cu-Fe-S update in this issue. Copper and nickel [both face-centered-cubic (fcc)] form a continuous solid solution over a wide range of temperature [Massalski2]. A miscibility gap arises below 354.5 °C, where the fcc phase splits into Cu-rich and Ni-rich phases. The Fe-Ni phase diagram [1991Swa] is characterized by a very narrow solidification range with a peritectic reaction at 1514 °C, between body-centered cubic (bcc) δ and liquid that yields the Fe-based fcc solid solution. A continuous solution denoted γ between fcc Fe and Ni is stable over a wide range of temperature. An ordered phase $FeNi_3$ forms congruently from γ at 517 °C. The Ni-S phase diagram [Massalski2] has a number of intermediate phases: NiS_2 (pyrite type cubic, mineral name vaesite denoted *vs*), Ni_3S_4 (Co_3S_4 type cubic, mineral name violarite, *vio*), $Ni_{1-x}S$ (NiAs type hexagonal) and its low-temperature form called millerite (*B*13 type rhombohedral), Ni_7S_6 (monoclinic) and its low-temperature form godlevskite, *gd* (end-centered orthorhombic), and Ni_3S_2 (fcc) and its low-temperature form heazlewoodite, *hz* (rhombohedral). The high-temperature form of Ni_3S_2 has a homogeneity range.

Ternary Systems

The review of the Cu-Fe-Ni system by [1990Gup] presented a liquidus projection, isothermal sections at 1250, 1150, 850, 750, 400, and 20 °C, the miscibility gap in the fcc (γ) phase between 1050 and 600 °C, and vertical sections at 50Cu-50Fe and 90Cu-10Fe (wt.%). A recent report [2000Qin] presents four isothermal sections at 600, 800, 1000, and 1050 °C. The Cu-Fe-S system reviewed by [1979Cha1] is updated in this issue. The Cu-Ni-S system reviewed by [1979Cha2] presented the liquid miscibility gap at 1200 °C, four isothermal sections at 780, 600, 500,

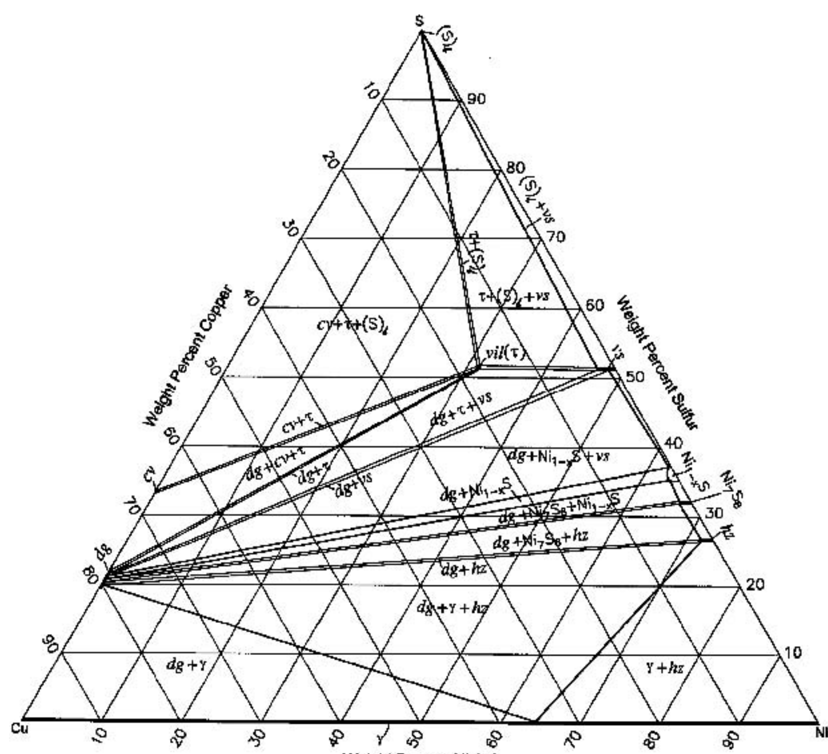

Fig. 1 Cu-Ni-S isothermal section at 500 °C [1979Cha]

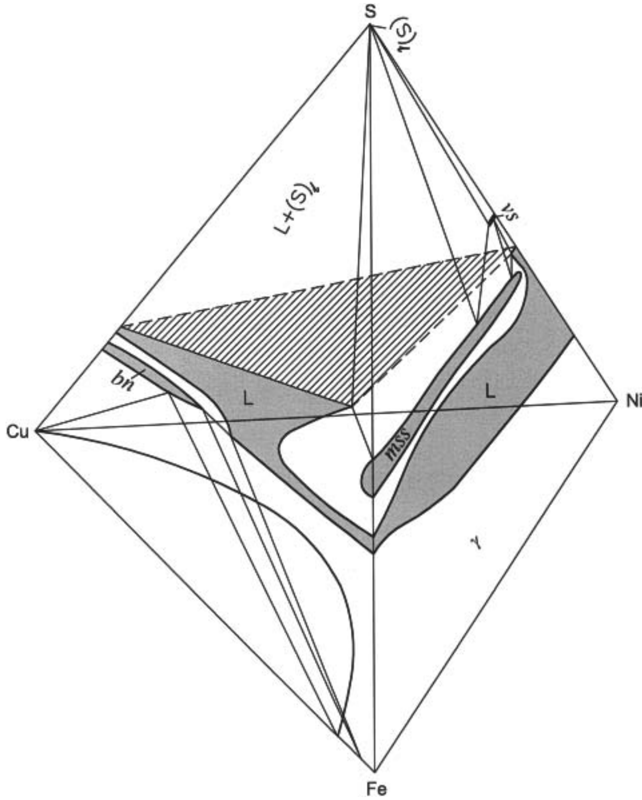

Fig. 2 Cu-Fe-Ni-S perspective view of the schematic phase relations at 1000 °C [after 1968Cra]

and 200 °C, a pseudobinary section along the Cu_2S-Ni_3S_2 join and a table of four-phase invariant reactions of the system. The isothermal section at 500 °C is redrawn in Fig. 1. The ternary compound $CuNi_2S_6$ (τ) (mineral name: villamaninite, *vil*), seen in Fig. 1, has the pyrite-type cubic structure and forms through a ternary peritectic reaction at ~503 °C [1979Cha2]. The Fe-Ni-S system reviewed by [2004Rag] presented a liquidus projection and nine isothermal sections at 1350, 1200, 1100, 1000, 900, 725, 600, 500, and 400 °C.

Quaternary Phase Equilibria

[1965Cra], [1968Cra], and [1969Cra] presented schematic (semiquantitative) sketches of the quaternary phase relationships of this system at 1000, 850, 650, 550, and 400 °C. The experimental charges were annealed in sealed silica tubes at the desired temperature and quenched in water. The phase equilibria were studied by reflected light microscopy and x-ray powder diffraction. Their results are shown as perspective views at 1000, 850, and 400 °C in Fig. 2-4. At 1000 °C (Fig. 2), the quaternary sulfide liquid L and the $Fe_{1-x}S$-$Ni_{1-x}S$ monosulfide solid solution are the dominant phases. For the Fe-Ni-S plane, the data of [1987Hsi] are used in Fig. 2. At 850 °C (Fig. 3), the phase field of the sulfide liquid has shrunk in size and tie-lines form between chalcopyrite (*cp*) and the monosulfide solid solution (*mss*). Ni_3S_2 appears as a phase in the ternary region. At 400 °C (Fig. 4), a number of binary and ternary compounds participate in the phase equilibria.

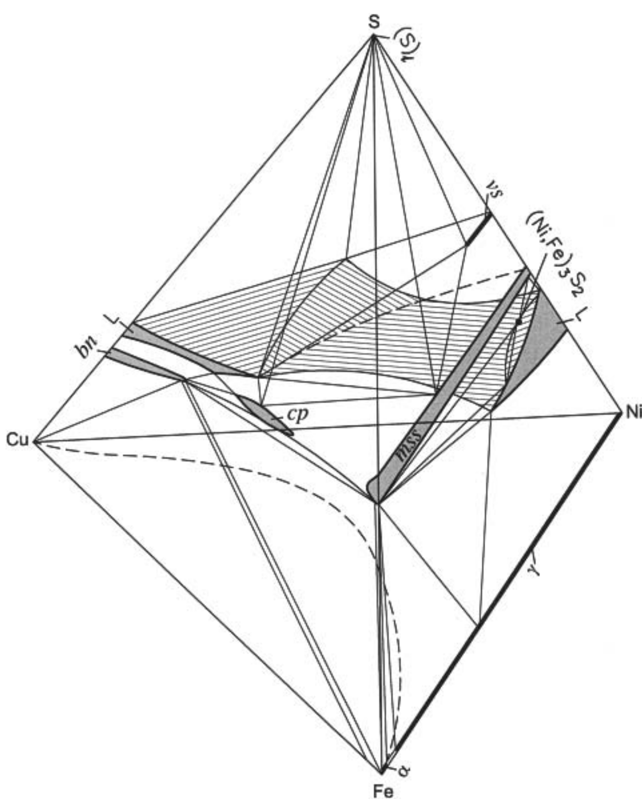

Fig. 3 Cu-Fe-Ni-S perspective view of the schematic phase relations at 850 °C [1968Cra]

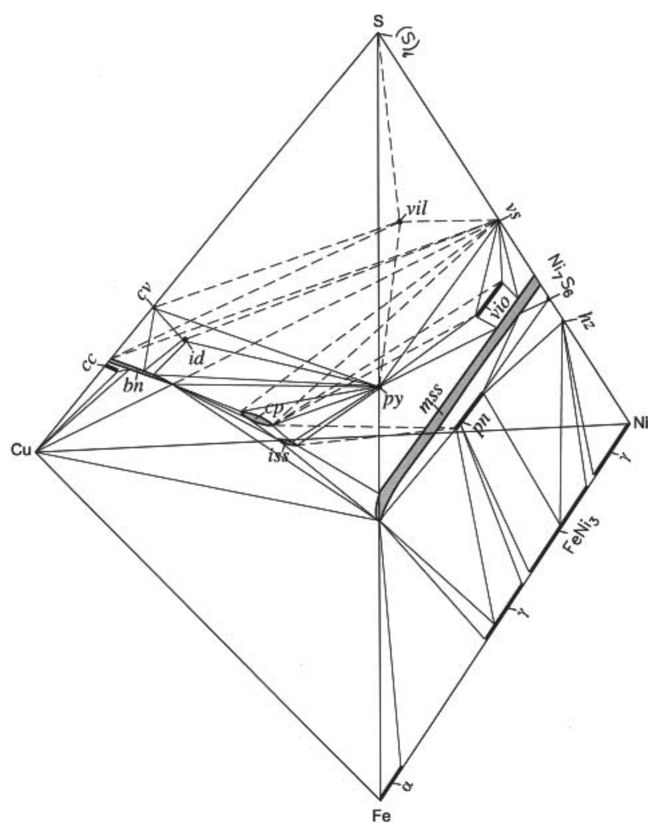

Fig. 4 Cu-Fe-Ni-S perspective view of the schematic phase relations at 400 °C [1968Cra]

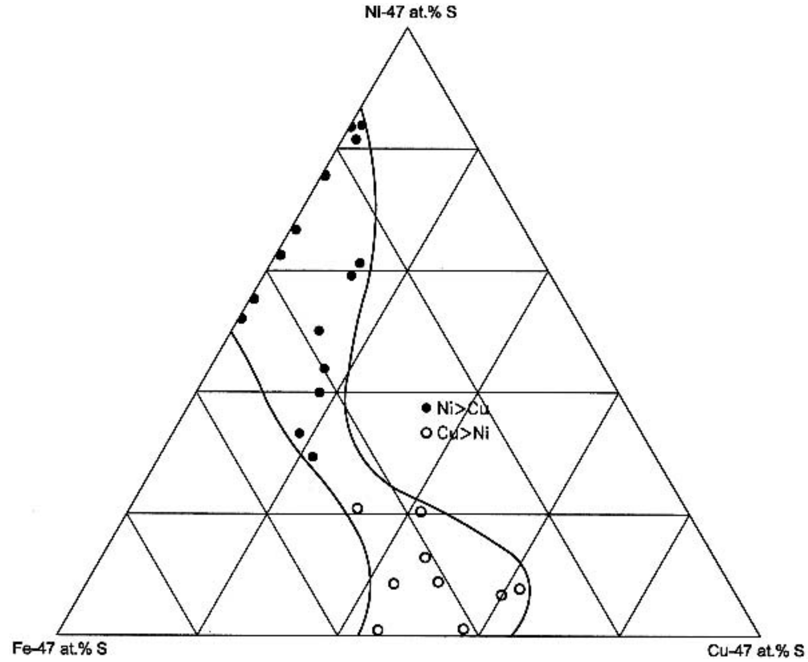

Fig. 5 Cu-Fe-Ni-S the continuous solid solution between *iss* and $(Ni,Fe)_3S_2$ at a constant S content of 47 at.% and at 760 °C [1995Per]

Among the other reports on this quaternary system, [1966Pop] presented a liquidus projection for the Cu_2S-FeS-NiS pseudoternary system. [1971Cab] measured the composition of both natural and synthetic Ni-bearing talnakhite, *tk* ($Cu_9Fe_5S_{16}$) and found that up to ~0.6 at.% (0.8 wt.%) Ni substitutes for Fe in this compound. [1995Per] investigated alloy compositions that lie on the section with a constant S content of 47 at.% and found that at 760 °C, there exists a continuous quaternary solid solution between the intermediate solid solution (*iss*) of the Cu-Fe-S ternary system and the solid solution based on the high-temperature form of Ni_3S_2 of the Fe-Ni-S system, which is known to dissolve large amounts of Fe (up to 33 at.% at 725 °C). These two ternary solutions have the same cubic symmetry and similar lattice parameters. Figure 5 shows this solid solution field at 760 °C. Compositions with Ni > Cu are notionally called $(Ni,Fe)_3S_2$ solid solution and those with Cu > Ni can be described as *iss*. The caption given to Fig. 5 by [1995Per] lists a constant S content of 45 at.%, whereas all the investigated compositions listed in several tables by [1995Per] give S = 47.06 at.%, corresponding to "$(Cu,Fe,Ni)_9S_8$." The sulfur fugacity of the solid solution measured by [1995Per] by the pyrrhotite method gave log f_{S2} (atm) = −13.8 at the most Fe-rich composition. This increases progressively with increasing Ni in the solution and further on with increasing Cu to a maximum value of −7.

References

1965Cra: J.R. Craig and G. Kullerud, The Cu-Fe-Ni-S System, *Carnegie Inst. Washington, Yearbook,* Vol 65, 1965-1966, p 329-335

1966Pop: G.B. Popova and V.V. Ershov, Physical and Chemical Conditions of Crystallization of Massive Ores in Cu-Ni Sulfide Deposits, *Geologiya Rudnykh Mestorozhdenii,* Vol 8 (No. 1) 1966, p 3-15 (in Russian)

1968Cra: J.R. Craig and G. Kullerud, The Cu-Fe-Ni-S System, *Carnegie Inst. Washington, Yearbook,* Vol 66, 1968, p 413-417

1969Cra: J.R. Craig and G. Kullerud, Phase Relations in the Cu-Fe-Ni-S System and Their Application to Magmatic Ore Deposits, *Écon. Geol. Monograph,* Vol 4, 1969, p 344-358

1971Cab: L.J. Cabri and D.C. Harris, New Compositional Data for Talnakhite $Cu_{18}(Fe,Ni)_{10}S_{32}$, *Econ. Geol.,* Vol 66, 1971, p 673-675

1976Lee: S.L. Lee, "Thermodynamic Properties of the Systems Cu-Ni-S and Fe-Cu-Ni-S," Doctoral Thesis, Columbia University, 1976, p 1-170

1979Cha1: Y.A. Chang, J.P. Neumann, and U.V. Choudary, Phase Diagrams and Thermodynamic Properties of Copper-Sulfur-Metal Systems, *INCRA Monograph VII,* The International Copper Research Association, 1979, p 58-88

1979Cha2: Y.A. Chang, J.P. Neumann, and U.V. Choudary, Phase Diagrams and Thermodynamic Properties of Copper-Sulfur-Metal Systems, *INCRA Monograph VII,* The International Copper Research Association, 1979, p 106-123

1983Chu: Y.Y. Chuang, "The Thermodynamics and Phase Relationships of the Cu-Ni-Fe-S Quaternary System and its Subsystems," Doctoral Thesis, University of Michigan, 1983, p 1-325

1984Din: A.T. Dinsdale, "Phase Diagrams and Thermodynamic Data for the Cu-Fe-Ni-S System," Doctoral Thesis, Brunel Univ., 1984

1987Hsi: K.C. Hsieh, K.C. Vlach, and Y.A. Chang, The Fe-Ni-S System. I. A Thermodynamic Analysis of the Phase Equilibria and Calculation of the Phase Diagram from 1173 to 1673 K, *High Temp. Sci.,* Vol 23, 1987, p 17-38

1990Gup: K.P. Gupta, The Cu-Fe-Ni (Copper-Iron-Nickel) System, *Phase Diagrams of Ternary Nickel Alloys,* Part 1, Ind. Inst. Metals, Calcutta, 1990, p 290-315

1991Swa: L.J. Swartzendruber, V.P. Itkin, and C.B. Alcock, The Fe-Ni (Iron-Nickel) System, *J. Phase Equilibria,* Vol 12 (No. 3), 1991, p 288-312

1995Per: A.V. Peregoedova, Z.N. Fedorova, and E.F. Sinyakova, Physicochemical Conditions of the Pentlandite Formation in Cu-Bearing Sulfide Paragenesis, *Geol. Geofiz.,* Vol 36 (No. 3), 1995, p 98-105 (in Russian); TR: *Russ. Geol. Geophys.,* 1995, Vol 36 (No. 3), p 91-98

2000Qin: G.W. Qin, G. Zhao, M. Jiang, H.X. Li, and S.M. Hao, The Isothermal Sections of the Cu-Fe-Ni Ternary System at 600, 800, 1000 and 1050°C, *Z. Metallkd.,* Vol 91 (No. 5), 2000, p 379-382

2004Rag: V. Raghavan, Fe-Ni-S (Iron-Nickel-Sulfur), *J. Phase Equilibria and Diffusion,* Vol 25 (No. 4), 2004, p 373-381