

Co-Fe-S (Cobalt-Iron-Sulfur)

V. Raghavan

The previous review of this system by [1988Rag] presented a liquidus projection for the Fe-FeS-CoS-Co region, a reaction scheme, and three isothermal sections at 800, 700, and 500 °C, based on the studies of [1953Vog], [1976Wys], and [1985Sch]. An update by [1998Rag] added two more isothermal sections at 1350 and 1200 °C from [1997Sol]. Recently, [2002Far] has clarified the phase relationships in the temperature range below 450 °C.

Binary Systems

The Co-Fe phase diagram [1984Nis] is characterized by an extremely narrow solidification range. The face-centered-cubic (fcc) Fe forms a continuous solid solution γ with α Co over a wide range of temperature. The $\gamma \rightarrow (\alpha$ Fe) body-centered-cubic (bcc) transformation temperature is initially raised by the addition of Co, reaching a maximum of 985 °C at 45 at.% Co. At 730 °C, the bcc phase of equiatomic composition orders to a CsCl type B2 structure.

The computed Co-S phase diagram [1979Cha] depicts five intermediate phases: Co_{1-x}S (NiAs type hexagonal), Co_4S_3 , Co_9S_8 ($D8_0$ type cubic, also known as cobalt pentlandite), Co_3S_4 (cubic), and CoS_2 (FeS_2 (pyrite) type cubic). The metal-deficient monosulfide Co_{1-x}S forms congruently

from the melt at 1180 °C and decomposes eutectoidally at 460 °C to Co_9S_8 and Co_3S_4 , Fig. 1(a) [1979Cha]. The recent experimental results of [1997Bry], however, show that Co_{1-x}S (denoted β) transforms congruently to β' (β' is presumably an ordered form) at ~ 545 °C, and there are two eutectoidal reactions at 475 and 425 °C on either side of the congruent point, Fig. 1(b). Details of the structural measurements identifying the phases were not reported by [1997Bry]. The ordering reactions are complex and play a central role in this low temperature range.

There are two intermediate phases in the Fe-S system [1982Kub]. The monosulfide pyrrhotite Fe_{1-x}S is stable at Fe-deficient (S-rich) compositions with a range of 50-55 at.% S. Fe_{1-x}S with 52 at.% S melts congruently at 1188 °C. In the Fe-FeS region, the solidification is through a eutectic reaction at 988 °C. In the FeS-S region, a monotectic reaction at 1082 °C yields Fe_{1-x}S of 54.2 at.% S and a sulfur-rich liquid (S). At 743 °C, cubic FeS_2 (pyrite) forms peritectically and undergoes a transition to the orthorhombic form (marcasite) at 425 °C.

The phase relations below 350 °C in the pyrrhotite region are complex with the occurrence of several ordered forms. At high temperatures, the NiAs-type unit cell of Fe_{1-x}S contains two formula units per cell, with the S atoms in hexagonal close packing and the metal atoms in octahedral

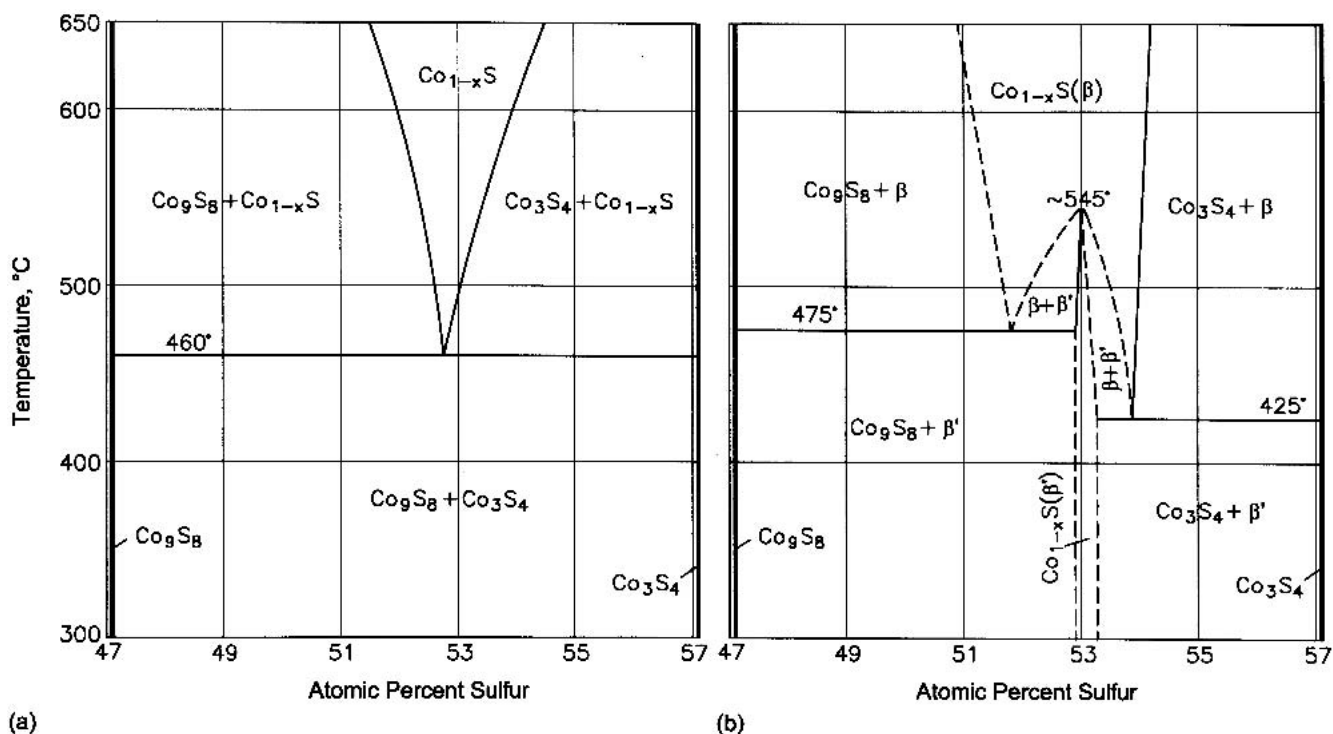


Fig. 1 Co_{1-x}S region of the Co-S phase diagram after (a) [1979Cha], and (b) [1997Bry]

Section II: Phase Diagram Evaluations

coordination. The phase with this unit cell is referred to as 1C. Superstructures arise by the clustering of metal atoms and by the ordering of vacancies in the metal sublattice. If A and C are the lattice parameters of the basic NiAs cell, the 2C structure of stoichiometric FeS (troilite) has $a = A\sqrt{3}$ and $c = 2C$ [1987Bar, 2002Far]. With $a = 2A$ and $c = nC$, numerous superstructures arise. For example, 3C refers to a superstructure with $a = 2A$ and $c = 3C$ [2002Far]. The ordering transitions are dependent on the deviation from stoichiometry of the monosulfide and the presence of metal atoms other than Fe.

Ternary Phase Equilibria

[1997Bry] investigated the composition range Fe_{1-x}S ($x = 0.079$)- Co_{1-x}S ($x = 0.112$) and found that the temperature of the eutectoidal transformation at 425 °C in Fig. 1(b) decreases with increasing Fe content. The transformation was not detected down to 0 °C, when the Fe content reaches the composition $(\text{Fe}_{41.6}\text{Co}_{58.4})_{0.908}\text{S}$.

The low temperature transformations in $(\text{Fe,Co})_{1-x}\text{S}$ were investigated among others by [1987Bar], [1987Col],

and [2002Far]. Phase separation in the $(\text{Fe,Co})_{1-x}\text{S}$ solid solution was studied in detail by [2002Far]. Stoichiometric FeS and CoS (actually a mixture of Co_{1-x}S and Co_9S_8) were prepared from high purity Fe and Co sponge and high purity S, which were heated in evacuated silica tubes up to 700 °C. Required molar proportions of FeS, CoS, and S were then annealed at 800 °C for 2 d and quenched in water. The final anneal was at temperatures between 425 and 105 °C for 7-28 d. The phase equilibria were studied by x-ray powder diffraction, scanning transmission electron microscopy (STEM), and electron probe microanalysis (EPMA). The temperature-composition diagram at an overall composition of S = 52 at.% determined by [2002Far] is redrawn in Fig. 2. It may be noted that a small amount of Co_9S_8 was present in the samples of [2002Far] and, as such, the section in Fig. 2 is not strictly pseudobinary. Between 425 and 400 °C, the single monosulfide phase splits into two phases. The horizontal line in Fig. 2 suggests a eutectoid type of decomposition. The Fe-rich phase has the 1C structure of NiAs. The Co-rich phase has the superstructure 3C. At 400 °C, the solvus of the Fe-rich phase is located at $\text{Fe}/(\text{Fe} + \text{Co}) = 0.83$, and this increases to 0.98 at 105 °C. The solvus of the Co-rich phase is $\text{Fe}/(\text{Fe} + \text{Co}) = 0.37$ at 400 °C and does not vary significantly with the fall in temperature. An isothermal section determined by [2002Far] at 325 °C in the monosulfide region is shown in Fig. 3. The extension of Co_9S_8 into the ternary region is schematic, as is the triangulation in Fig. 3.

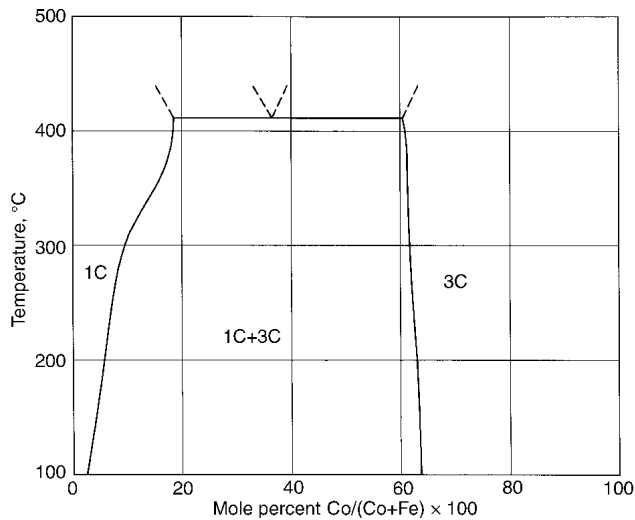


Fig. 2 Co-Fe-S vertical section at an overall S content of 52 at.%, in the presence of Co_9S_8 [2002Far]

References

- 1953Vog:** R. Vogel and G.F. Hillner: "Phase Diagram of Iron-Iron Sulfide-Cobalt Sulfide-Cobalt," *Arch. Eisenhüttenwes.*, 1953, 24(3-4), pp. 133-41 (in German).
- 1976Wys:** P. Wyszomirski: "Experimental Studies of the Ternary Fe-Co-S System in the Temperature Range of 500-700 °C," *Mineral. Polon.*, 1976, 7(1), pp. 39-49.
- 1979Cha:** Y.A. Chang and R.C. Sharma: "Application of an Associated Solution Model to the Metal-Sulfur Melts and the Calculation of the Metal-Sulfur Phase Diagrams," in *Calculation of Phase Diagrams and Thermochemistry of Alloy Phases*, Y.A. Chang and J.F. Smith, ed., Metall. Soc. AIME, Warrendale, PA, 1979, pp. 145-74.
- 1982Kub:** O. Kubaschewski: "Iron-Sulfur," *Iron—Binary Phase Diagrams*, Springer-Verlag, Berlin, 1982, pp. 125-28.
- 1984Nis:** T. Nishizawa and K. Ishida: "The Co-Fe (Cobalt-Iron) System," *Bull. Alloy Phase Diagrams*, 1984, 5(3), pp. 250-59.

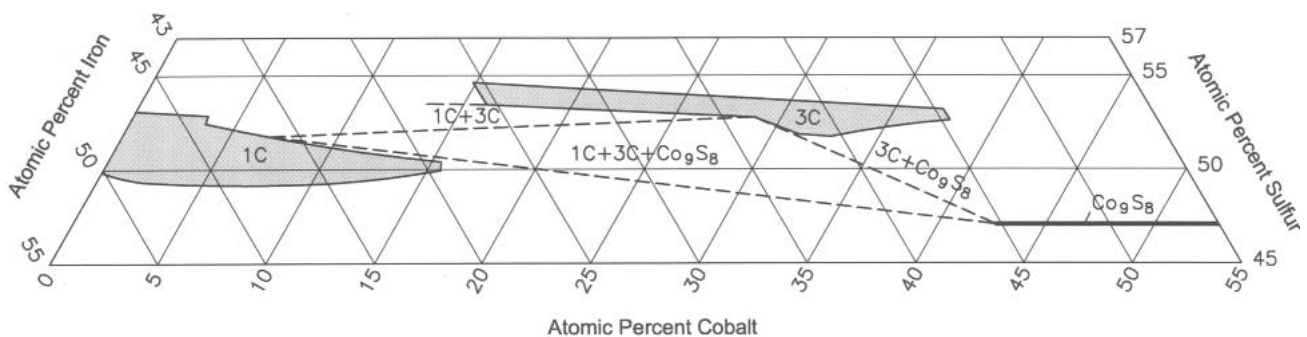


Fig. 3 Co-Fe-S partial isothermal section at 325 °C [2002Far]

- 1985Sch:** R. Schmid, O. Musbah, and Y.A. Chang: "Phase Relations and Thermodynamics of the Fe-Co-S System at 1073 K," *Z. Metallkd.*, 1985, 76(1), pp. 1-16.
- 1987Bar:** E. Barthelemy and C. Carcaly: "Phase Relations and Ageing Effects in $\text{Fe}_{1-x}\text{Co}_x\text{S}$ System," *J. Solid State Chem.*, 1987, 66, pp. 191-203.
- 1987Col:** G. Collin, M.F. Gardette, and R. Gomes: "The $\text{Fe}_{1-x}\text{Co}_x\text{S}$ System ($x < 0.25$); Transition and the High Temperature Phase," *J. Phys. Chem. Solids*, 1987, 48(9), pp. 791-802.
- 1988Rag:** V. Raghavan: "The Co-Fe-S (Cobalt-Iron-Sulfur) System," *Phase Diagrams of Ternary Iron Alloys. Part 2*, Ind. Inst. Metals, Calcutta, 1988, pp. 93-106.
- 1997Bry:** V.A. Bryukvin and L.I. Blokhina: "Phase Equilibria in the System Iron-Cobalt-Sulfur," in *Pyrometall. Fundam. Process Dev. Proc. Nickel-Cobalt 97, Int. Symp.*, C.A. Levac and R.A. Berryman, ed., Canad. Inst. Min. Metall. Petroleum, Montreal, Quebec, 1997, pp. 337-41.
- 1997Sol:** M. Soltaneih, J.M. Toguri, and R. Sridhar: "The Liquidus Surface and Tie-Lines in the Fe-Co-S System between 1473 and 1623 K," *Metall. Mater. Trans. B*, 1997, 28B, pp. 647-50.
- 1998Rag:** V. Raghavan: "Co-Fe-S (Cobalt-Iron-Sulfur)," *J. Phase Equilibria*, 1998, 19(3), p. 264.
- 2002Far:** S.P. Farrell and M.E. Fleet: "Phase Separation in $(\text{Fe,Co})_{1-x}\text{S}$ Monosulfide Solid-Solution below 450 °C, with Consequences for Coexisting Pyrrhotite and Pentlandite in Magmatic Sulfide Deposits," *Canadian Mineralogist*, 2002, 40, pp. 33-46.