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

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The study of this system is of practical importance in the extraction of Ni from its ores. It is also relevant to the hot corrosion of high temperature alloys in S-bearing atmospheres. An evaluation of this system from the liquid range to 700 °C by [1982Hsi] presented a liquidus projection, a reaction scheme, a vertical section at 40 at.% S, and seven isothermal sections at 1100, 1005, 900, 850, 800, 750, and 700 °C. Many new reports have since appeared on the experimental and computed phase relationships of this system.

Binary Systems

The Fe-Ni phase diagram [1991Swa] is characterized by a very narrow solidification range with a peritectic reaction at 1514 °C, between bcc δ and liquid that yields the Fe-based face-centered-cubic (fcc) solution. A continuous solid solution denoted γ between fcc Fe and Ni is stable over a wide range of temperature. At lower temperatures, an ordered phase $FeNi_3$ ($AuCu_3$ type, cubic) forms congruently at 517 °C from γ. The γ→α [body-centered-cubic (bcc) Fe] transition temperature is lowered by Ni. There are two intermediate phases in the Fe-S system [1982Kub]. The monosulfide $Fe_{1-x}S$ (NiAs type hexagonal; mineral name: pyrrhotite denoted *po*) 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 $(S)_l$. At 743 °C, cubic FeS_2 (pyrite, *py*) forms peritectically and undergoes a transition to the orthorhombic form of marcasite at 425 °C. The phase relations below 350 °C in the pyrrhotite region are complex with the occurrence of several ordered forms. The Ni-S phase diagram is not fully established [Massalski2]. There are a number of intermediate phases in the system: NiS_2 (pyrite type cubic, mineral name vaesite denoted *vs*), Ni_3S_4 (Co_3S_4 type cubic, 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. It is sometimes represented as two phases within this range [1978Lin], as a consequence of a break seen in the S fugacity curve plotted as a function of composition within this range [1976Rau]. [1994Sto] reinvestigated the Ni-S phase diagram in the range of 44-48 at.% S and labeled a phase as Ni_9S_8, but it falls within the homogeneity range of Ni_7S_6. For lattice parameter data, see [Pearson3, 1998Sug, 2000Uen].

Ternary Phases

The isostructural phases $Fe_{1-x}S$ (pyrrhotite) and $Ni_{1-x}S$ form a continuous solid solution from solidus temperatures down to ~300 °C. This solution is denoted *mss* (monosulfide solid solution). The ternary solid solution $(Fe,Ni)_9S_8$ with the mineral name pentlandite (denoted *pn*) has been studied extensively. It had the Co_9S_8 type of cubic structure. Widely varying data have been reported for its homogeneity range. [1970She] used *d*-spacing measurements to determine the range (in at.%) as 29.0-20.7 Fe; 24.7-31.3 Ni at 600 °C, 34.0-14.8 Fe; 19.4-37.1 Ni at 500 °C and 35.5-20.7 Fe; 18.0-31.8 Ni at 400 °C. [2003Kos] recommended a Ni range of 22.5-32 at.% at 600 °C, whereas [1973Mis], from results of electron microprobe analysis, gave a range of ~20-41 at.% Ni at 600 °C. The S range is small in all cases, about 1 at.% or less, around the stoichiometric composition of 47.1 at.%. Pentlandite forms through a peritectoid reaction at 610 °C between Ni_3S_2 and *mss*. Recently, [1998Sug] reported a high temperature form of *pn,* stable between 865 and 584 °C, with its cubic lattice parameter being half of that of *pn* that exists below 610 °C. According to [1998Sug], the high temperature *pn* phase forms through a peritectic reaction at 865 °C. It is not clear whether the thermal effect observed by [1998Sug] at 865 °C could be associated with the peritectic formation of the high temperature form of Ni_3S_2 at 862 °C in the ternary region [1982Hsi]. It may be noted that the high temperature form of Ni_3S_2 has the same crystal symmetry (fcc) as *pn*, similar lattice parameter as the high temperature version of *pn* as found by [1998Sug], and also dissolves a considerable amount of Fe (26 at.% at 600 °C [2003Kos] and 33 at.% at 725 °C [1995Kar]). In fact, at 725 °C, [1995Kar] interpreted the high temperature phase as a part of the broad solid solution field of Ni_3S_2.

Thermodynamic Models

A comprehensive thermodynamic analysis of this system was reported by Chang and coworkers [1983Chu, 1987Hsi1, 1987Hsi2, 1987Hsi3]. The presence of vacancies in the metal-deficient monosulfide solid solution *mss* was modeled. The other phases were treated as pseudobinaries of the two binary sulfides, using subregular solution models. The ternary sulfide melts were described by an associated solution model. A liquidus projection and 12 isothermal sections at 1350, 1300, 1200, 1100, 1050, 1017, 1000, 900, 850, 800, 750, and 700 °C were computed. Stability diagrams, which are plots of the partial pressure of S versus composition, were also calculated at 1100, 1017, 900, 850, 800, 750, and 700 °C [1987Hsi1, 1987Hsi3].

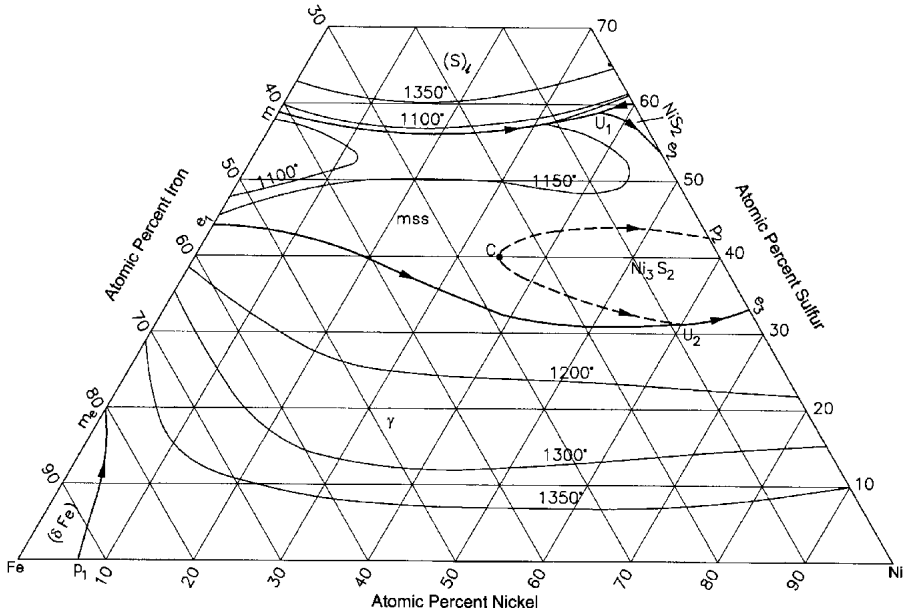

Fig. 1 Fe-Ni-S computed liquidus projection [1987Hsi1]

Liquidus Projection

The liquidus projection computed by [1987Hsi1] is redrawn in Fig. 1. There are two U-type transition reactions. $L + (S)_l \leftrightarrow NiS_2 + mss$ (U_1) is at 1005 °C in [1982Hsi] and 1017 °C in [1987Hsi1] and $L + mss \leftrightarrow \gamma + Ni_3S_2$ (U_2) is at ~740 °C. The binary phase Ni_3S_2 forms in the ternary region at 862 °C at the upper critical point *C*.

The liquidus surface in the Fe-FeS-NiS-Ni region was studied recently by [1999Sin]. With starting materials of 99.99% Fe, 99.99% Ni, and 99.9999% S, [1999Sin] prepared samples that were sealed in evacuated quartz tubes and thermal analysis was carried out at a heating rate of 10-20 °C/min and a cooling rate of 20-30 °C/min. The phase equilibria were studied by x-ray diffraction and optical and electron microscopy. The liquidus surface constructed by [1999Sin] disagrees with that given by [1982Hsi] and [1987Hsi1] in several respects. The peritectic formation of Ni_3S_2 at 862 °C through the reaction between liquid and *mss* was not observed by [1999Sin]. More importantly, point *D* in Fig. 3 and Table I of [1999Sin] was interpreted as a ternary eutectic reaction at 961 °C. This is impossible, as two of the three liquidus lines meeting at *D* approach the point with an increase in temperature. If one assumes point *D* to be the ternary peritectic formation of Ni_3S_2, the temperature of 961 °C appears too high, as compared with 862 °C [1982Hsi] and the composition of the liquid at point *D* [1999Sin] is quite different from the liquid composition at the critical point *C* in Fig. 1. Due to this uncertainty, the results of [1999Sin] are not discussed further.

The liquidus and the solidus of *mss* ($Fe_{0.96}S$-$Ni_{0.96}S$) were determined by [1998Sin], and these are redrawn in Fig. 2 and compared with a few data points from [1963Kul]. The liquidus and solidus temperatures T_l and T_s are given by the following empirical equations:

$$T_l\,(°C) = 1184 - 318.222X + 55.7803X^2 + 68.3025X^3$$

and

$$T_s\,(°C) = 1180 - 514.82X + 407.816X^2 - 113.837X^3$$

where X is the mole fraction of $Ni_{0.96}S$ [1998Sin]. At neither end does the composition of the monosulfide (containing 51 at.% S) correspond to its congruent melting point.

Isothermal Sections

The review of [1982Hsi] presented seven isothermal sections at 1100, 1005, 900, 850, 800, 750, and 700 °C, based primarily on the work of Kullerud and coworkers [1963Cla, 1963Kul, 1969Kul], with additional input from later work. A number of isothermal sections have since been reported. [1978Len] determined partial isothermal sections at 1350, 1300, and 1200 °C, by quenching samples equilibrated in the ($L + \gamma$) region and determining the composition by the electron probe microanalyzer. The other isothermal sections are at 900 °C [1993Fed, 1998Kar], 850 °C [1987Hsi4], 820 °C [1993Fed], 800 °C [1987Hsi4], 750 °C [1987Hsi4], 725 °C [1995Kar], 700 °C [1987Hsi4], 600 °C [1993Fed, 2001Sin, 2003Kos], 500 °C [2000Uen], and 400 °C [2000Uen]. Partial sections mainly depicting the tie lines between $Fe_{1-x}S$ and the Fe-Ni phases were reported by [1998Ma] at 700, 600, 500, 400, and 300 °C. The earlier literature reporting isothermal sections includes: [1963Kul] (1100, 1000, 900, 860, 650, 600, 575, 550, 500, and 400 °C); [1968Cra] (400 °C); [1970She] (600, 500, and 400 °C); and [1973Cra] (300, 250, and 200 °C).

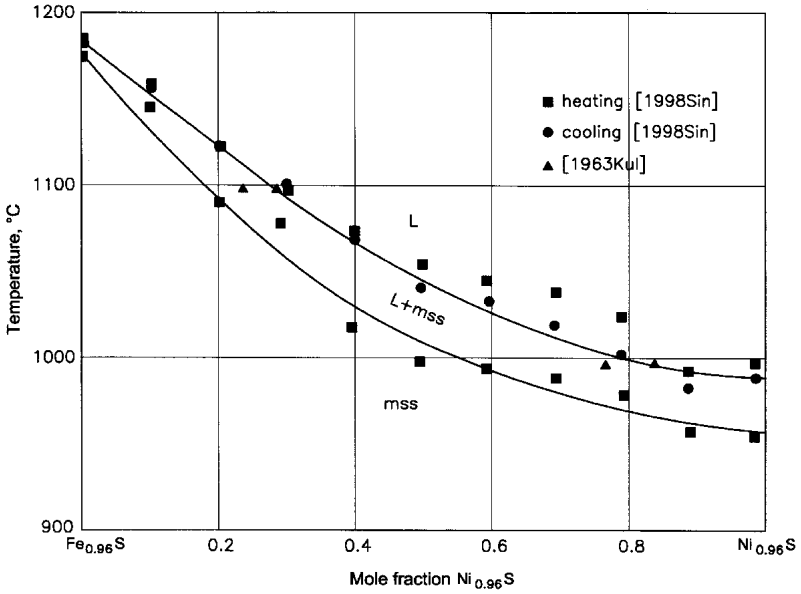

Fig. 2 Fe-Ni-S vertical section along the $Fe_{0.96}$-$Ni_{0.96}S$ join [1998Sin]

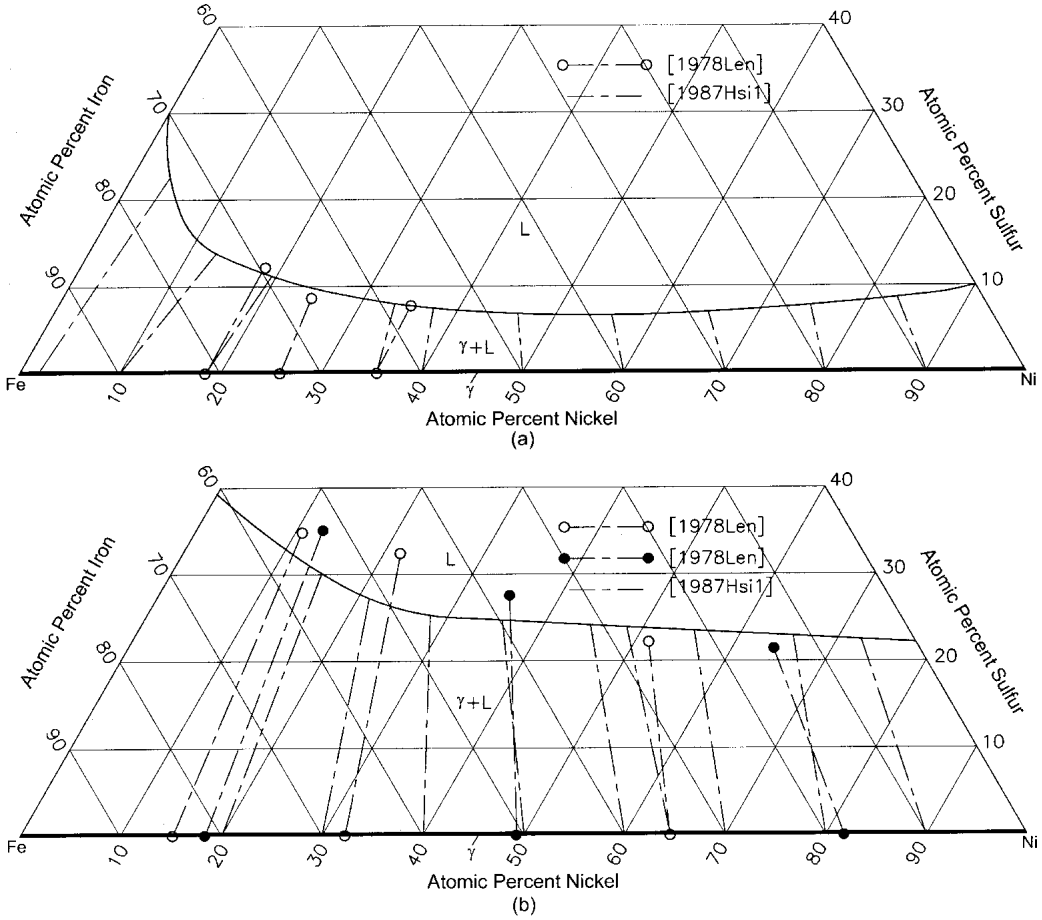

Fig. 3 Fe-Ni-S computed isothermal sections at **(a)** 1350 °C, and **(b)** 1200 °C [1987Hsi1]. Tie lines marked with filled circles are from samples containing residual oxygen.

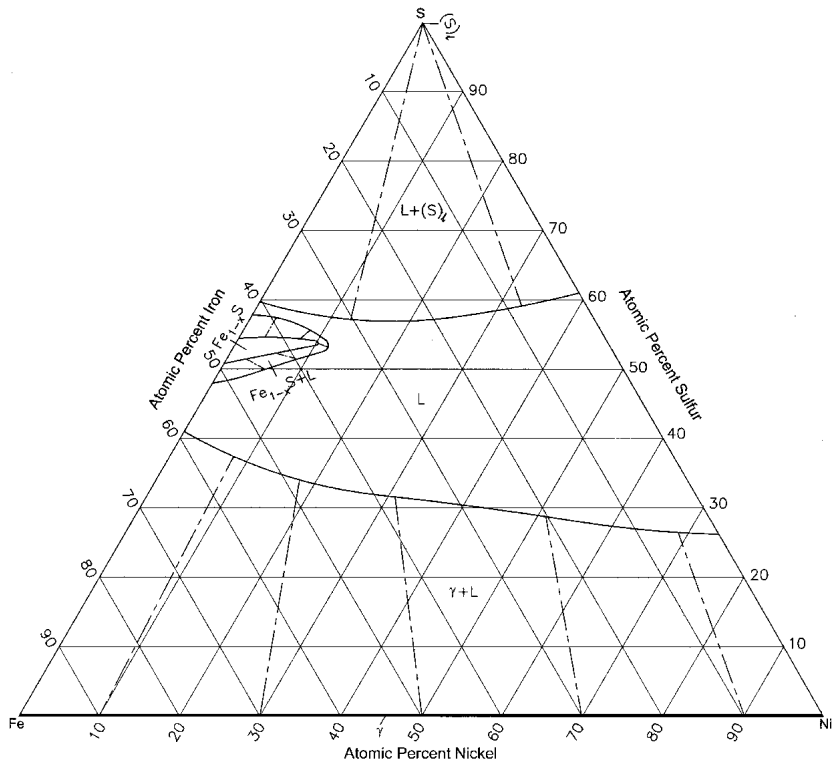

Fig. 4 Fe-Ni-S computed isothermal section at 1100 °C [1987Hsi1]

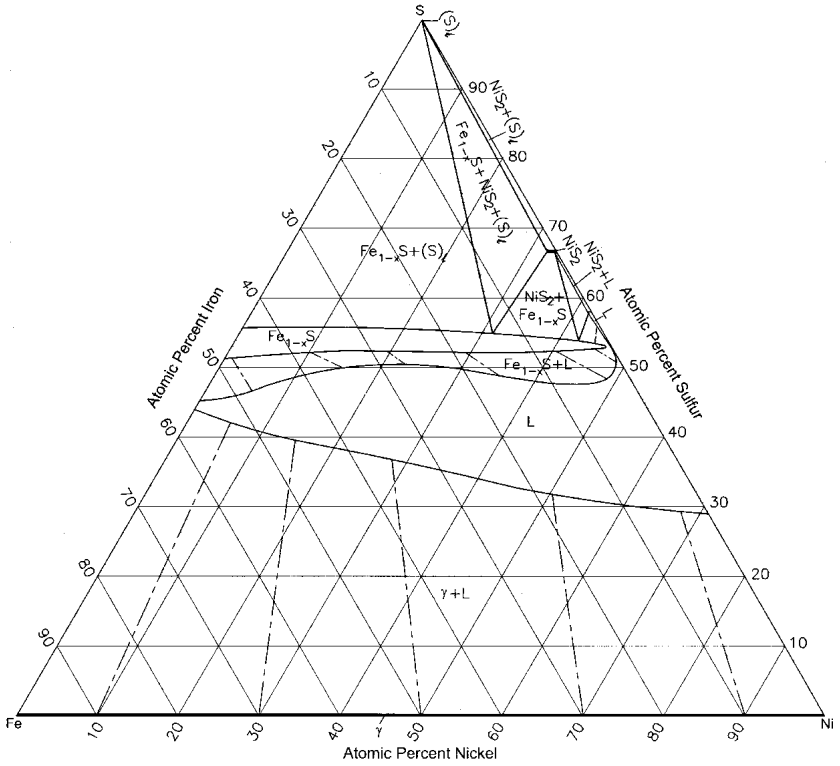

Fig. 5 Fe-Ni-S computed isothermal section at 1000 °C [1987Hsi1]

The computed tie lines [1987Hsi1] for the two-phase equilibrium between γ and the sulfide melt at 1350, 1300, and 1200 °C agree well with the experimental results of [1978Len]. Figure 3 compares the experimental tie lines with the computed ones at 1350 and 1200 °C. [1987Hsi1] and [1987Hsi3] computed isothermal sections at 1100 and

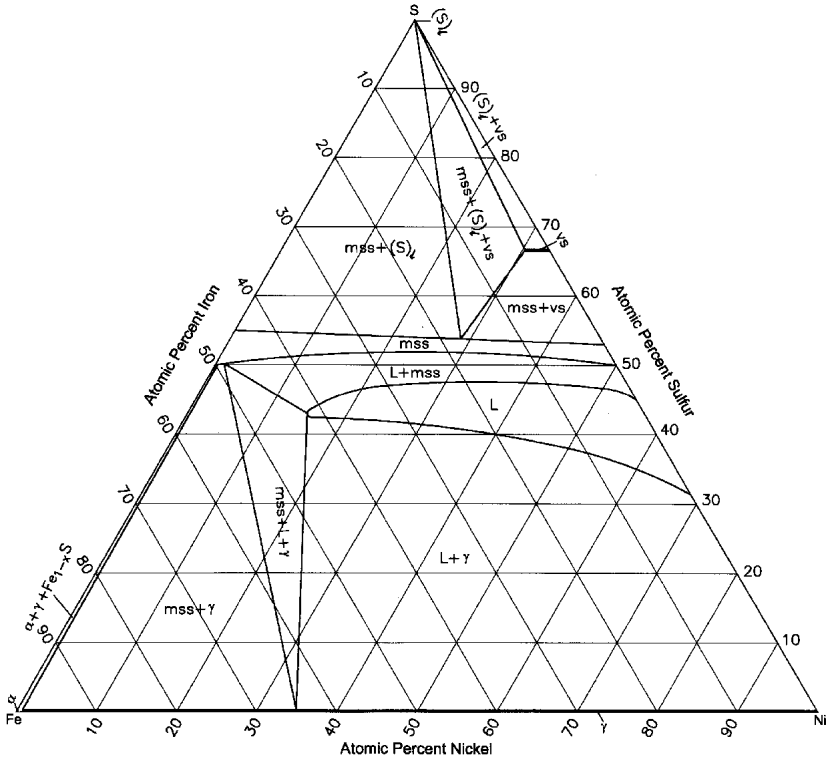

Fig. 6 Fe-Ni-S isothermal section at 900 °C [1998Kar]

1000 °C (Fig. 4 and 5), which are in satisfactory agreement with the experimental diagrams of [1963Kul].

With starting materials of spectroscopically pure Fe (15 ppm of metallic impurities), spectroscopically pure Ni (20 ppm of metallic impurities), and 99.99+% S, [1998Kar] heated a total of 63 binary and ternary compositions to 900 °C. The final anneal was at 900 °C for 15 d, followed by water quenching. The phase equilibria were studied by reflected light microscopy and electron probe microanalysis. The measured compositions of the coexisting phases were listed. The isothermal section at 900 °C constructed by [1998Kar] is redrawn in Fig. 6. The liquid phase originating on the Ni-S side extends far into the ternary region, dissolving up to 42 at.% Fe. The γ phase extends over all of the Fe-Ni side, except for a small region near the Fe end. The low S boundary of the monosulfide solid solution *mss* starts from the stoichiometric composition at the Fe end and recedes to higher S contents over most of the solid solution field. $Fe_{1-x}S$, in three-phase equilibrium with alloy (35 at.% Ni) and sulfide melt (15 at.% Ni, 43 at.% S), dissolves up to 1.1 at.% Ni. NiS_2 (*vs*), in three-phase equilibrium with *mss* (28.8 at.% Ni, 53.5 at.% S) and the sulfur-rich liquid $(S)_1$, dissolves up to 3 at.% Fe. Using starting materials of the same purity as above, [1995Kar] heated 54 compositions in evacuated silica tubes, which were given a final anneal at 725 °C for 15 d and quenched. The phase equilibria were studied by reflected light microscopy and electron probe microanalysis. The measured compositions of the coexisting phases were listed. The isothermal section at 725 °C of [1995Kar] is redrawn in Fig. 7. The boundaries of the *mss* phase field are linear on both the S-rich side and the metal-rich side. The sulfide melt along the Ni-S side has a range of 34-38.4 at.% S and dissolves up to 11.9 at.% Fe. Ni_3S_2 has a range of 39.3-45 at.% S and dissolves up to 32.6 at.% Fe. FeS_2 and NiS_2 dissolve, respectively, at 3.6 at.% Ni and 9.6 at.% Fe.

With starting materials of 99.99% Fe, 99.99% Ni, and 99.9999% S, [2003Kos] synthesized about 25 ternary compositions in evacuated quartz tubes, which were given a final anneal at 600 °C for 2 months and quenched. The phase equilibria were studied with optical microscopy, x-ray powder diffraction, and electron probe microanalysis. Combining their results with other results from their own group [2001Sin] and literature data, [2003Kos] constructed an isothermal section for this ternary system at 600 °C, which is redrawn in Fig. 8. Empirical polynomial equations were developed by [2003Kos] to describe the boundaries of *mss*, *pn*, and *hz* as a function of composition.

[2003Kos] measured the S fugacity (f_{S2}) by the pyrrhotite technique, which makes use of the established relationships between the composition of pyrrhotite ($Fe_{1-x}S$), temperature, and S fugacity. Pyrrhotite and the ternary composition to be investigated are placed in the same evacuated tube and annealing is done to allow the transfer of S through the vapor phase. The attainment of equilibrium is deduced by using two pyrrhotite samples of differing initial composition. These compositions become equal on attainment of equilibrium. [2003Kos] determined the S fugacity in the *mss, mss* + *pn, mss* + Ni_3S_2, and *mss* + *pn* + Ni_3S_2 fields. As an example, the isofugacity curves in the *mss* single-phase field are shown in Fig. 9 [2003Kos]. A few fugacity lines in the two-phase fields of *mss* + *pn* and *mss* + Ni_3S_2 (which are

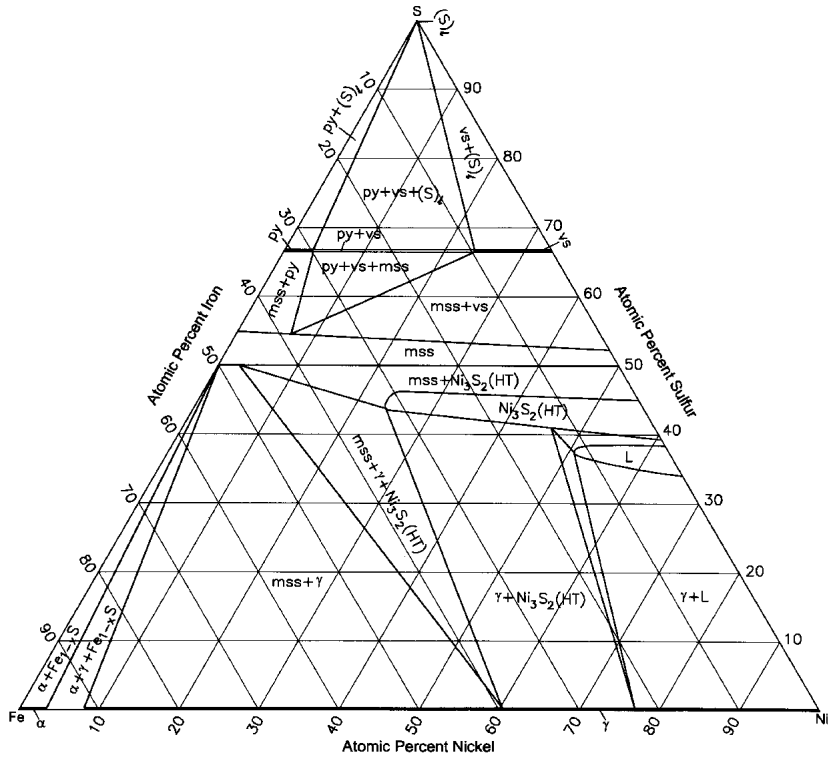

Fig. 7 Fe-Ni-S isothermal section at 725 °C [1995Kar]

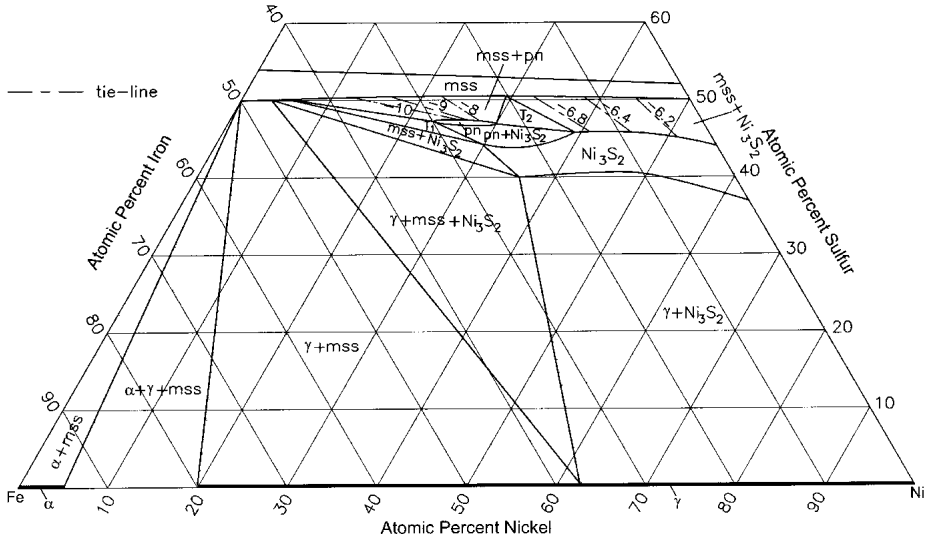

Fig. 8 Fe-Ni-S isothermal section at 600 °C [2003Kos]. The numbers on tie lines are log f_{S2} values.

tie lines) are shown in the isothermal section at 600 °C (Fig. 8). The two tie-triangles of (*mss* + *pn* + Ni_3S_2) in Fig. 8 have log f_{S2} values of −11.19 in the Fe-rich field marked T_1 and −7.27 in the Ni-rich field marked T_2. [2003Kos] developed empirical equations to describe the fugacity as a function of composition. [1987Hsi4] also measured S activities between 900 and 700 °C, by equilibrating metallic (or sulfide) samples in H_2/H_2S gas mixtures.

With starting materials of 99.99% Fe, 99.99% Ni, 99.999% S, and synthetic monosulfides, [2000Uen] heated appropriate mixtures of over 100 compositions, which were annealed at 500 °C for 10-20 d and at 400 °C for 35-74 d and quenched in water. The phase equilibria were studied by reflected light microscopy, x-ray powder diffraction, and electron probe microanalysis. In the isothermal sections at 500 and 400 °C, [2000Uen] did not distinguish between γ

and $FeNi_3$. The Ni contents of the Fe-Ni alloys that are in two-phase equilibrium with *pn* are skewed more toward Ni-rich compositions in the results of [2000Uen], as compared with those of [1970She] and [1968Cra]. The microprobe measurements of [2000Uen] for the (α+γ)/γ boundary in Fe-Ni alloys are likewise shifted toward the Ni end and do not agree with the binary data accepted here. In view of this, the isothermal section constructed earlier by [1970She] at 500 °C appears more reliable and is given in Fig. 10. [1970She] used starting materials of 99.999% Fe, 99.99% Ni, and 99.999% S and studied the phase equilibria by optical microscopy and x-ray powder diffraction.

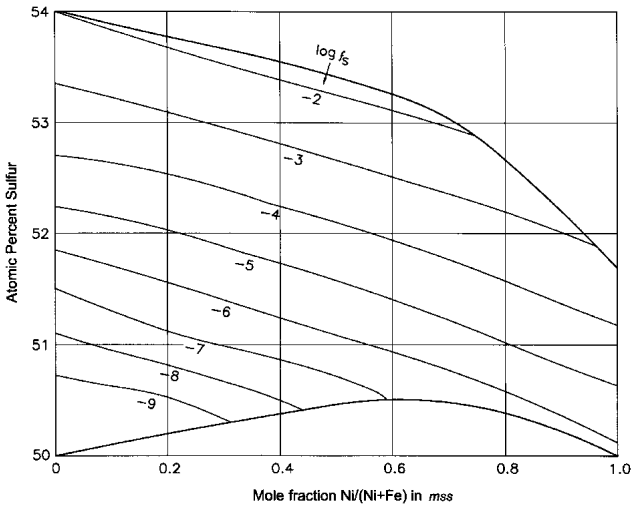

Fig. 9 Fe-Ni-S sulfur fugacity curves in the *mss* phase field at 600 °C [2003Kos]

The isothermal section constructed by [1968Cra] at 400 °C is shown in Fig. 11. The continuous solid solution *mss* persists at 400 °C. Pentlandite (*pn*) has a Ni range of 21-36 at.%. Ni_3S_4 (violarite, *vio*) is present in the ternary region only, with a Ni range of 29-37 at.%. The formation temperature of the binary Ni_3S_4 is 356 °C. Apparently, Fe stabilizes this phase at higher temperatures. Solubility of the third component (in at.%) in the binary compounds is limited, typically ~1 at.% or less. The Fe-Ni phases dissolve a negligible amount of S. The isothermal section in Fig. 11 is in satisfactory agreement with that of [1970She].

[1973Cra] studied the phase relationships at still lower temperatures of 300, 250, and 200 °C. Long annealing times of 1-12 months were used. The phase equilibria were studied by optical microscopy, x-ray powder diffraction, and electron probe analysis. A miscibility gap arises in the central portion of the continuous monosulfide solid solution *mss* below 263 ± 13 °C [1973Cra]. A second miscibility gap appears in the Ni-rich portion of this solid solution at 225 ± 25 °C. Tie lines extend from pentlandite to pyrite through the central gap in the isothermal section at 200 °C (not shown here). Ni_3S_4 (violarite) extends up to the composition $FeNi_2S_4$ at 300, 250, and 200 °C. In addition to the complicated phase transitions in the binary monosulfides at low temperatures, the phase relations are admittedly vitiated by nucleation difficulties and the occurrence of metastable equilibria, e.g., between $Fe_{1-x}S$ and Ni_3S_4.

[1996Kos] analyzed the topology of the phase evolution in this system. Using the known experimental information,

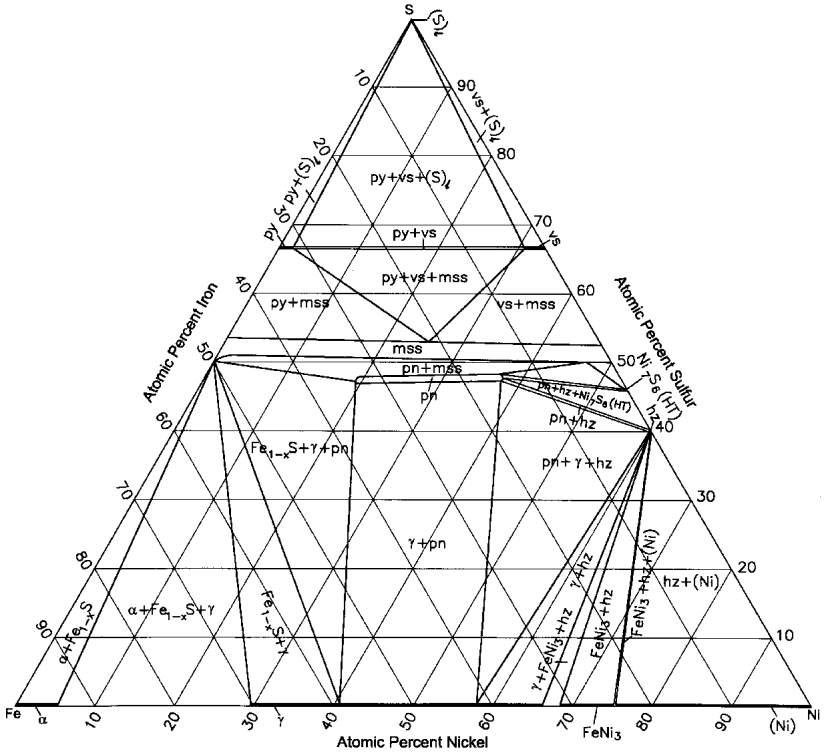

Fig. 10 Fe-Ni-S isothermal section at 500 °C [1970She]

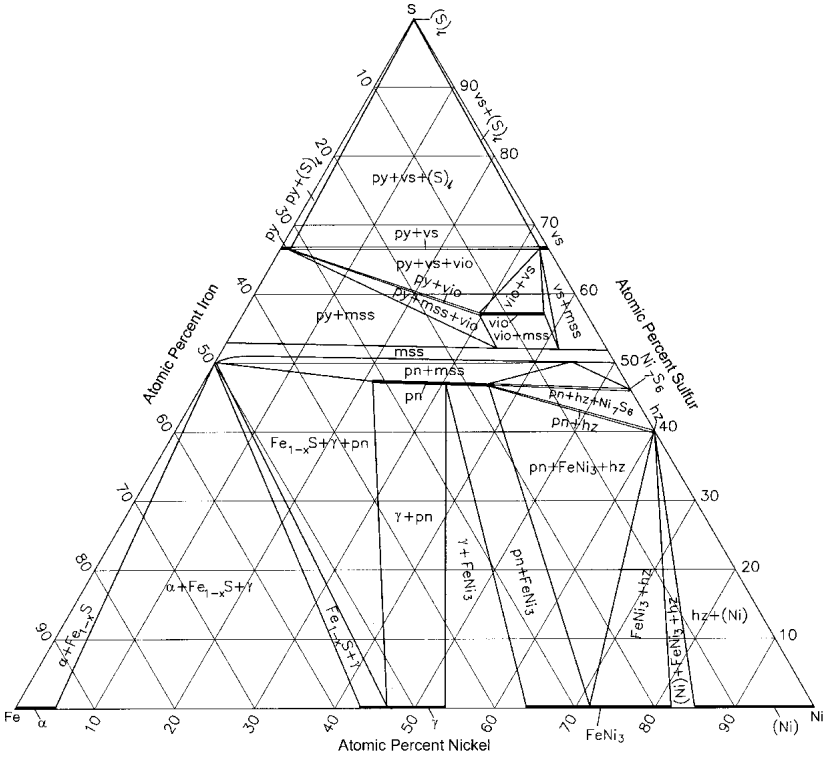

Fig. 11 Fe-Ni-S isothermal section at 400 °C [1968Cra]

they derived schematic isothermal and vertical sections on the basis of topologocal considerations.

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