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Fe-Mn-S (Iron-Manganese-Sulfur)

V. Raghavan

The previous review of this system [1988Rag] presented a schematic liquidus surface, four isothermal sections at 1600, 1300, 1100, and 800 °C mainly for the Fe-FeS-MnS-Mn region, a pseudobinary section along the FeS-MnS join, the same section in the presence of Fe, a liquidus projection near the Fe corner, and a reaction scheme. Two thermodynamic treatments of the Fe-FeS-MnS-Mn region have been reported recently [1998Mie, 2000Oht].

Binary Systems

The Fe-Mn phase diagram [1982Kub1] contains no intermediate phases. A continuous solid solution denoted γ forms between fcc Fe and γMn. There are two intermediate phases in the Fe-S system [1982Kub2]. The monosulfide pyrrhotite $Fe_{1-x}S$ (NiAs type hexagonal) 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) 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. The only intermediate phase of the Mn-S system, MnS, has the NaCl type cubic structure and melts at 1655 °C [Massalski2]. The system is characterized by the presence of a miscibility gap between Mn-rich and MnS-rich liquids, with the monotectic temperature at 1570 °C and the final eutectic solidification near the Mn-end.

Thermodynamic Assessments

The thermodynamic treatments of this system by [1998Mie] and [2000Oht] pertain to the Fe-FeS-MnS-Mn region of the system. The solubility of FeS in cubic MnS is up to 79 mol% [1988Rag]. This phase, labeled (Mn,Fe)S by [1988Rag], is called the Q phase after [1937Vog, 1998Mie, 2000Oht]. The solubility of MnS in hexagonal $Fe_{1-x}S$ is only 8 mol% [1988Rag]. This phase is denoted P [1937Vog, 1998Mie, 2000Oht].

[1998Mie] treated the liquid phase on the basis of a two sublattice model (Fe,Mn)(S,Va), where Va stands for vacancies. The two sublattice model was also applied to the sulfide solid solution (Fe,Mn)S, omitting the vacancies. The solid phases, fcc, bcc, and the cubic forms of Mn, were considered as substitutional solutions. The description of the Fe-FeS system was basically from [1984Din], with a reassessment of the interaction parameters using the SGTE phase stability data. The description of the Mn-MnS system by [1976Sta] was used by [1998Mie]. For the Fe-Mn system, the assessment of [1989Hua] was adopted. The ternary interaction parameters $L_{Fe,Mn:S}$ and $L_{Fe,Mn:S,Va}$ were evaluated by [1998Mie]. The computed results were presented as the FeS-MnS pseudobinary system, the same system in the presence of Fe, the liquidus projection, the liquid miscibility gap at 1600 °C, and the solubility of S in the fcc phase in the temperature range of 1335-1100 °C. The computed liquid miscibility gap of [1998Mie] near the Fe corner shown in Fig. 1 is in good agreement with experimental data.

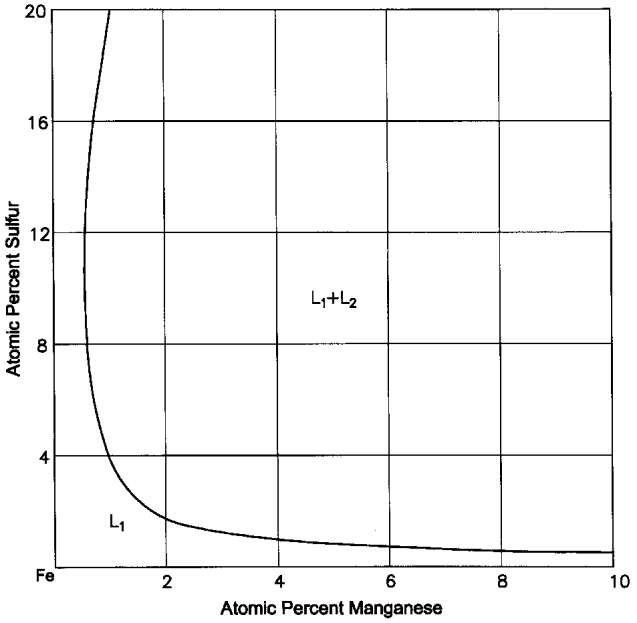

Fig. 1 Fe-Mn-S computed liquid miscibility gap near the Fe corner at 1600 °C [1998Mie]

The thermodynamic treatment of [2000Oht] is similar to that of [1998Mie]. The parameters optimized by [1986Oht] for the Fe-FeS system were used. Using the approach of [1976Sta], the parameters for the Mn-MnS system were reevaluated by [2000Oht]. The description of the Fe-Mn system by [1989Hua] was used. The sulfide solid solution between the two compound phases FeS and MnS was described by a regular solution model. The computed results were presented as a FeS-MnS pseudobinary section, the same section in the presence of Fe, a liquidus projection, seven isothermal sections at 100° intervals between 1600 and 1000 °C, and four vertical sections at Fe:Mn weight ratios of 97:3 and 90:10, at 0.3 wt.% S and along the Fe-MnS join, respectively. Satisfactory agreement of the computed diagrams was found with the available experimental results. To supplement the experimental data reviewed by [1988Rag], four isothermal sections of [2000Oht] at 1500, 1400, 1200, and 1000 °C are redrawn in Fig. 2 and 3. The liquid miscibility gap, which has origins in the Mn-MnS

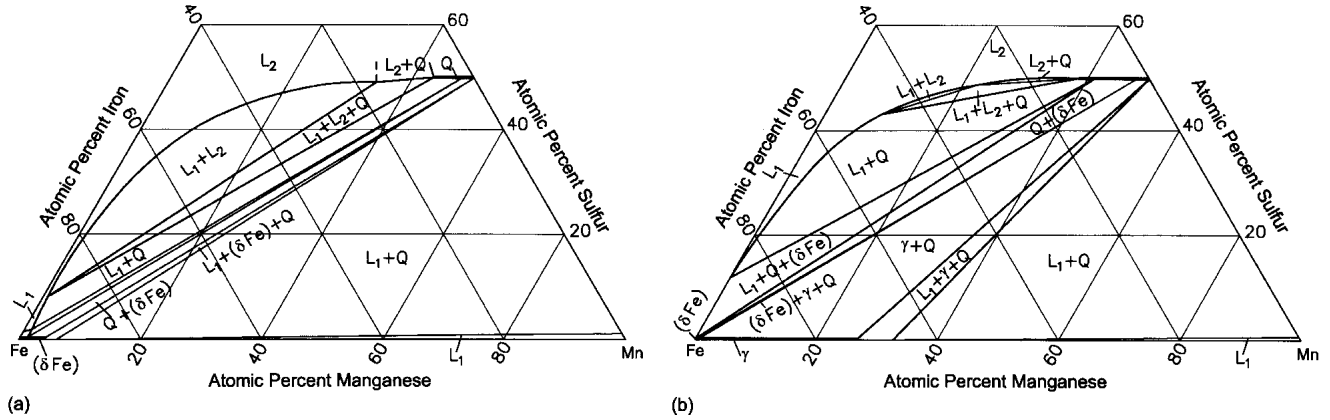

Fig. 2 Fe-Mn-S computed isothermal sections at **(a)** 1500 °C, and **(b)** 1400 °C [2000Oht]

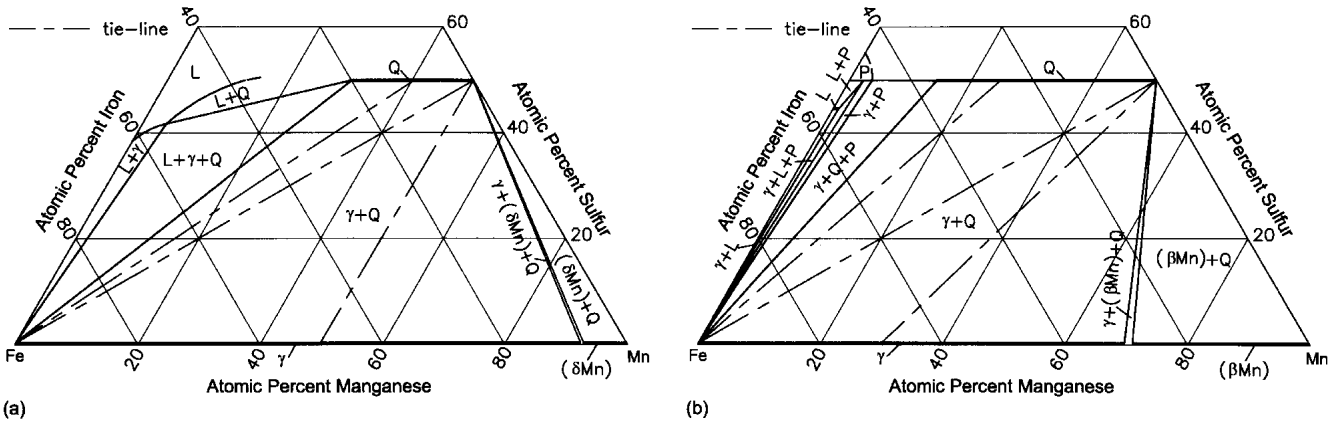

Fig. 3 Fe-Mn-S computed isothermal sections at **(a)** 1200 °C, and **(b)** 1000 °C [2000Oht]

system, has an appreciable range at 1500 °C, Fig. 2(a). It is hardly seen at 1400 °C (Fig. 2b), as it disappears at the lower critical point of 1370 °C [1937Vog]. At 1200 °C (Fig. 3a), the dominant two-phase field is (γ + Q). Almost pure Fe forms tie lines with almost pure MnS. The P phase based on pyrrhotite appears at 1000 °C, Fig. 3(b).

[1998Vda] reported a computed isothermal section at 1487 °C for Fe-rich alloys of this system.

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