JPEDAV (2004) 25:368-370
DOI: 10.1361/15477030420142
1547-7037/$19.00 ©ASM International

Cr-Fe-S (Chromium-Iron-Sulfur)

V. Raghavan

The previous review of this system by [1988Rag] presented a liquidus surface, three isothermal sections at 950, 700, and 600 °C and a reaction scheme, based primarily on the work of [1938Vog] and [1969Elg]. An update of this system [1998Rag] summarized the results of [1982Ind] on the pseudobinary section FeS-Cr_2S_3 and of [1988Fuj] on the isothermal section at 1300 °C. Recently, [2000Oik] carried out a thermodynamic evaluation of this system.

Binary Systems

In the Fe-Cr phase diagram [1993Itk], a minimum occurs in the liquidus-solidus line at 1513 °C and at 21 at.% Cr. A gamma loop restricts the face-centered-cubic (fcc) phase γ to about 12 at.% Cr. The body-centered-cubic (bcc) phase α is stable over a large region. The intermediate phase σ ($D8_b$, tetragonal) forms from α at 820 °C around the midcomposition and decomposes eutectoidally at 545 °C to Fe-rich and Cr-rich bcc phases. In the Cr-S phase diagram [1938Vog, 1969Elg, Massalski2], a liquid miscibility gap exists between a metal-rich liquid and a sulfide liquid, with a monotectic reaction at 1550 °C. [2000Oik] quote a pre-1950 publication that places the monotectic reaction above 1760 °C. The computed Cr-CrS diagram of [2000Oik] shows the monotectic reaction to be at ~1850 °C. Clearly, more modern experimental results are necessary to resolve these differences. $Cr_{1-x}S$ (NiAs type hexagonal) is metal-deficient, has a homogeneity range of 50-59 at.% S, and forms congruently between 1550 and 1600 °C. At lower temperatures, several other phases occur in this region, see [Massalski2] for a summary. There are two intermediate phases in the Fe-S system [1982Kub]. $Fe_{1-x}S$ (pyrrhotite) 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.

Ternary Phase Equilibria

In their thermodynamic calculation of this system, [2000Oik] described the liquid phase by a two sublattice model, one containing the metal atoms and the other S atoms and vacancies. The fcc and bcc solid solution phases were also described by a two sublattice model. The magnetic contribution to the free energy was taken into account. The continuous monosulfide solid solution denoted λ was treated as stoichiometric (with respect to S), with two sublattices for the metal atoms (Cr and Fe) and S atoms, respectively. The computed results were presented as a liquidus projection for the Fe-FeS-CrS-Cr region, isothermal sections at 1600, 1500, 1370, 1300, 1090, and 950 °C and as vertical sections at 19.5 wt.% S, Fe:Cr weight ratio of 4:1, and along the Fe-CrS join. The isothermal sections computed at 1600, 1500, 1370, and 1090 °C by [2000Oik] are redrawn in Fig. 1 and 2 to supplement the data reviewed earlier [1988Rag, 1998Rag]. The liquid miscibility gap [1938Vog] is present at 1600 and 1500 °C (Fig. 1). It disappears at some temperature between 1500 and 1370 °C. Three-phase regions of (α + γ + L) and (α + λ + L) are schematically indicated in Fig. 2(a). The computed isothermal section of [2000Oik] at 1300 °C (not shown here) is in agreement with that of [1988Fuj] (reviewed in [1998Rag]) and the computed section at 950 °C (not shown) is in agreement with that of [1938Vog] (reviewed in [1988Rag]).

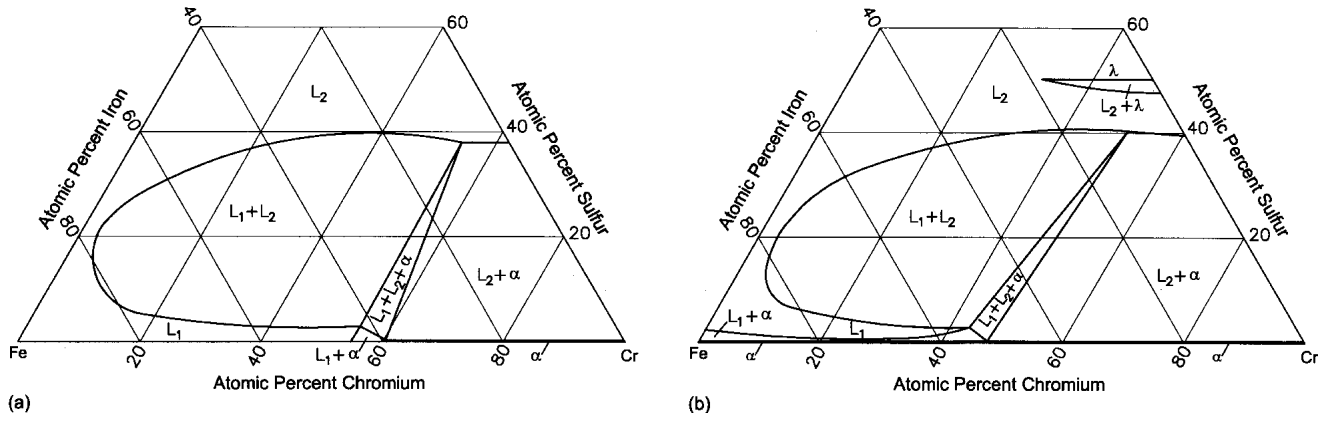

Fig. 1 Cr-Fe-S computed isothermal sections at **(a)** 1600 °C, and **(b)** 1500 °C [2000Oik]

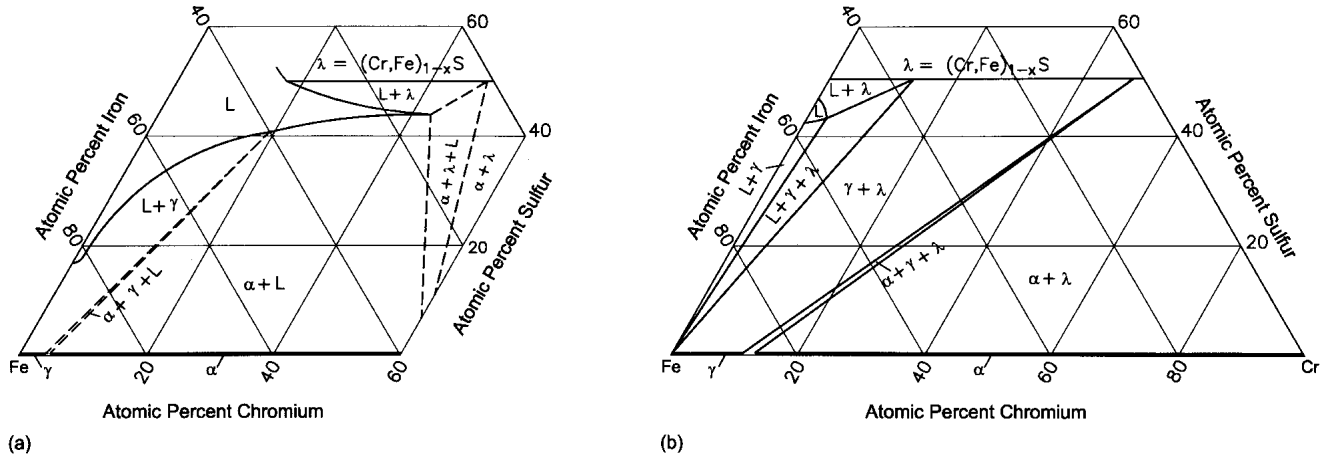

Fig. 2 Cr-Fe-S computed isothermal sections at **(a)** 1370 °C, and **(b)** 1090 °C [2000Oik]

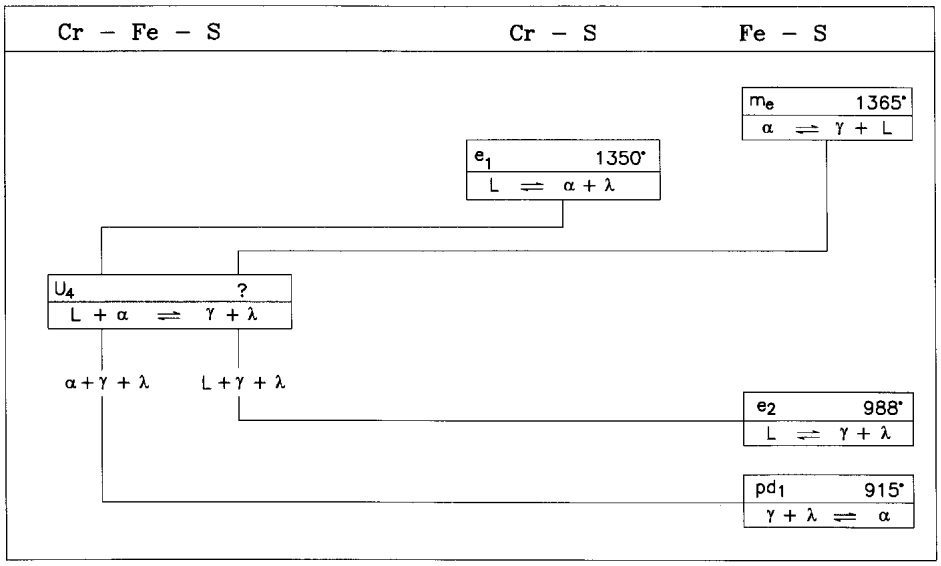

Fig. 3 Cr-Fe-S reactions involving α, γ, λ, and liquid [1988Rag]

Differences between the results of [1938Vog] and the computations of [2000Oik] center around the temperature of the U-type four-phase invariant reaction U_4 in the reaction table of [1988Rag]. The relevant part of the table is reproduced in Fig. 3. The eutectic reaction e_1 at 1350 °C in the Cr-S binary system and the metatectic reaction m_e at 1365 °C in the Fe-S system move into the ternary region and meet on the U_4 plane. The products of the U_4 reaction reach the Fe-S side and end at the reaction e_2 at 988 °C and pd_1 at 915 °C. The temperature of the U_4 reaction estimated from the computed vertical section of [2000Oik] at 19.5 wt.% S is 1325 °C, which is 275 °C higher than that reported by [1938Vog]. Between these temperatures, a large (γ + λ) two-phase field is present in the computed vertical section [2000Oik], in place of the (α + λ) field in the experimental vertical section of [1938Vog]. The isothermal section of [1988Fuj] at 1300 °C supports the computed results. It is possible that the early results of [1938Vog] failed to identify the high temperature existence of the (γ + λ) field from metallographic observations made on quenched samples.

The ternary compound Cr_2FeS_4 (denoted τ by [1988Rag]) occurs in the S-rich part, which falls outside the region discussed in the above results.

References

1938Vog: R. Vogel and R. Reinbach: "The System Fe-Cr-CrS-FeS," *Arch. Eisenhuttenwes.,* 1938, *11*(9), pp. 457-62 (in German).

1969Elg: A. El Goresy and G. Kullerud: "Phase Relations in the System Chromium-Iron-Sulfur," in *Proc. Symp. On Meteorite Res.,* P.M.D. Millman, ed., Reidel Publ. Co., Dordrecht, The Netherlands, 1969, pp. 638-56.

1982Ind: V.M. Indosova, E.G. Zhukov, and T. Kalinnikov: "The

FeS-Cr_2S_3 System," *Zh. Neorg. Khim.,* 1982, *27*(2), pp. 533-36 (in Russian); TR: *Russ. J. Inorg. Chem.,* 1982, *27*(2), pp. 303-05.

1982Kub: O. Kubaschewski: "Iron-Sulfur," *Iron—Binary Phase Diagrams,* Springer-Verlag, Berlin, 1982, pp. 125-28.

1988Fuj: T. Fujisawa, M. Asano, T. Suzuki, C. Yamauchi, and H. Sakao: "Activity of Sulfur in Solid Fe-Cr Alloys and Their Equilibrium Relations with Sulfides at 1573 K," *Tetsu to Hagane,* 1988, *74*(6), pp. 1013-20 (in Japanese).

1988Rag: V. Raghavan: "The Cr-Fe-S (Chromium-Iron-Sulfur) System," *Phase Diagrams of Ternary Iron Alloys. Part 2,* Ind. Inst. Metals, Calcutta, 1988, pp. 107-20.

1993Itk: V.P. Itkin: "Cr-Fe (Chromium-Iron)," in *Phase Diagrams of Binary Iron Alloys,* H. Okamoto, ed., ASM International, Materials Park, OH, 1993, pp. 102-29.

1998Rag: V. Raghavan: "Cr-Fe-S (Chromium-Iron-Sulfur)," *J. Phase Equilibria,* 1998, *19*(3), pp. 265-66.

2000Oik: K. Oikawa, H. Mitsu, H. Ohtani, and K. Ishida: "Thermodynamic Calculations of Phase Equilibria in the Fe-Cr-S System," *ISIJ Int.,* 2000, *40*(2), pp. 182-90.