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Fe-Rh-S (Iron-Rhodium-Sulfur)

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The previous review of this system by [1988Rag] was limited to a summary of the data on the spinel-type cubic ternary phase ~$FeRh_2S_4$. An update by [1998Rag] reviewed the results of [1990Bry] and presented two pseudobinary sections along the $Fe_{1-x}S$-FeRh and $Fe_{1-x}S$-Rh_2S_3 joins, a liquidus projection and a reaction sequence for the solidification reactions. Recently, Makovicky et al. [2002Mak] determined two isothermal sections at 900 and 500 °C for this system.

Binary Systems

The Fe-Rh phase diagram [1993Swa] is known experimentally only for Fe-rich alloys and is estimated at compositions richer in Rh. The Fe-based face-centered cubic (fcc) phase forms a continuous solid solution γ with fcc Rh down to about 1300 °C. At 1300 °C, a CsCl-type ordered phase α' forms congruently from γ. [1993Swa] presented the Fe-based bcc phase (αFe) $\rightarrow$ α' transition as a second-order transition without an intervening two-phase field. The results of [2002Mak], however, indicate the presence of a two-phase field both at 900 and 500 °C. The new results of [2002Mak] is tentatively accepted here. There are two intermediate phases in the Fe-S system [1982Kub]. The monosulfide pyrrhotite $Fe_{1-x}S$ (hexagonal NiAs type) is stable at Fe-deficient (S-rich) compositions with a range of 50-55 at.% S. $Fe_{1-x}S$ at 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 orthorhombic FeS_2 (marcasite) at 425 °C. The phase relations below 350 °C in the pyrrhotite region are complex with the occurrence of several ordered forms. In the Rh-S system [Massalski2], there are four intermediate phases: $Rh_{17}S_{15}$ (cubic $Pd_{17}Se_{15}$ type), Rh_3S_4, Rh_2S_3 (orthorhombic) and $RhS_{\sim3}$ (cubic pyrite type). A eutectic reaction occurs between (Rh) and $Rh_{17}S_{15}$ at 925 °C. The phase relationships in the S rich region are not known.

Ternary Isothermal Sections

Following up their preliminary work [1986Mak], [2002Mak] used starting materials of Rh (40 ppm of metallic impurities), Fe (20-25 ppm of metallic impurities) and

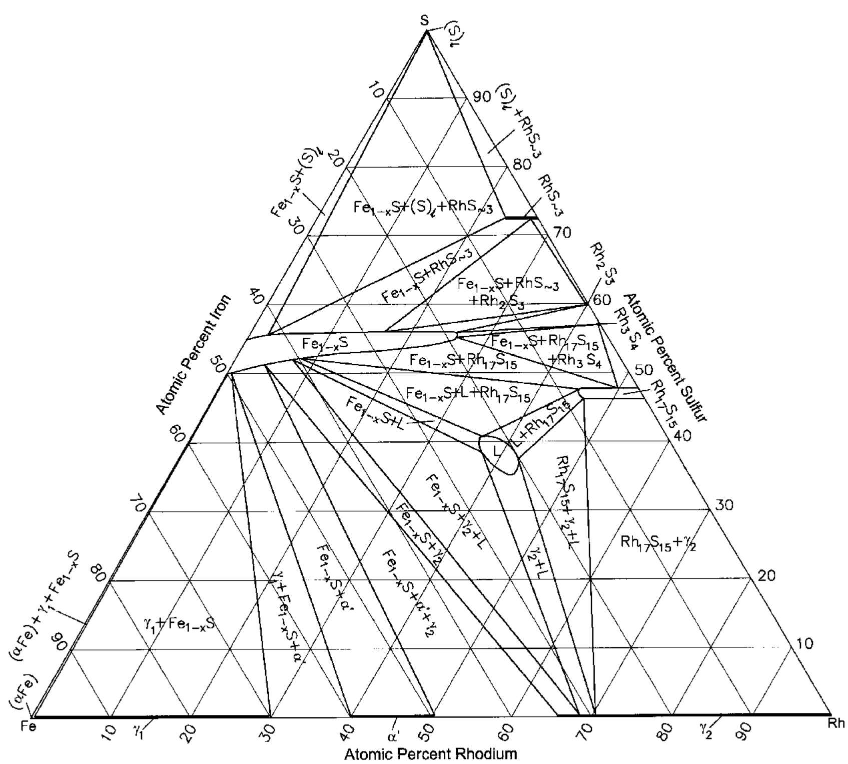

Fig. 1 Fe-Rh-S isothermal section at 900 °C [2002Mak]

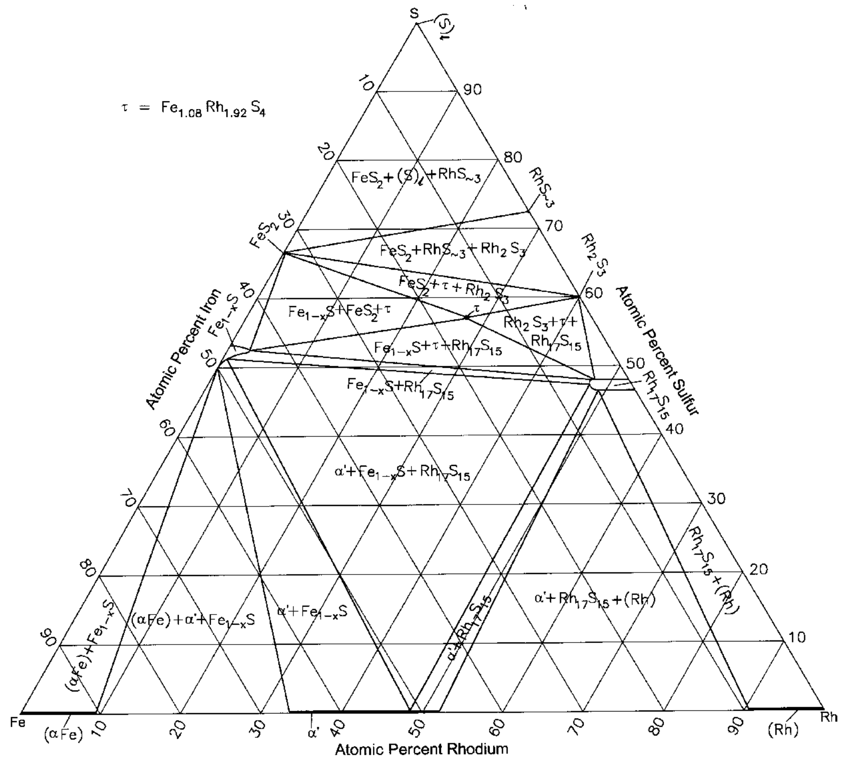

Fig. 2 Fe-Rh-S isothermal section at 500 °C [2002Mak]; narrow two-phase regions around tie-triangles are omitted.

>99.999% S to melt 56 samples in evacuated tubes. The samples were given a final anneal of 60-90 d at the desired temperature 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 sections constructed by [2002Mak] at 900 and 500 °C are redrawn in Fig. 1 and 2. At 900 °C (Fig. 1), the composition ranges of Fe-rich fcc phase γ_1, α', and Rh-rich fcc phase γ_2 are ~0.5-29.7, 40-50.4, and 65.7-100 at.% Rh, respectively. $Rh_{17}S_{15}$ shows a homogeneity range of 1-2 at.% Rh. The solubility of Rh in pyrrhotite attains as high as 25.7 at.%, with S content increasing with increasing Rh. $Rh_{17}S_{15}$ and $RhS_{\sim 3}$ dissolve 7.5 and 4 at.% Fe, which substitutes for Rh. A small ternary liquid field centered around the composition 22.5Fe-40Rh-37.5S (at.%) is present at 900 °C. According to the results of [1990Bry] reviewed in [1998Rag], this liquid disappears at 895 °C through a ternary eutectic reaction yielding $Fe_{1-x}S$, $Rh_{17}S_{15}$ and γ_2, which is consistent with the isothermal section of [2002Mak].

At 500 °C (Fig. 2), the composition ranges of Fe-based bcc phase (αFe), α', and (Rh) are 0-9.5, 33.5-52.2, and 90.5-100 at.% Rh, respectively. The lower limit of the composition of (Rh) is uncertain, due to the scatter in the results [2002Mak]. A distinct two-phase field was observed by [2002Mak] between (αFe) and α'. The ternary compound $Fe_{1.08}Rh_{1.92}S_4$ (denoted τ) is present, which forms presumably through a peritectoid reaction between 900 and 500 °C. [2002Mak] did not find a homogeneity range for the ternary compound at 500 °C. The binary compound Rh_3S_4 was not found. The solubility of Rh in $Fe_{1-x}S$ is 2.8 at.% and of Fe in $Rh_{17}S_{15}$ is 5.5 at.% at 500 °C.

References

1982Kub: O. Kubaschewski: "Iron-Sulphur" in *Iron – Binary Phase Diagrams*, Springer-Verlag, Berlin, Germany, 1982, pp.125-28.

1986Mak: M. Makovicky, E. Makovicky, and J. Rose-Hansen: "Experimental Studies on the Solubility and Distribution of Platinum Group Elements in Base Metal Sulfides in Platinum Deposits" in *Metallogeny of Basic and Ultrabasic Rocks,* M.J. Gallagher, R.A. Ixer, C.R. Neary, and H.M. Prichard, ed., Institution Min. and Metall., London, UK, 1986, pp. 415-25.

1988Rag: V. Raghavan: "The Fe-Rh-S (Iron-Rhodium-Sulphur) System" in *Phase Diagrams of Ternary Iron Alloys. Part 2,* Indian Inst. Metals, Calcutta, India, 1988, pp. 251-52.

1990Bry: V.A. Bryukvin, B.A. Fishman, V.A. Reznichenko, V.A. Kukoev, and N.A. Vasileva: "Investigation of the Fe-Rh-S Phase Diagram in the Fe-Rh-Rh_2S_3-$FeS_{1.09}$ Composition Range," *Metally,* 1990, (2), pp. 23-28 (in Russian); TR: *Russ. Metall.,* 1990, (2), pp. 18-22.

1993Swa L.J. Swartzendruber: "Fe-Rh (Iron-Rhodium)" in *Phase Diagrams of Binary Iron Alloys,* H. Okamoto, ed., ASM International, Materials Park, OH, 1993, pp. 353-58.

1998Rag: V. Raghavan: "Fe-Rh-S (Iron-Rhodium-Sulfur)," *J. Phase Equilibria,* 1998, *19*(3), pp. 276-78.

2002Mak: E. Makovicky, M. Makovicky, and J. Rose-Hansen: "The System Fe-Rh-S at 900° and 500°C," *Canadian Mineralogist,* 2002, *40,* pp. 519-26.