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Fe-Os-S (Iron-Osmium-Sulfur)

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Very recently, [2002Kar] determined three isothermal sections for this ternary system between 1180 and 900 °C.

Binary Systems

A partial Fe-Os phase diagram has been determined experimentally for Fe-rich alloys [1982Kub1]. By analogy with the Fe-Ru phase diagram, a tentative full diagram has been proposed [1982Kub1, 1993Swa]. This tentative diagram shows only solid solutions based on the terminal phases. The work on this ternary system by [2002Kar], however, shows the presence of an intermediate phase of rhombohedral symmetry along the Fe-Os side, as discussed below. There are two intermediate phases in the Fe-S system [1982Kub2]. 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 Os-S phase diagram, a eutectic reaction $L \leftrightarrow$ (Os) + OsS_2 (cubic pyrite type) occurs at ~2000 °C and ~51 at.% S [1992Fis].

Ternary Isothermal Sections

Using Os and Fe with 15 ppm of metallic impurities and S of 99.999% purity, [2002Kar] heated 71 alloy compositions in evacuated tubes, which were finally annealed between 1180 and 900 °C up to 30 d and quenched in water. The phase equilibria were studied with reflected-light microscopy, electron probe microanalyzer and the x-ray powder diffraction technique. The measured compositions of the coexisting phases were listed. Three isothermal sections at 1180, 1100, and 900 °C were constructed by [2002Kar]. An intermediate phase with rhombohedral symmetry (denoted β here) was found along the Fe-Os side at all three temperatures. The (hexagonal) lattice parameters of rhombohedral β are shown in Fig. 1. The two-phase region between β and (Os) [hexagonal close packed (hcp)] could not be ascertained by electron probe measurements by [2002Kar], due to the fine intergrowth of the phases and the very small grain size. The x-ray diffraction measurements by [2002Kar], however, indicated two pairs of hexagonal parameters. One pair of a and c parameters was independent of composition and the values of a = 0.2734 nm and c = 0.4320 nm for this phase agree with those listed by [Pearson3] for pure Os (cph). The a and c parameters of the other pair (for the rhombohedral phase) are lower and increase with increasing Os content as shown in Fig. 1. Pending further confirmation of the existence of the rhombohedral phase, the results of [2002Kar] are accepted tentatively and are shown in Fig. 2 and 3.

At 1180 °C (Fig. 2), the γ phase has a homogeneity range of 0-21.5 at.% Os. The rhombohedral phase (β) is stable between 27.3 and ~85 at.% Os. The (Os) phase (hcp) has a range of 98.5-100 at.% Os. The measured S content in all the three alloys is less than 0.1 at.%. Along the Fe-S side, at 1180 °C, there are two sulfide melts L_1 and L_2 on either side of pyrrhotite ($Fe_{1-x}S$; Fig. 2). The entire composition range of γ and most of the range of β coexist with the S-poor (Fe-rich) sulfide melt L_1 (Fig. 2). In the three-phase equilibrium of L_1, γ and β, L_1 contains 43.3 at.% S. The Os content of L_1 for the end poorest in S is 0-0.02 at.% and at the other end (50 at.% S), it is 0.06-0.1 at.%. In the three-phase equilibrium of L_1, $Fe_{1-x}S$ and (Os), $Fe_{1-x}S$ contains 0.4 at.% Os. It increases to 0.7 at.% in the three-phase equilibrium of $Fe_{1-x}S$ (53.4 at.% S), (Os) and OsS_2. In the three-phase equilibrium of $Fe_{1-x}S$, L_2 and OsS_2, OsS_2 contains 0.2 at.% Fe and this increases to 1.1 at.% Fe at the three-phase equilibrium of L_2, OsS_2 and $(S)_l$. In the isothermal section at 1100 °C [2002Kar] not shown here, the triangulation is the same as at 1180 °C. The homogeneity ranges of γ, β, and (Os) are 0-20.2, 26.1-80, and 98.4-100 at.% Os. OsS_2 dissolves up to 2.9 at.% Fe.

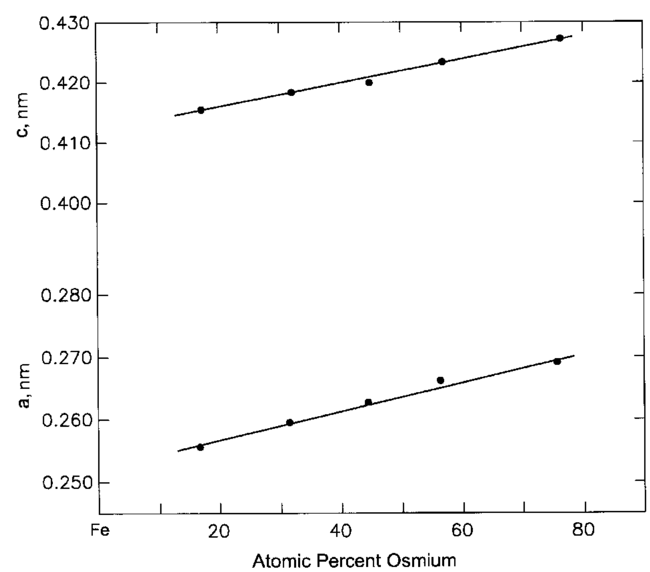

Fig. 1 Fe-Os-S lattice parameters of the rhombohedral Fe-Os phase (β) [2002Kar]

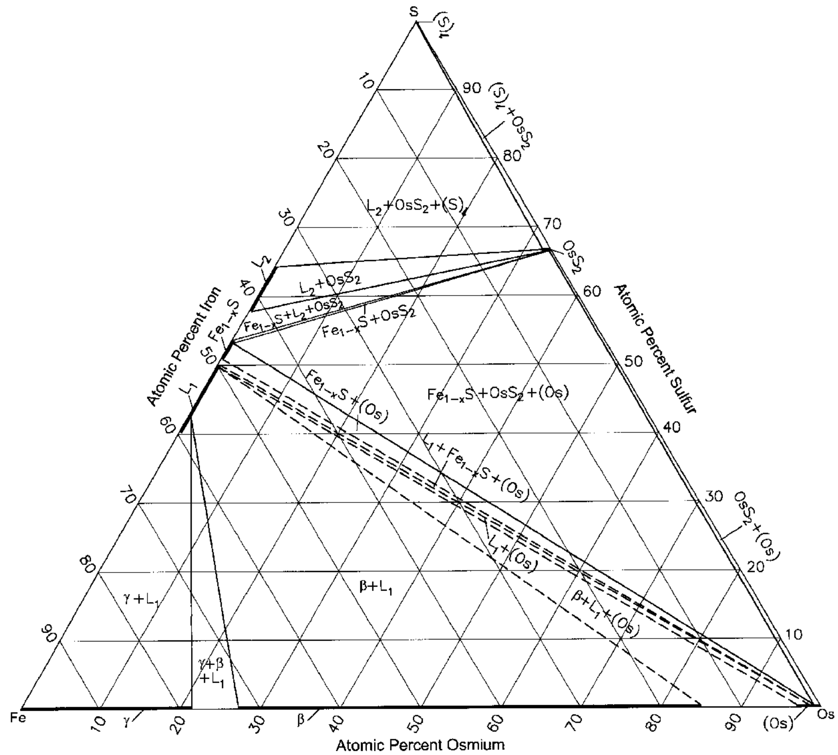

Fig. 2 Fe-Os-S isothermal section at 1180 °C [2002Kar]

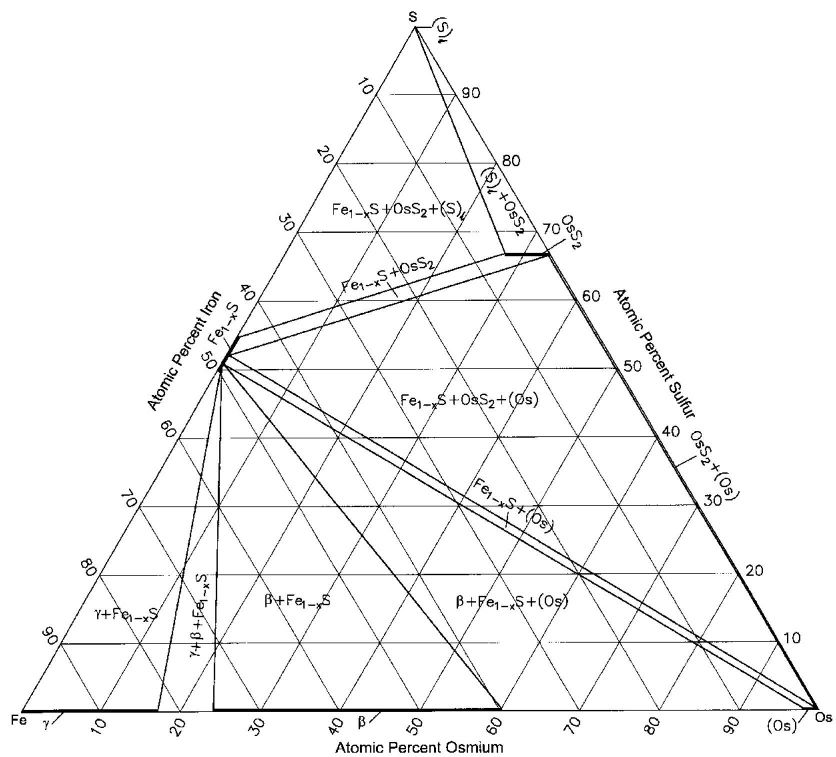

Fig. 3 Fe-Os-S isothermal section at 900 °C [2002Kar]

At 900 °C (Fig. 3), the γ phase has a homogeneity range of 0-17.2 at.% Os. The rhombohedral phase (β) is stable between 24.2 and ~60 at.% Os. (Os) dissolves Fe up to ~2 at.% Fe. In the three-phase equilibrium of $Fe_{1-x}S$-OsS_2-$(S)_l$, OsS_2 dissolves 5.7 at.% Fe. In the equilibrium $Fe_{1-x}S$-OsS_2-(Os), OsS_2 dissolves only 0.2 at.% Fe [2002Kar].

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