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Fe-Se-Tl (Iron-Selenium-Thallium)

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The previous review of this system by [1992Rag] presented a pseudobinary section along the FeSe-TlSe join, based on the work of [1986Gur]. Recently, Kerimova et al. [1999Ker] reinvestigated this section and reported quite different results.

Binary Systems

The Fe-Se phase diagram [1991Oka] depicts a number of modifications of the monoselenide around the midcomposition: $\beta Fe_{1.04}Se$, $\gamma Fe_{1-x}Se$, $\gamma' Fe_{1-x}Se$, $\delta Fe_{1-x}Se$, and $\delta' Fe_{1-x}Se$. $\beta Fe_{1.04}Se$ has the tetragonal PbO type structure. $\delta Fe_{1-x}Se$ is a NiAs-type hexagonal phase. The other phases are NiAs related phases. $FeSe_2$ has the FeS_2 (marcasite) type orthorhombic structure. For more structural details, see [1991Oka]. The Fe-Tl phase diagram is not known. Fe and Tl do not measurably react with each other even at the boiling point of Tl, which is below the melting point of Fe [1982Kub]. The Tl-Se phase diagram [1981Mor] has two intermediate phases: TlSe and Tl_2Se. The other reported phases Tl_2Se_3 and $TlSe_3$ were not found by [1981Mor].

The Ternary Compounds

Two ternary compounds $FeTlSe_2$ (monoclinic) and Fe_2TlSe_2 (tetragonal) are known in this system. The structural details are summarized by [1992Rag]. The lattice parameters of $FeTlSe_2$ determined by [1999Ker] are: a = 0.1202 nm, b = 0.550 nm, c = 0.713 nm, and β = 118.52°, in agreement with the data reviewed by [1992Rag].

The Pseudobinary Section

Using high purity starting materials, [1999Ker] melted 14 alloy compositions in evacuated quartz tubes. The slowly cooled samples were homogenized by annealing at 567 °C for 23 d for Fe-rich alloys and at 137 °C for 21 d for Tl-rich alloys. The phase equilibria were studied by x-ray diffraction and differential thermal analysis at a heating rate of 2-4 K/min. The FeSe-TlSe pseudobinary section determined by [1999Ker] is redrawn in Fig. 1. The FeSe phase of [1999Ker] is presumably the NiAs-type δ phase of [1991Oka]. In the absence of more data, the FeSe end is depicted in Fig. 1 as given by [1999Ker]. The ternary compound $FeTlSe_2$, which occurs at the midcomposition along the FeSe-TlSe join, forms congruently from the melt at 630 °C [1999Ker]. It is of fixed stoichiometry and divides the pseudobinary section into two parts. On the FeSe side, a eutectic reaction occurs at 597 °C and 44 mol% TlSe, which yields FeSe and $FeTlSe_2$. On the TlSe side, the solid solution based on TlSe forms peritectically at 400 °C. TlSe

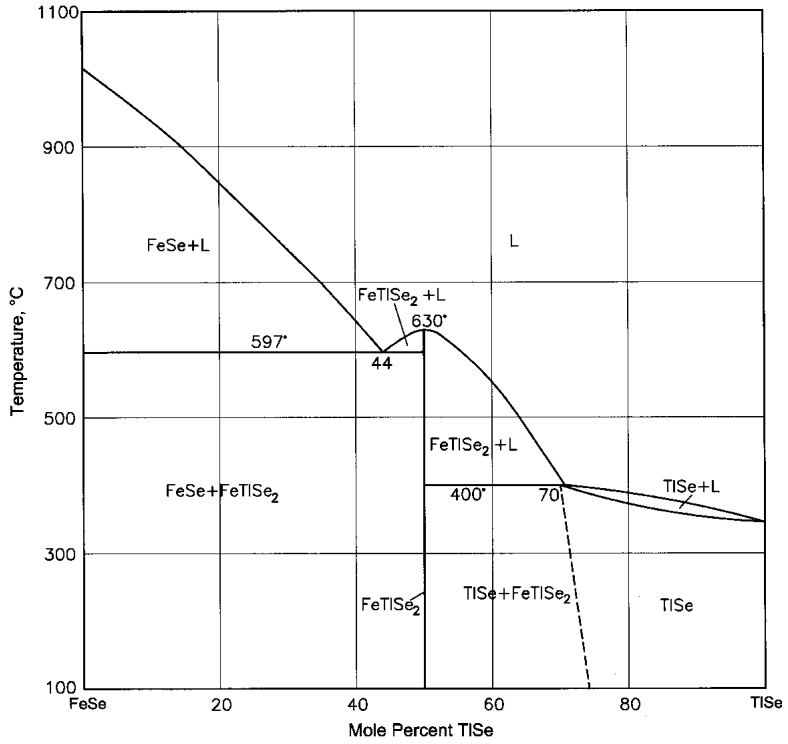

Fig. 1 Fe-Se-Tl pseudobinary section along the FeSe-TlSe join [1999Ker]

dissolves up to 30 mol% FeSe, whereas FeSe shows no solubility for TlSe.

Based on the work of [1986Gur], [1992Rag] presented a pseudobinary section along the FeSe-TlSe join. Here, the ternary compound $FeTlSe_2$ forms by a peritectic reaction at 320 °C between $Fe_{1.04}Se$ and a liquid containing about 90 mol% TlSe. FeSe dissolves over 10 mol% TlSe. These results are in disagreement with the new results of [1999Ker]. It is difficult to reconcile the differences with the available information. No attempt is made here to do so.

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