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Fe-Ni-Sb (Iron-Nickel-Antimony)

V. Raghavan

The previous review of this system [1992Rag] presented the pseudobinary section along the Fe-NiSb join, depicting a eutectic between (Fe) and NiSb at 60 mol% NiSb and at 1000 °C. Recently, [1997Ric1] determined a liquidus surface, an isothermal section at 600 °C and several vertical sections of this system in the composition range of 42-100 at.% Sb.

Binary Systems

The Fe-Ni phase diagram [1993Swa] is characterized by a very narrow solidification range with a peritectic reaction at 1514 °C, between bcc δ and liquid that yields the Fe-based fcc solid solution. A continuous solid solution (denoted γ) between fcc Fe and Ni is stable over a wide range of temperature. At lower temperatures, an ordered phase $FeNi_3$ forms congruently at 517 °C from γ. The Fe-Sb phase diagram [1993Oka] depicts two intermediate phases. The NiAs type $B8_1$ phase Fe_3Sb_2 (ε) has a homogeneity range of 40-47 at.% Sb. The other intermediate phase $FeSb_2$ is stoichiometric and has orthorhombic symmetry. [Pearson3] lists two orthorhombic types for this phase: FeS_2-type (*Pnnm*) and $FeSb_2$-type (*Pnn*2). The Ni-Sb phase diagram [Massalski2] shows three intermediate phases. Ni_3Sb has the βCu_3Ti type orthorhombic structure. The high temperature form of Ni_5Sb_2 is monoclinic and the low temperature form (denoted Ni_7Sb_3 by [Massalski2]) is tetragonal. NiSb has a composition range of 43-52 at.% Sb and has a NiAs type $B8_1$ structure. $NiSb_2$ is orthorhombic with FeS_2 (marcasite) as the prototype. The existence of a Ni rich phase $Ni_{15}Sb$ below 460 °C [Massalski2] needs to be confirmed.

Ternary Phase Equilibria

[1997Ric1] confirmed the existence of the ternary compound $FeNiSb_6$ reviewed by [1992Rag]. It has the $CoAs_3$ (skutterudite) type cubic structure with a = 0.90881 nm [1997Ric1] and is denoted τ here.

A detailed study of the phase equilibria of this system was reported by Richter and Ipser [1997Ric1,2]. Using starting materials of purity of 99.99% Sb, 99.9% Fe and 99.99% Ni, [1997Ric1] heated alloy compositions to 1200 °C in evacuated quartz tubes. For differential thermal analysis (DTA) measurements, the furnace-cooled samples were

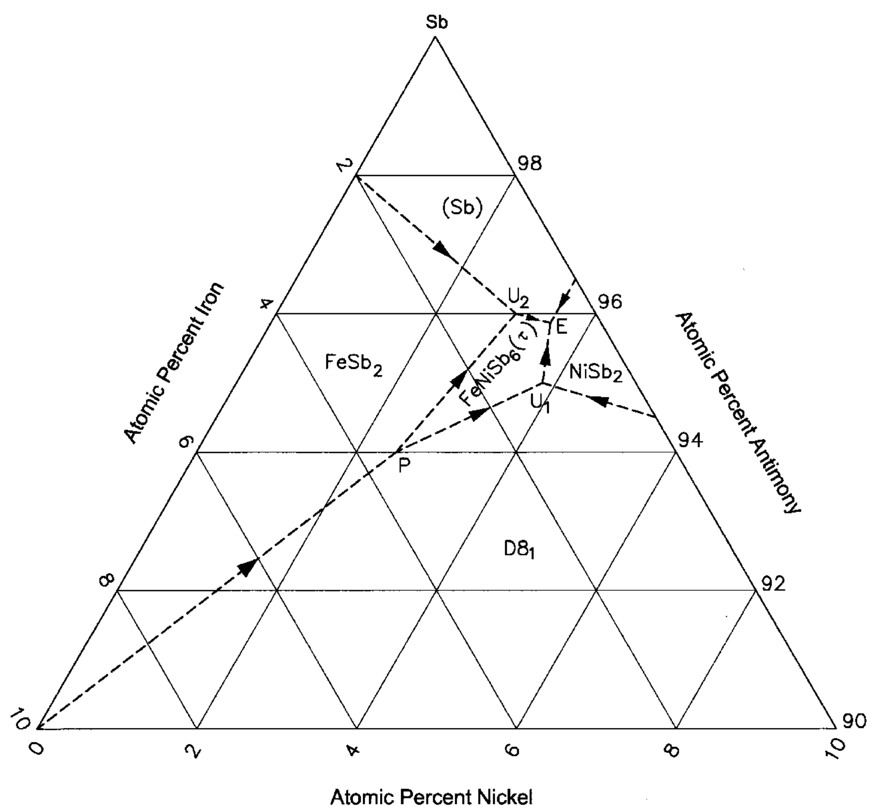

Fig. 1 Fe-Ni-Sb tentative liquidus projection for Sb rich alloys

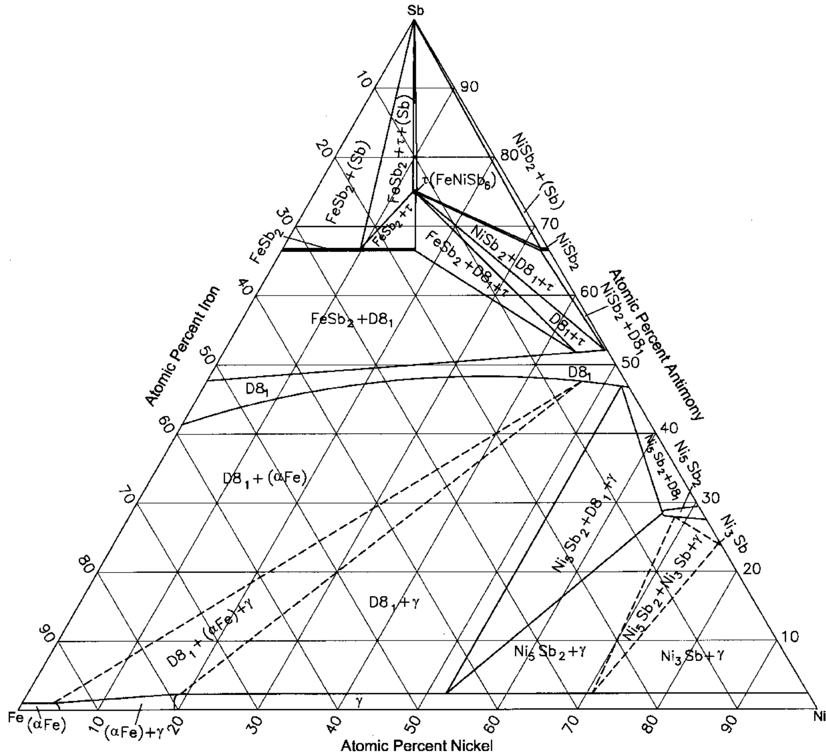

Fig. 2 Fe-Ni-Sb isothermal section at 600 °C (after [1997Ric1])

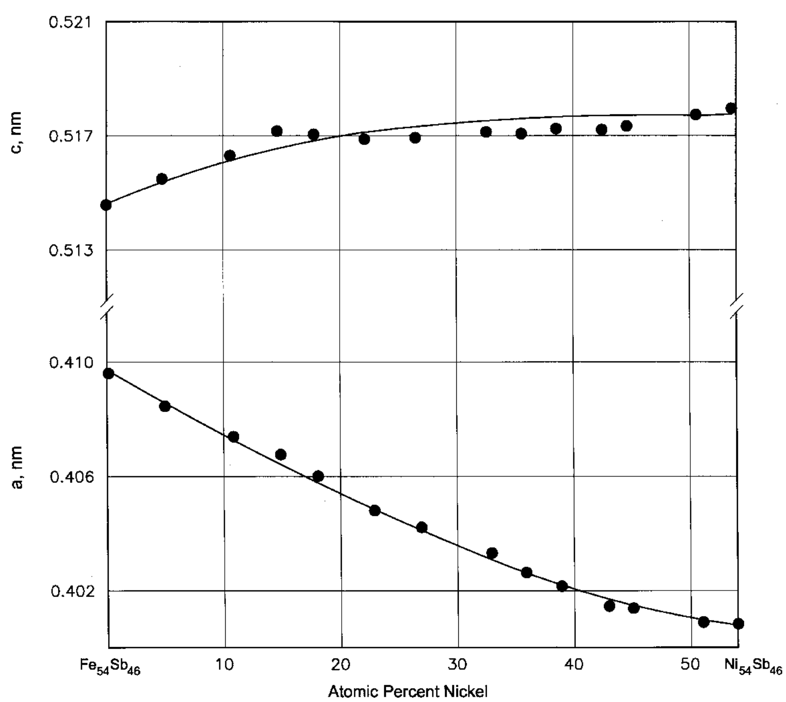

Fig. 3 Fe-Ni-Sb lattice parameter variation of the NiAs type solid solution ε [1997Ric1]

heated at the rate of 2 K per min. For determining the isothermal section at 600 °C, the samples cooled from 1200 °C were crushed and given a final anneal for 6-9 weeks at 600 °C. The phase equilibria were studied by metallography, x-ray powder diffraction (XRD) and electron probe microanalysis (EPMA).

From the DTA measurements, [1997Ric1] identified four ternary invariant reactions in Sb rich alloys, all occurring in

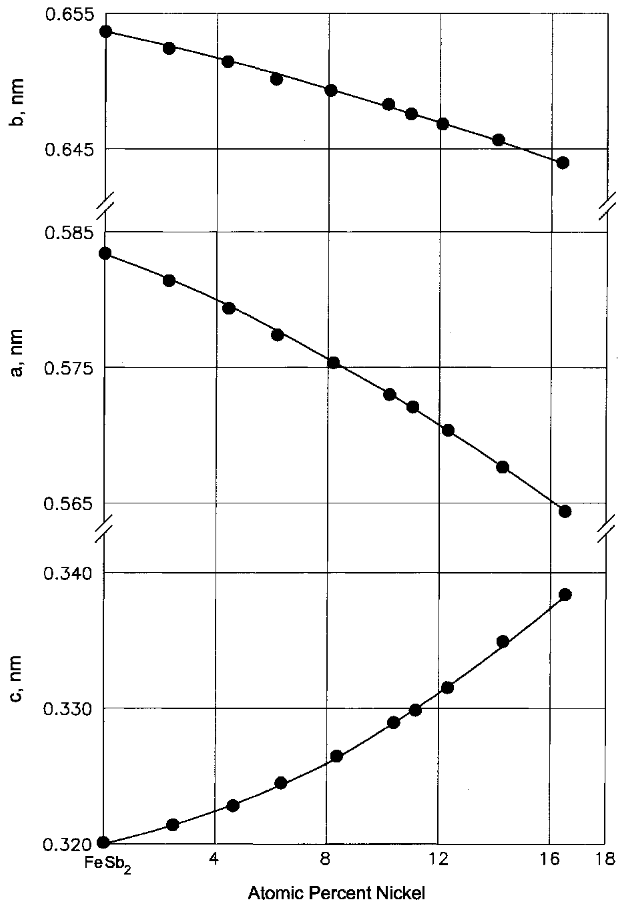

Fig. 4 Fe-Ni-Sb lattice parameter variation of the (Fe,Ni)Sb_2 solid solution [1997Ric1]

a narrow temperature range of 642-615 °C. At 642 °C, a ternary peritectoid reaction P yields the ternary compound $FeNiSb_6$ (τ). Two U-type transition reactions U_1 and U_2 follow at 625 and 620 °C. The final solidification is through a ternary eutectic reaction E at 615 °C. Using the compositions of the binary and ternary invariant reactions listed by [1997Ric1] and the reaction scheme given by them, a tentative liquidus surface for Sb rich alloys is drawn in Fig. 1. The composition of the ternary eutectic reaction E has been shifted slightly in Fig. 1 to comply with the rules of construction. The invariant reactions in Fig. 1 are in the Fe range of 0-10 at.%. A liquidus surface for the region with Fe in the range of 10-60 at.%, depicting constant-temperature contours at 20 °C intervals, is given by [1997Ric1].

The isothermal section at 600 °C constructed by [1997Ric1] for Sb contents of 40-100 at.% is redrawn in Fig. 2. The section has been extended tentatively to the Sb poor region. The ternary compound $FeNiSb_6$ (τ) is present in this section. The isostructural phases Fe_3Sb_2 and NiSb form a continuous solid solution (denoted $B8_1$ in Fig. 2). The lattice parameters of this NiAs type hexagonal phase were determined by [1997Ric1] at 46 at.% Sb. They are seen to vary nonlinearly with Ni content (Fig. 3). Fig. 2 indicates that the Sb range of this solid solution decreases towards the mid-composition, pointing to the possibility of a miscibility gap arising at lower temperatures. The orthorhombic phases $FeSb_2$ and $NiSb_2$ do not form a continuous solution. The solubility of Ni in $FeSb_2$ is up to the composition $Fe_{0.5}Ni_{0.5}Sb_2$, whereas at the other end the solubility is more limited and is given by the composition $Fe_{0.03}Ni_{0.97}Sb_2$. The lattice parameters of the solid solution based on $FeSb_2$ determined by [1997Ric1] are shown in Fig. 4. They vary nonlinearly with Ni content. Ni_5Sb_2 dissolves up to 5 at.% Fe at 600 °C [1997Ric1]. The Sb solubility in (αFe) and γ were measured by [1997Ric1] to be about 1 and 2 at.%, respectively.

[1997Ric1] used DTA data to plot four vertical sections at 66.7, 70, 75, and 85 at.% Sb. [1997Ric2] determined another vertical section at Fe:Ni ratio of 1:1. The vapor pressure of Sb was determined by [1997Ric2] by an isopiestic method over the solid solution $(Fe_{0.5}Ni_{0.5})_{1\pm x}Sb$ in the range of 45.5-51.5 at.% Sb and 1037-747 °C. The data were used to calculate the thermodynamic properties of this solid solution.

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