

Fe-Ni-Pd-S (Iron-Nickel-Palladium-Sulfur)

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[1990Mak] studied the phase relationships in this quaternary system at 900, 725, and 550 °C.

Binary Systems

For brief descriptions of the Fe-Ni, Fe-S, and Ni-S systems, see the Fe-Ni-S update in this issue. The Fe-Pd phase diagram [1982Kub] is characterized by the presence of a continuous solid solution γ in the temperature range of 1300-900 °C between the Fe-based fcc phase and Pd. Two superstructures, FePd (AuCu type tetragonal) and FePd₃ (AuCu₃ type cubic), form congruently from γ at 790 and 820 °C and have appreciable homogeneity ranges at lower temperatures. The Ni-Pd system [Massalski2] is an isomorphous one, with the face-centered-cubic (fcc) phase (γ) present at all subsolidus temperatures. A partial Pd-S phase diagram [Massalski2] depicts several intermediate phases: Pd₄S (Pd₄Se type tetragonal), Pd₃S (orthorhombic), Pd_{2,2}S (cubic), PdS (B34 type tetragonal), and PdS₂ (PdSe₂ type orthorhombic).

Ternary Systems

[1992Rag] reviewed the limited information on the Fe-Ni-Pd system and presented a liquidus surface. The pre-

dominant phase of primary crystallization on this surface is the continuous fcc solid solution γ . An update on the Fe-Ni-S system appears in this issue. The review of the Fe-Pd-S system by [1988Rag] gave a liquidus projection, a reaction scheme, and an isothermal section at 1000 °C. An update by [1998Rag] added three more isothermal sections at 900, 725, and 550 °C from [1993Mak]. For the Ni-Pd-S system, [1993Kar] presented four isothermal sections at 900, 725, 550, and 400 °C. Three of these sections at 900, 725, and 550 °C are redrawn in Fig. 1-3. The broad liquid field that extends from the Ni-S side to the Pd-S side at 900 and 725 °C becomes more restricted at 550 °C. A ternary compound Ni_{5.3}Pd_{3.8}S₈ is present at 550 °C; the details of its structure are not known.

Quaternary Phase Equilibria

With spectroscopically pure (or high purity) starting materials, weighed mixtures were heated in evacuated silica tubes and given a final anneal for several weeks at the desired temperature and quenched [1990Mak]. The phase equilibria were studied by reflected light microscopy and electron probe microanalysis. The phase relations at 900 °C are shown in Fig. 4 in a perspective sketch of the compo-

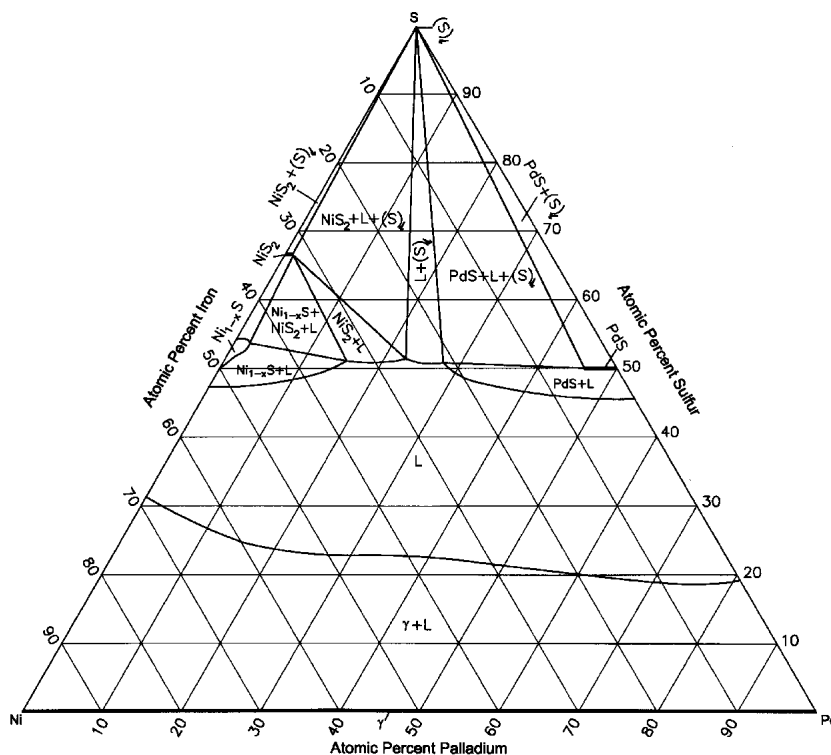


Fig. 1 Ni-Pd-S isothermal section at 900 °C [1993Kar]

sition tetrahedron [1990Mak]. An extensive field of sulfide melt lies in the middle region. In the lower portion, tie lines form between the melt and the γ phase. For low Pd contents,

the Fe/Ni ratio is similar in the melt and the alloy. For medium and large Pd contents, Fe segregates preferentially in the alloy for all Fe/Ni ratios. The alloy comes into equi-

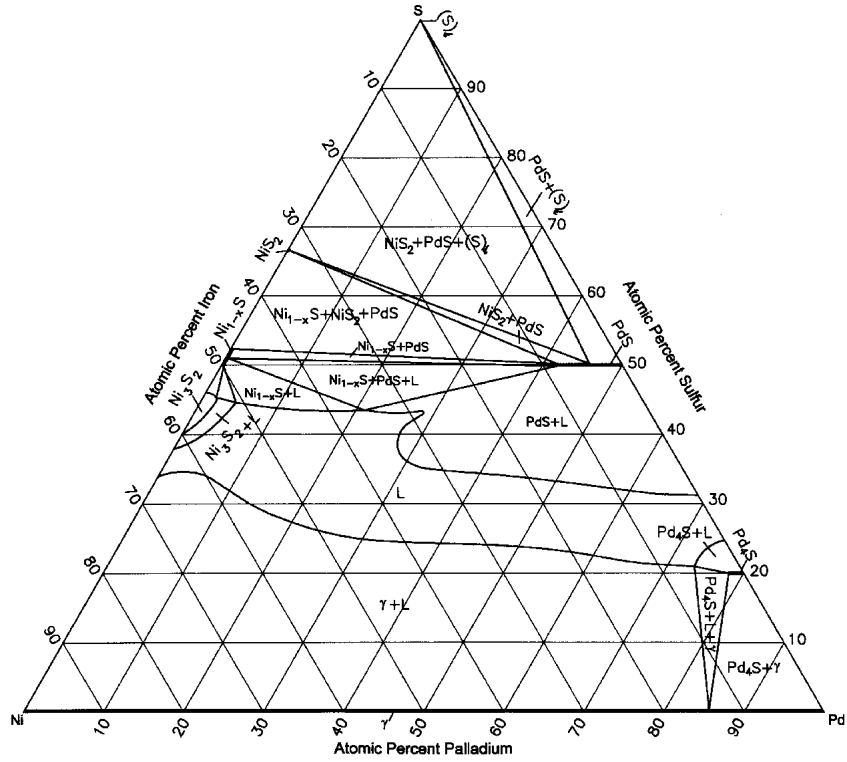


Fig. 2 Ni-Pd-S isothermal section at 725 °C [1993Kar]

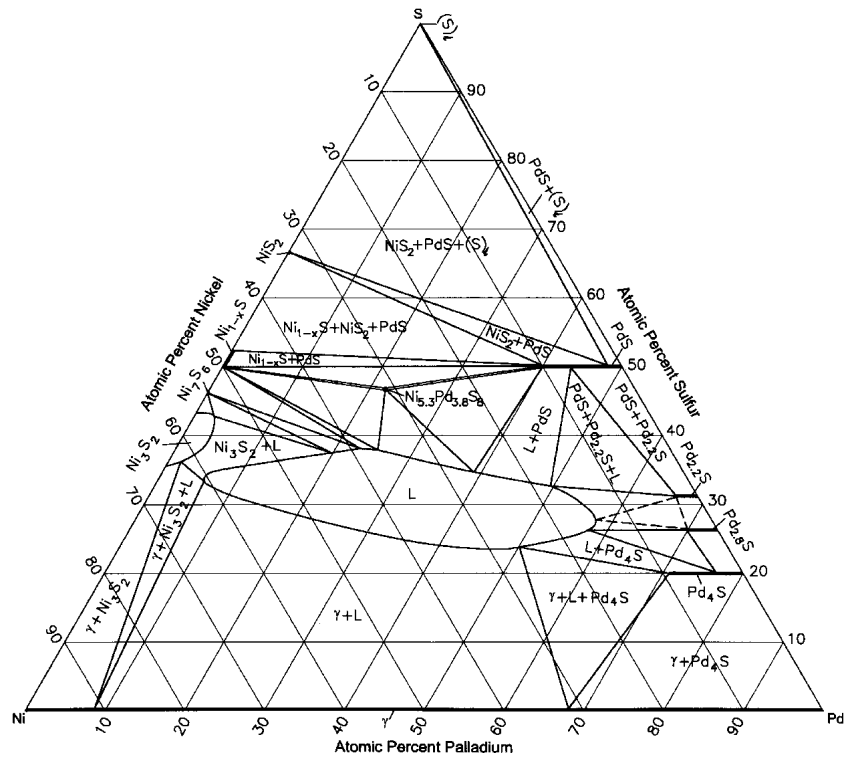


Fig. 3 Ni-Pd-S isothermal section at 550 °C [1993Kar]

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librium with low-Fe or nearly Fe-free sulfide melt. For Fe-rich compositions, $(\text{Fe}_{1-x}\text{S} + \text{melt})$ and $(\text{Fe}_{1-x}\text{S} + \text{melt} + \gamma)$ equilibria are observed. Above the melt region, the continuous monosulfide solid solution *mss* is present. On the S-rich

side, *mss* dissolves up to 5 at.% Pd at the Fe-rich end and 2.1 at.% Pd at the Ni-rich end. The solubility of Pd becomes negligible at the metal rich side of *mss*. NiS_2 coexists with *mss*, the sulfide melt, and $(\text{S})_1$, but not with PdS. PdS dis-

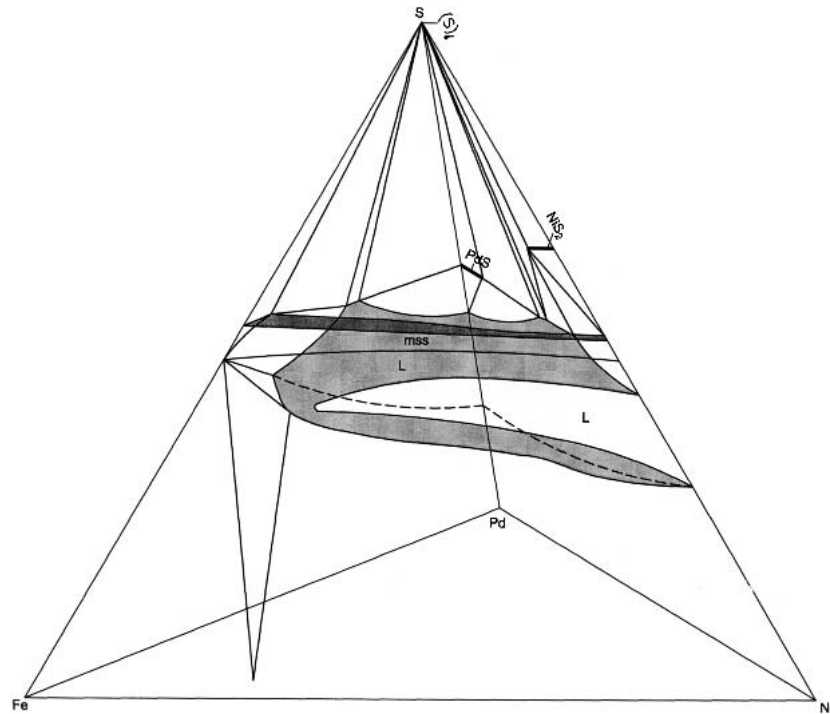


Fig. 4 Fe-Ni-Pd-S perspective view of the phase relationships at 900 °C [1990Mak]

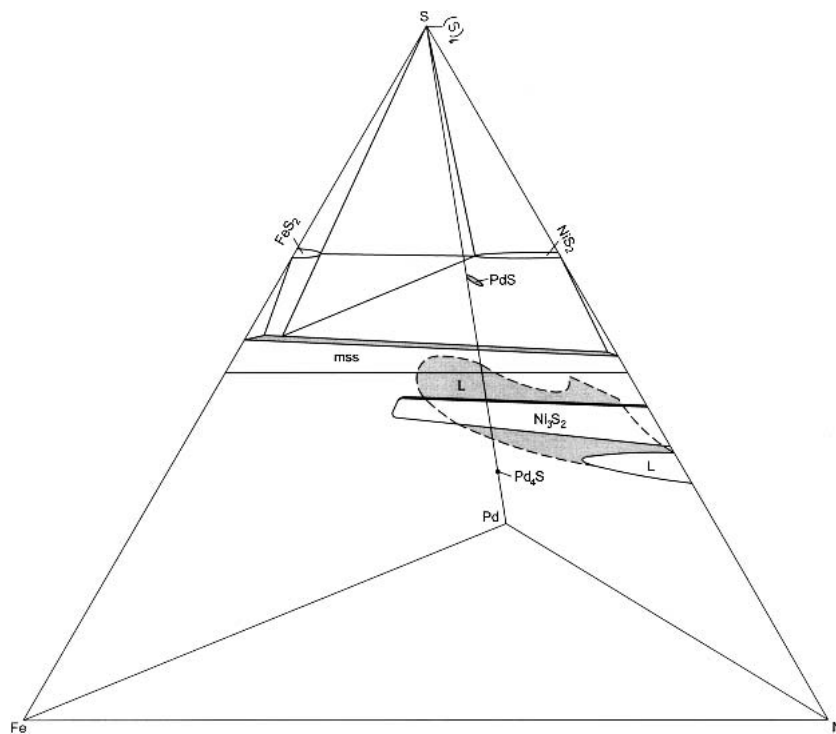


Fig. 5 Fe-Ni-Pd-S perspective view of the phase relationships at 725 °C [1990Mak]

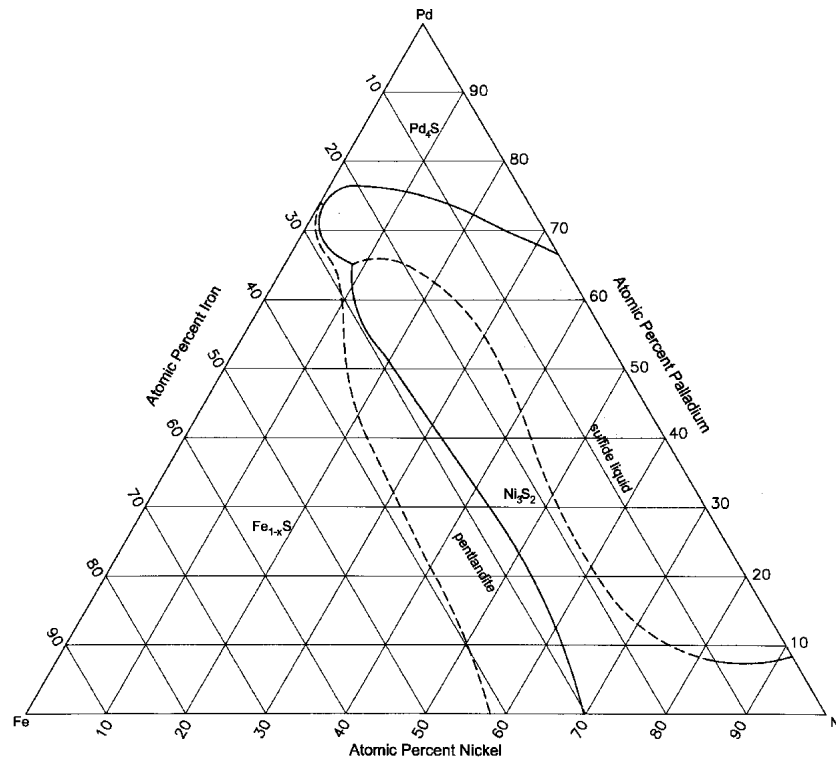


Fig. 6 Fe-Ni-Pd-S alloy compositions in equilibrium with various sulfide phases at 550 °C [1990Mak]

solves 4.9 at.% Ni and 0.3 at.% Fe. NiS_2 dissolves 1 at.% Pd [1993Kar]. FeS_2 is not stable at this temperature.

At 725 °C (Fig. 5), the sulfide melt decreases in volume as compared with 900 °C (Fig. 4). The possible presence of the “high-temperature form” of *pn* indicated by [1990Mak] with a question mark is omitted, as it is now considered to be an extension of the solid solution based Ni_3S_2 , see Fig. 6 of the Fe-Ni-S update in this issue. Ni_3S_2 dissolves 2.1 at.% Pd. In the upper region, the prominent three-phase equilibrium is ($\text{NiS}_2 + mss + \text{PdS}$). NiS_2 dissolves at least 10 at.% Fe. The Pd solubility, which is less than 0.5 at.% in pure NiS_2 , reaches 1-1.4 at.% in the presence of Fe [1990Mak]. FeS_2 (*py*) is present at 725 °C.

At 550 °C, the sulfide melt decreases further in volume as compared with 725 °C. The melt area seen in Fig. 3 in the central portion of the Ni-Pd-S ternary system penetrates into the composition tetrahedron up to the median plane at Fe:Ni = 1:1. With the appearance of Ni_7S_6 , several lower sulfides of Pd (Fig. 3) and the ordered forms of γ (FePd and FePd_3), the phase equilibria become complicated at 550 °C. Figure 6 depicts the compositions of the alloys that are in equilibrium with the various sulfides (below the monosulfide line) at 550 °C [1990Mak]. The ternary compound $\text{Ni}_{5.3}\text{Pd}_{3.8}\text{S}_8$ does not extend into the quaternary region. On the S-rich side, FeS_2 dissolves 1.5 at.% Ni and NiS_2 dissolves 2.0 at.% Fe. The solubility of Pd in the disulfides is small or negligible. The Pd content of pentlandite varies from traces to 4 at.% in various phase associations [1990Mak]. At 400 °C, due to sluggishness of the reactions, the attainment of equilibrium was often found to be incomplete [1990Mak]. No sulfide melt persists at 400 °C. An incomplete perspective

sketch of the composition tetrahedron was given by [1990Mak] (not shown here). At this temperature, PdS dissolves 12.8 at.% Ni and 0.9 at.% Fe. The solubility of other components in the disulfides is minimal. Pentlandite dissolves Pd up to the composition $\text{Pd}(\text{Fe,Ni})_8\text{S}_8$ [1990Mak]. A second ternary phase $\text{Pd}_{1.2}\text{Ni}_{3.9}\text{S}_4$ was found on the Ni-Pd-S plane, and it does not extend into the tetrahedron.

Recently, [1998Sin] studied the segregation behavior of Pd, when 1 wt.% Pd (~0.4 at.% Pd) is added to Fe-Ni-S alloys with 40-51 at.% S. As the S content (or S fugacity) and the Ni:Fe ratio are increased, the preferential segregation of Pd changes successively from Fe-Pd alloys to pentlandite (*pn*) and heazlewoodite (*hz*) and finally to PdS and $\text{Pd}_{2.2}\text{S}$. The Pd content of *pn*, which forms through a peritectoid reaction between *mss* and *hz* is 0.1-3.0 at.%. The maximum Pd of 5.8 at.% is found in Ni-rich *pn*, which precipitates from *mss*. At 600 °C and higher, the solubility of Pd in S-enriched *mss* is 0.4 at.%. This segregation behavior of Pd is in contrast to that of Pt, which segregates in the alloys over a wide range of composition [1998Sin].

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