Table 2 Mg-Se Lattice Parameter Data

Phase	Composition, at.% Se	Lattice parameters, nm a	c	Comment	Reference
(Mg)	0	0.32093	0.52107	At 25° C	[King1]
MgSe	50	0.546	...	At RT	[27Bro]
(Se)	100	0.43655	0.49576	At 25° C	[King1]

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Mg-Se evaluation contributed by **A.A. Nayeb-Hashemi** and **J.B. Clark,** Department of Metallurgical Engineering, The University of Missouri-Rolla, MO 65401. This work was supported by ASM International. Literature searched through 1984. Professor Clark is the ASM/NBS Data Program Category Editor for binary magnesium alloys.

The Ag-Ni (Silver-Nickel) System

107.8682 58.69

By M. Singleton and P. Nash
Illinois Institute of Technology

Equilibrium Diagram

The Ni-Ag system is an apparently simple monotectic system that has not been studied much since the evaluation of [Hansen]. The equilibrium phase diagram (Fig. 1) is based on the evaluation of [Hansen], with some modifications. Invariant reaction temperatures and compositions are given in Table 1. The melting points of the pure

Fig. 1 Assessed Ni-Ag Phase Diagram

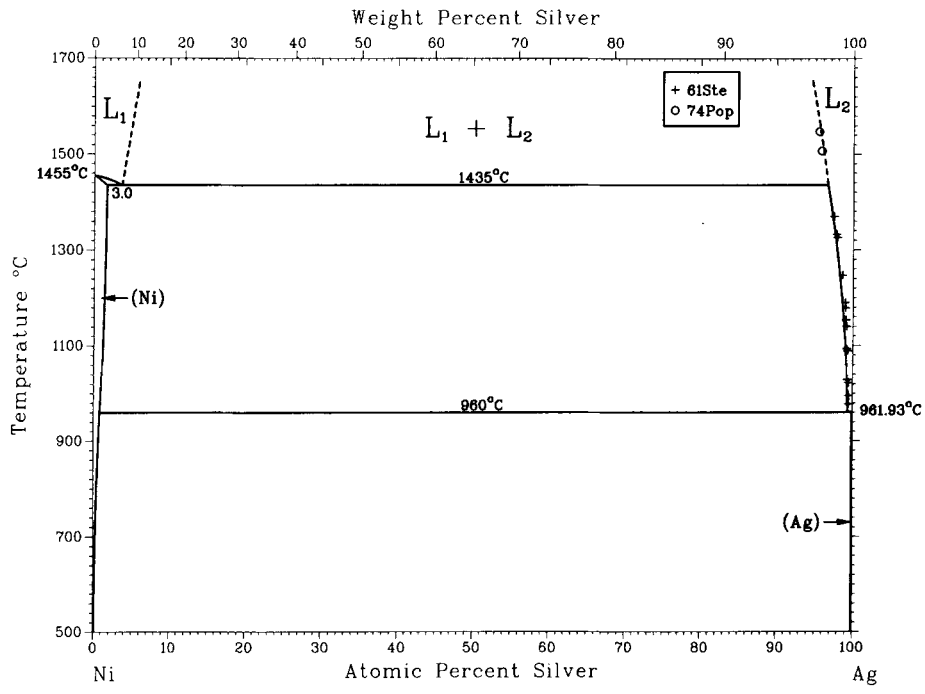

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Table 1 Special Points of the Assessed Ni-Ag Phase Diagram

Reaction	Compositions of the respective phases, at.% Ag			Temperature, °C	Reaction type
$L_1 \rightleftarrows (Ni) + L_2$	3	1	96.11	1435	Monotectic
$L \rightleftarrows (Ni) + (Ag)$	99.679	>1	99.8	960	Eutectic

Table 2 Solubility of Ni in (Ag)

Reference	Composition, at.% Ag	Reaction °C
[30Tam]	99.813	922
	99.846	860
	99.879	785
	99.919	702
	99.941	640
	99.952	600
	99.967	510
	99.978	400
[76Lad]	99.790	912
	99.813	881
	99.831	865
	99.862	834
	99.890	808
	99.903	788
	99.916	767
	99.936	750
	99.924	748
	99.941	733
	99.937	724
	99.957	674
	99.974	631

elements in Fig. 1 have been taken from [Melt] as 1455 °C for Ni (reported as 1453 °C in [Hansen] and 1451 °C in [77Sie]) and 962 °C for Ag (reported as 960.5 °C in [Hansen] and 961 °C in [77Sie]).

The Ag-rich liquidus was investigated by [61Ste], who used a liquid sampling technique followed by accurate chemical analysis to obtain the data points shown in Fig. 1. These data were shown by [61Ste] to fit the following analytical representation:

$$\log_{10} N = \frac{-A}{T} + B \qquad \text{(Eq 1)}$$

where $A = 4800$, $B = 1.4$ (for 1370 °C > T > 1000 °C), N is the mole fraction, and T is the absolute temperature.

By extrapolating this expression, the eutectic composition at the eutectic temperature (960 °C, taken from [Hansen]) was fixed in Fig. 1 at 99.679 at.% Ag. Similarly, the liquidus composition at the monotectic temperature (1435 °C, taken from [Hansen, 77Sie]) was fixed at 96.11 at.% Ag.

Calculation of the Ag-rich eutectic composition is possible, assuming a eutectic temperature of 960 °C and employing the following relation [81Gas]:

$$X_{Ni} = (T_M - T_E)x\frac{\Delta H_m}{T_M^2(1-k)R}$$

where R is the gas constant = 8.3143 J/mol · K; X_{Ni} is the atom fraction of Ni; T_M is the melting point of Ag, K; T_E is the eutectic temperature, K; ΔH_m is the enthalpy of fusion of pure Ag, J/mol; and k is the distribution coefficient (equal to zero if ideal mixing is assumed).

Assuming ideal mixing and taking ΔH_m to be 11 300 J/mol [83Cha], Eq 2 yields a eutectic composition of 99.822 at.% Ag, which is in reasonable agreement with the value extrapolated from the experimental data (99.679 at.% Ag) and used in Fig. 1.

The position of the monotectic point was placed by [Hansen] at approximately 3 at.% Ag on the basis of earlier work using solidified layer analyses [07Pet, 13Ces]. Figure 1 is drawn accordingly. Data pertaining to the liquid miscibility gap are largely unavailable. The phase boundary is estimated (dashed line) in Fig. 1. The two data points included in Fig. 1 are taken from work by [74Pop] on Fe-Ni-Ag and Co-Ni-Ag ternary melts.

The limit of solid solubility of Ni in (Ag) was determined by [30Tam] through measurements of the specific magnetization of equilibrated and quenched alloys. Data are presented in Table 2 with the more recent data of [76Lad]. Although the solid solubility of Ag in (Ni) decreases with decreasing temperature, no quantitative data are available. The estimate of 1 at.% Ag obtained by [Hansen] for the maximum solubility is used in Fig. 1.

Crystal structure data for the Ni-Ag system are provided in Table 3.

Metastable Phases

[69Ric] used condensation of co-evaporated Ni and Ag onto an amorphous backing to extend the maxium solid solubility of Ni in (Ag) to approximately 14 at.% Ni at the eutectic temperature.

Thermodynamics

[61Ste] reasoned that, for a dilute solution obeying Henry's law in which pure solid metal is in equilibrium with the solution:

$$\ln N = -\Delta H/RT \pm \Delta S/R \qquad \text{(Eq 3)}$$

where N is the mole fraction solute (Ni), ΔH is the sum of the differential heat of solution and heat of fusion, R is the gas constant, T is the absolute temperature (1000 °C < T < 1375 °C), and ΔS is the sum of the entropy of fusion and the excess partial molar entropy.

The data plotted in Fig. 2 indicate that Eq 3 is valid for compositions up to $N = 3 \times 10^{-2}$. Figure 2 is based on the data of [61Ste], who reported the entropy data in "e.u" without defining the units. It has been assumed that an "e.u" is an entropy unit, which is 1 cal/mol · K.

Measurement of the gradient of the curve in Fig. 2 yields:

$$\Delta H = 93\,004 \text{ J/mol} \qquad \text{(Eq 4)}$$

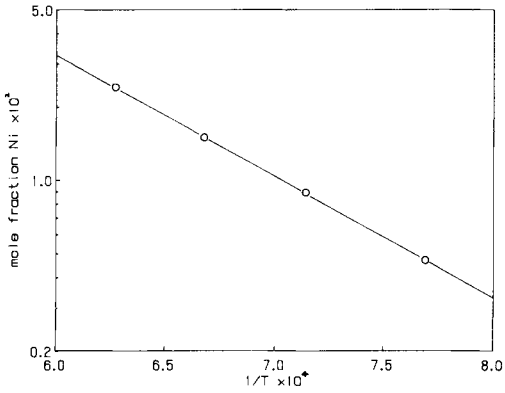
$$\Delta S = 26.8 \text{ J/mol} \cdot \text{K}.$$

Using values for the heat and temperatures of fusion taken from [58Kub], the differential heat of solution ΔH

Table 3 Ni-Ag Crystal Structure Data

Phase	Composition, at.% Ag	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
Ni	0 to 1	*cF*4	*Fm*3*m*	*A*1	Cu	[King1]
Ag	99.8 to 100	*cF*4	*Fm*3*m*	*A*1	Cu	[King1]

Fig. 2 Solubility of Ni in Liquid (Ag)



M. Singleton and P. Nash, 1987.

and the excess partial molar entropy were calculated as 75 402 J/mol and 16.8 J/mol · K, respectively.

Later work by [76Lad] on the solubility of Ni in (Ag) presented in Table 1 fit the expression (similar to Eq 3 [61Ste]):

$$C_o = \exp S/k \cdot \exp - \Delta H/kT \qquad \text{(Eq 5)}$$

where C_o is the atom fraction solute (Ni); ΔS is the excess entropy per atom of solute, J/mol · K; ΔH is the enthalpy per atom of solute, J/mol; and k is Boltzmans constant = 1.3805 J/K.

The data fit yielded:

$$C_o = \exp 6.445 \exp - 33\,722/T$$

giving

$$\Delta S/k = 6.445,\ H/k = 33\,722$$

which in turn yields:

$$\Delta S = 8.898 \text{ J/mol} \cdot \text{K}$$

$$\Delta H = 102.350 \text{ J/mol}$$

These values are on the order of those determined by [61Ste].

[68Gup] studied the diffusion of Ni in liquid Ag in approximately the same range of temperatures and compositions as [61Ste] and represented the behavior analytically as:

$$D_{Ni} = (7.4 \pm 1.6) \times 10^{-4} \exp(-(8120 \pm 620)/\text{RT}) \text{ cm}^2/\text{s} \qquad \text{(Eq 6)}$$

Using this expression, the activation energy for Ni diffusion in liquid Ag was calculated as 34 015 ± 2 513 J/mol, from which value the partial molar energy $\Delta_{sol}G_{Ni}$ of solution of Ni in liquid Ag was determined to be 101 793 J/mol. The positive sign of $\Delta_{sol}G_{Ni}$ is consistent with the experimental observation that the solubility of Ni in (Ag) is very limited [Elliott], because a large positive $\Delta_{sol}G_{Ni}$ implies solvent-solute immiscibility.

Suggestions for Further Work

Although the general form of the Ni-Ag equilibrium diagram is agreed upon, there is a lack of information regarding certain regions of the diagram. In particular, the variation of solid solubility of Ag in (Ni) with temperature and the extent of the liquid/liquid miscibility gap need to be determined.

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Ag-Ni evaluation contributed by **M. Singleton** and **P. Nash,** Illinois Institute of Technology, Metallurgical and Materials Engineering, 10 West 33rd Street, Chicago, IL 60616. This work was funded by NASA, Grant No. NAG3-302 through ASM International. Literature searched through 1983. Professor Nash is the ASM/NBS Data Program Category Editor for binary nickel alloys.