The Ag-Si (Silver-Silicon) System

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Equilibrium Diagram

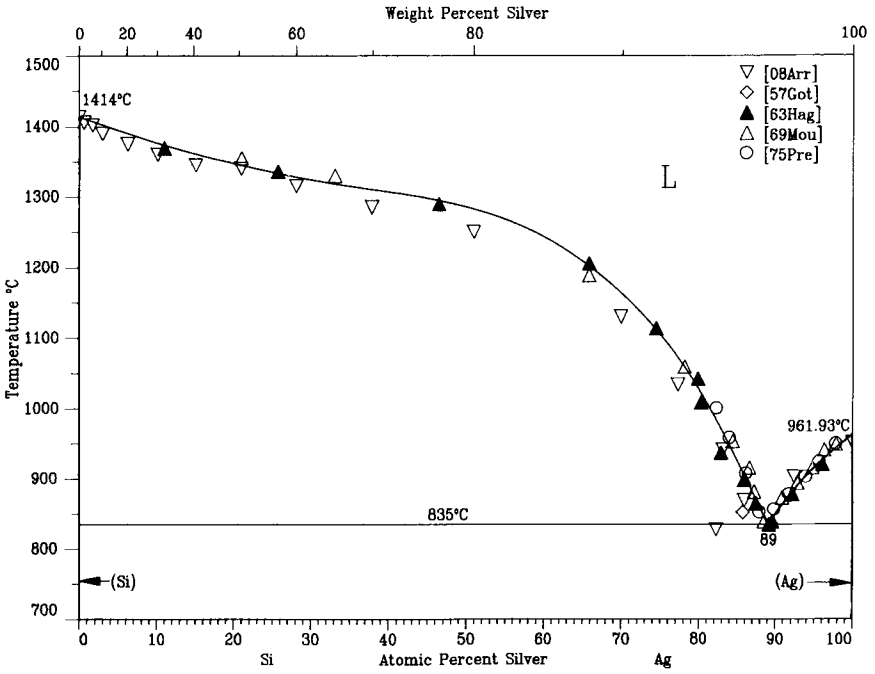
The assessed equilibrium phase diagram of the Si-Ag system is presented in Fig. 1. The system has a eutectic reaction around 845 °C and 89 at.% Ag. The mutual solubilities of Si and Ag in the solid state are negligible.

The main features of the Si-Ag phase diagram were determined first by [08Arr] by means of thermal analysis. The measurements were of understandably low accuracy: the melting temperature of Ag was reported 10 °C below the now accepted value (961.93 °C [Melt]), and the eutectic point differs considerably from coordinates determined more recently. The most comprehensive thermal analysis study of the system was performed by [63Hag], who heated Si-Ag alloys to about 100 to 200 °C above the estimated liquidus temperature, cooled them at an average rate of 2 to 7 °C/min, and determined the liquidus and eutectic temperatures from the cooling curves; the measurements were conducted using 99.86% pure Si and 99.95% pure Ag in an alumina crucible under an atmosphere of Ar. The liquidus coordinates, which were claimed to be accurate within 1 °C and 0.3 at.%, are reproduced in Tables 1 and 2 and Fig. 1; the temperatures are averages of two reported measurements for each composition. Data of [63Hag] are in good agreement with thermal analysis results obtained by other investigators [69Mou, 75Pre]. [69Mou] took their cooling curves at a rate of 5 °C/min and used 99.9% pure Si with Ag of "spectrographic purity;" [75Pre] conducted their measurements only in the Ag-rich side of the diagram, using 99.995% Ag and Si of unspecified purity. Results of both references are included in Tables 1 and 2 and Fig. 1, those of [75Pre] having been transcribed from graphical data.

The coordinates of the eutectic point reported by various investigators are listed in Table 3, together with those assessed on the basis of experimental data and the thermodynamic calculations presented later.

The (Si) solidus in the high-temperature range is reproduced in Fig. 2 [61Bol]. The authors determined solid solubilities from radiotracer diffusion experiments performed in quartz ampules in an atmosphere of He. The solidus is retrograde in character with a maximum solubility of 4×10^{-4} at.% Ag at about 1350

Fig. 1 Assessed Si-Ag Phase Diagram



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°C. The reported data agree with the earlier assessment of [57Col], indicating the solubility to be in the range 10^{-6} to 6×10^{-5} at.% Ag at 1200 °C.

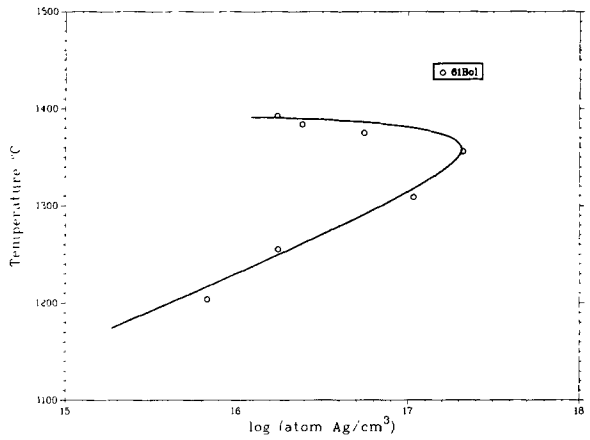
Metastable Phases

The occurrence of two metastable phases was reported in the Ag-rich side of the diagram: a cph structure in the composition range 75 to 95 at.% Ag [65Luo, 66Ana]; and an orthorhombic phase (Ag_2Si) containing about 70 at.% Ag [74Sur]. Both phases were obtained in alloys solidified rapidly at cooling rates above 10^5 °C/s by the melt spinning technique on Cu substrates. The cph phase starts decomposing above 100 °C [65Lou], and the orthorhombic phase decomposes to the equilibrium phases upon heating to "high temperatures" [74Sur].

The lattice parameters of the metastable phases are presented in Table 4. The structure of the orthorhombic phase described in [74Sur] was also indexed by him on the basis of the tetragonal unit cell (a = 0.5556 and c = 0.8340 nm), but this indexing did not prove satisfactory for all the interplanar spacings observed. No evidence of extended solid solubility of Si in (Ag) was discovered [65Luo], although a decrease of Ag lattice parameter to 0.40795 nm in the rapidly quenched alloys was interpreted by [74Sur] as implying that a small amount of Si does dissolve in (Ag).

The crystallization of Si-Ag amorphous films vapor deposited on NaCl substrates was investigated by [72Her]. The films were prepared in the form of a triple layer sandwich of 40 nm Si between two 25 nm films of Ag. The crystallization temperature of Si was reported as 540 °C.

Fig. 2 Solid Solubility of Ag in (Si)



From [61Bol].
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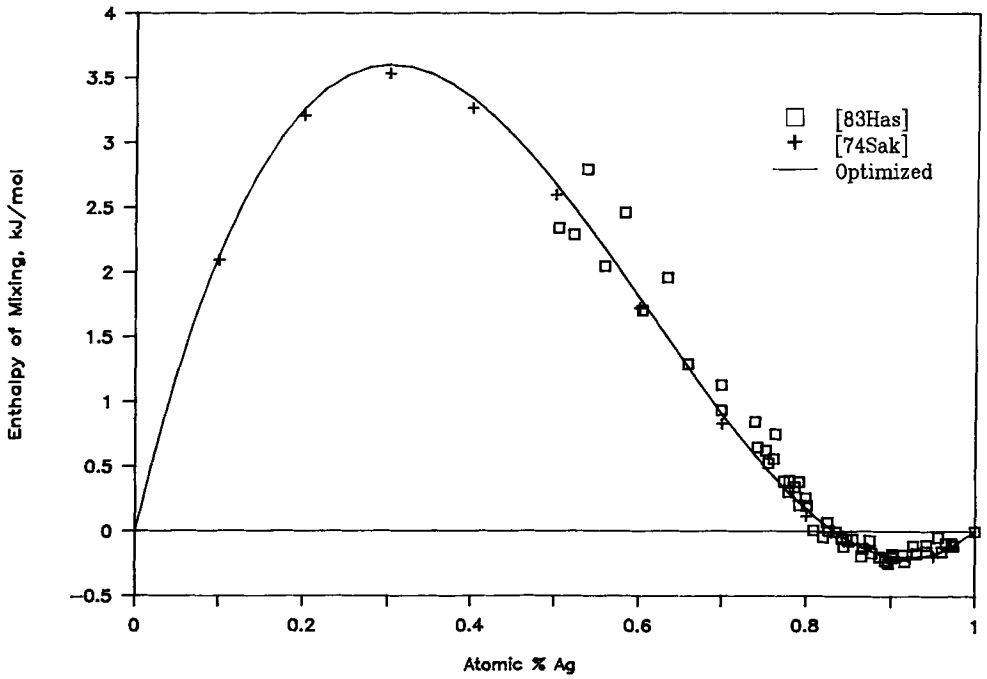
Fig. 3 Si-Ag Liquid Enthalpy of Mixing



From [83Has] and [74Sak].
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Crystal Structures and Lattice Parameters

At normal pressure, Si has a cubic C (diamond)-type structure. The high-pressure structure of Si is tetragonal, of the βSn type. Ag has an fcc structure of the Cu type. Crystallographic data for pure Si and Ag are included in Table 5.

Table 1 Experimental (Si) Liquidus Coordinates

Temperature, °C	Composition, at.% Ag	Temperature, °C	Composition, at.% Ag
From [63Hag]		**From [69Mou]**	
1369	10.7	1350	20.7
1335	25.6	1325	32.7
1289	46.4	1190	66
1206	66.1	1060	78.6
1113	74.7	955	84.8
1045	80	918	86.8
1010	80.6	885	87.6
938	83.8	**From[75Pre](a)**	
901	86.2	1000	82.5
868	87.8	960	84.2
		910	86.4
		854	88.2

(a) Values transcribed from graphical data.

Table 2 Experimental (Ag) Liquidus Coordinates

Temperature, °C	Composition, at.% Ag	Temperature, °C	Composition, at.% Ag
From [63Hag]		**From [75Pre](a)**	
922	96.3	950	98.3
881	92.4	925	96
844	89.7	905	94.3
From [69Mou]		880	92
955	98.2	856	90
945	96.8		
920	95.3		
898	93.3		
880	91.2		

(a) Values transcribed from graphical data.

Table 3 Coordinates of the Si-Ag Eutectic Transformation

Temperature, °C	Composition, at.% Ag	Reference
855	86.8	[57Got]
848	89.3	[75Pre]
845	88.85	[69Mou]
840	89.4	[63Hag]
830	82.7	[08Arr]
835	89	Assessed (from experimental)
830	89.3	Assessed (from thermodynamic calculation)

[33Jet] determined lattice parameters of the coexisting (Ag) and (Si) obtained in the whole composition range on melting the pure components, annealing between 635 and 825 °C, and quenching. The authors reported that the lattice parameters of (Ag) and (Si) increase with alloying by up to 0.00008 and 0.00016 nm, respectively.

However, these values are within their experimental error, estimated as ±0.0001 nm. Because of the negligible solubility in the solid state, the lattice parameters of (Si) and (Ag) phases can be regarded identical with those of the pure components.

Thermodynamics

The activities of the liquid components were measured by [50Sch, 63Den, 63Tur, 64Smi, 65Oke, 68Tup, 70Ver, 71Rob, 74Sak], but the measurements were confined mostly to Ag-rich solutions and the results obtained are very contradictory, sometimes erroneous [50Sch]. The most comprehensive study was conducted by [71Rob], who measured vapor pressures of Ag by a dynamic method in the temperature range 1450 to 1600 °C over the entire range of compositions. However, the reported activities are not compatible with the experimental enthalpy of mixing data of [83Has], whose results are believed by the present evaluators to be of superior accuracy. [83Has] calorimetrically measured the enthalpy of mixing in the liquid for alloys containing more than 50 at.% Ag at 1150 and 1277 °C. Because no temperature dependence was observed, the experimental values at both temperatures could be represented by:

$$\Delta_{mix}H = X_{Ag}(1 - X_{Ag})(27.12 - 32.14\,X_{Ag})\ \text{kJ/mol}$$

The partial enthalpy of mixing for Si in liquid alloys, calculated from the activity data of [74Sak], agreed best with the data of [83Has]. Because the data of [74Sak] covered the entire composition range, the two sets of data have been combined in the present evaluation to obtain an optimized expression for the enthalpy of mixing. The procedure used for the optimization was as follows: partial enthalpies of mixing for Si were calculated from the data of [83Has]. Of these, one value was chosen on the basis of an exact match with

Table 4 Si-Ag Lattice Parameter Data

Phase	Composition range, at.% Ag	Lattice parameters, nm a	b	c	Reference
(Si)	~0	0.54306	...	...	[King1]
SiII(H.P.)	0	0.4686	...	0.2585	[Pearson2]
(Ag)	~100	0.40861	...	...	[King1]
Metastable Phase					
Ag_2Si	~70	0.556	0.916	0.849	[74Sur]
β	75 to 95	0.2870	...	0.4528	[65Luo]

Note: H.P. ≡ high pressure.

that of [74Sak] (which occurred at $X_{Ag} = 0.397$). At this composition, the partial enthalpy of mixing for Ag was calculated from the [83Has] integral enthalpy of mixing data and used together with the partial enthalpy of mixing of Si data of [74Sak] to perform the Gibbs-Duhem integration. The integral enthalpies of mixing thus calculated could be represented as:

$$\Delta_{mix}H = X_{Ag}(1 - X_{Ag})(26.5 - 32.2\,X_{Ag})\ \text{kJ/mol}$$

The two expressions for the integral enthalpy of mixing ([74Sak] and [83Has]) were averaged to obtain the optimized enthalpy of mixing function:

$$\Delta_{mix}H = X_{Ag}(1 - X_{Ag})(26.8 - 32.15\,X_{Ag})\ \text{kJ/mol}$$

The optimized function is plotted together with the experimental data of [83Has] and [74Sak] in Figure 3 and indicates that the two sets of data are well represented by the expression.

Using this expression for the enthalpy of mixing and the experimental solubility data (obtained from a smooth liquidus drawn "by eye" through the reported data), the excess entropy of mixing was calculated as a function of composition as follows:

$$S^{ex}_{mix} = X_{Ag}(1 - X_{Ag})(3.8 - 5.6\,X_{Ag} - 2.1X^2_{Ag})\ \text{J/mol·K}$$

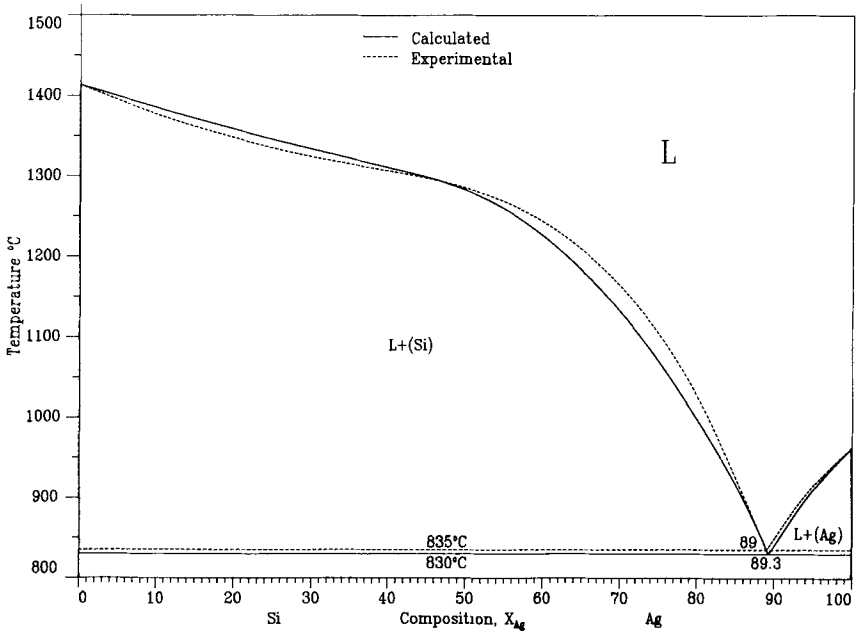
The enthalpy and excess entropy functions were used together with the Gibbs energy of fusion functions of the pure components to calculate the phase diagram. For the calculation, it was assumed that the enthalpy and excess entropy are temperature independent and that the mutual terminal solid solubilities of the pure components are nil. The calculated and experimental

Table 5 Si-Ag Crystal Structure Data

Phase	Composition, at.% Ag	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Si)	~0	*cF*8	$Fd\bar{3}m$	*A*4	C(diamond)
SiII(H.P.)	0	*tI*4	$I4_1/amd$	*A*5	βSn
(Ag)	~100	*cF*4	$Fm\bar{3}m$	*A*1	Cu
Metastable phases					
Ag_2Si	~70	Orthorhombic	...	...	...
β	75 to 95	cph	...	...	...

Note: H.P. ≡ high pressure.

Fig. 4 Comparison Between Calculated and Experimental Liquidus in Si-Ag



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liquidus curves shown in Figure 4 indicate that the phase diagram can be calculated with reasonable accuracy using the thermodynamic expressions derived in this evaluation.

The Gibbs energy of fusion functions for Si and Ag used in the calculations are as follows:

$$\Delta_{fus}G_{Si} = 48\,531 + 0.5298T + 1.9288 \times 10^{-3}\,T^2 - 4.3723T \ln T - 1.77 \times 10^{5}\,T^{-1}\ \text{J/mol}$$

and

$$\Delta_{fus}G_{Ag} = 1221 + 90.709T + 4.799 \times 10^{-3}\,T^2 - 13.738T \ln T + 2.655 \times 10^{5}\,T^{-1}\ \text{J/mol}$$

The heat capacities and heat of fusion for Si are from [73Bar] and those for Ag from [77Bar].

The Ag-Si liquid solution exhibits an interesting behavior. It is endothermic up to 83.4 at.% Ag, with a maximum heat absorption of 3602 J/mol at 30.2 at.% Ag. It is exothermic beyond 83.4 at.% Ag with a maximum heat evolution of 205 J/mol at 92.1 at.% Ag. The latter characteristic clearly indicates the tendency toward the formation of Ag-rich intermediate phases, possibly those observed during rapid solidification experiments by earlier investigators [65Luo, 66Ana, 74Sur]. The tendency was confirmed by liquid viscosity measurements of [69Abr]. The total excess entropy of mixing is close to zero (*i.e.*, the entropy of mixing is nearly ideal), which may be construed as mutual balancing of thermal and excess configurational entropies of mixing. Thermodynamic analysis of the liquid solution was attempted by [60Thu] and [70Rao], based solely on the rather obsolete data of [08Arr].

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*Indicates key paper.

#Indicates presence of a phase diagram.

Si-Ag evaluation contributed by **R.W. Olesinski, A.B. Gokhale**, and **G.J. Abbaschian**, Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611. This program was supported by ASM, under Grant No. FG 101-1 to the University of Florida. Thermodynamic calculations were made by using the computer program developed by Drs. A.D. Pelton, W.T. Thompson, and C.W. Bale, of McGill University, Montréal, Québec. Literature searched through 1983. Professor Abbaschian is the ASM/NIST Data Program Category Editor for binary silicon alloys.

The Ag-Nb (Silver-Niobium) System

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[63Kie] used a powder metallurgical infiltration process to prepare alloys of Ag and Nb. X-ray diffraction, electrical conductivity, and metallography were used to study the structural characteristics of the alloys. Their results showed that the solubility of Nb in liquid Ag is negligible from 1400 to 1700 °C. In addition, the solid solubility of Ag in (Nb) is extremely small over the same temperature range. No phase diagram is available, and no intermediate compounds have been reported for the Ag-Nb system, which apparently is similar to the Ag-W, Ag-Mo, and Ag-V systems [63Kie]. The crystal structure and lattice parameter data for Ag and Nb are reported in Table 1.

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Table 1 Ag-Nb Crystal Structure Data at 25 °C

Phase	Composition, at.% Nb	Pearson symbol	Space group	Strukturbericht designation	Prototype	Lattice parameter, nm
Ag	0	*cF*4	$Fm\bar{3}m$	*A*1	Cu	0.40861
Nb	100	*cI*2	$Im\bar{3}m$	*A*2	W	0.33007

From [King1].

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