82Jei: W. Jeitschko and B. Jaberg, "Structure Refinement of Ni_3Sn_4," *Acta Crystallogr., B38,* 598-600 (1982). (Crys Structure; Experimental)

*Indicates key paper.
#Indicates presence of a phase diagram.

Ni-Sn evaluation contributed by **P. Nash** and **A. Nash,** Metallurgical and Materials Engineering Department, Illinois Institute of Technology, 10 West 33rd Street, Chicago, Illinois 60616. This work was funded by NASA Grant No. NAG3-302, through the American Society for Metals. Literature searched through 1983. Professor P. Nash is Category Editor for binary nickel alloys.

The Bi-Si (Bismuth-Silicon) System

208.9804 28.0855

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Equilibrium Diagram

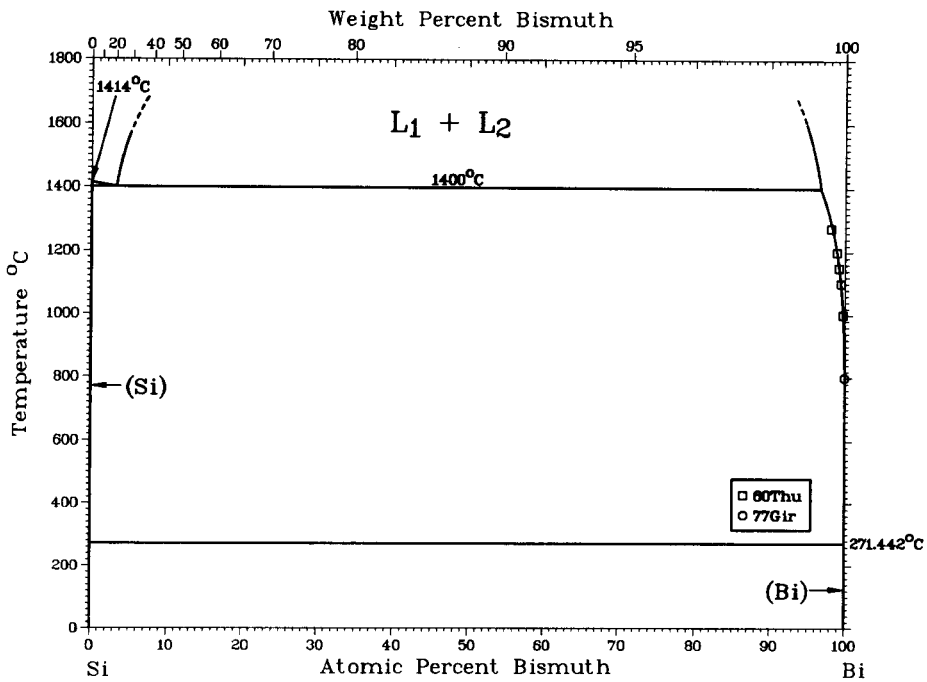
The assessed equilibrium phase diagram of the Si-Bi system is presented in Fig. 1. It shows a monotectic transformation at 1400 °C and a eutectic transformation at a temperature very close to the melting point of Bi (271 °C). The equilibrium phases are as follows:

- The liquid, L, with a monotectic composition at 3.3 at.% Bi
- The terminal (Si) solid solution, which is retrograde in character with a maximum solubility of about 0.0018 at.% Bi at 1350 °C
- The terminal (Bi) solid solution, with negligible solubility of Si

Liquid Solution. The approximate features of the Si-Bi system were first examined by [07Wil] by means of thermal analysis. Si used in these investigations contained almost 2% impurities, mainly Fe and Al, which might be responsible for inaccuracies of the reported diagram (for example, the eutectic temperature was reported as being several degrees below the melting point of Bi).

Liquidus coordinates experimentally determined by [60Thu] and [77Gir] are listed in Table 1. Both investigators used a weighing technique to determine the composition of the melt. [60Thu] sealed a known amount of Bi with an excess amount of Si in an evacuated silica tube, and annealed it for up to 19 h. The composition of the saturated melt was determined from the weight loss of Si caused by its dissolution in (Bi). The accuracy of the temperature measurements was reported to be ±2 °C, and the materials were reported to be of "high" purity. [77Gir] specified the purity only of his Bi as 5 N and did not report the accuracy of his temperature measurements.

Fig. 1 Assessed Si-Bi Phase Diagram



R. W. Olesinski and G. J. Abbaschian, 1985.

Data of [60Thu] and [77Gir] have been optimized by the present evaluators using least-squares regression analysis and a thermodynamic model discussed below. The calculated Gibbs energy function for the liquid phase and those for solid phases were used to calculate the phase boundaries. All calculations were based on the assumption that the enthalpies and entropies of mixing are temperature independent and that mutual solid solubilities of Si and Bi are nil. Invariant points of the phase diagram are listed in Table 2 together with those estimated by [60Thu], who calculated a critical temperature of the liquid miscibility gap as 2187 °C, whereas the present calculations imply a critical temperature of about 2900 °C. However, no information is available to indicate whether or not the miscibility gap extends beyond the boiling point of Bi (1564 °C).

Table 1 Experimental Coordinates of the Si-Bi Liquidus

Temperature, °C	Composition, at.% Bi	Reference
1275	98.07	[60Thu]
1200	98.87	
1150	99.168	
1100	99.456	
1000	99.738	
800	99.938	[77Gir]

Solid Solution, (Si). The solidus adopted in this evaluation (Fig. 2) is based on the results of [56Ful] and those of F. X. Hassion and L. J. Russo as reported in [60Tru]. [56Ful] reduced Bi from its oxide at temperatures between 1220 and 1380 °C and used the p-n junction method to measure the surface concentration. Their results agree fairly well with the data in [60Tru], which were obtained from capacitance measurements not described.

The equilibrium distribution coefficient of Bi near the melting point of Si was reported as 0.0007 (quoted by [60Tru] from a patent issued to S. M. Christian).

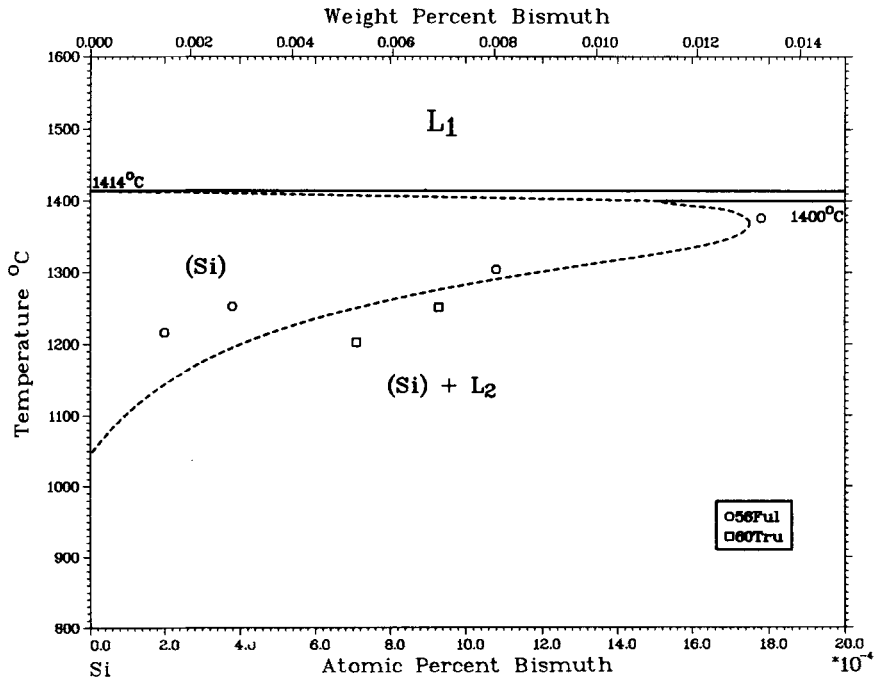
Metastable Phases

Solid solubility of Bi in (Si) was extended to 0.8 at.% Bi by ion implantation and subsequent laser annealing [80Whi]. The implantation was conducted into Si wafers with a dose of 1.2×10^{-15} cm^{-2} and 250 keV at room temperature; laser annealing was performed with a 15 ns pulse at an energy density of 1.5 J × cm^{-2}. [81Bae] used similar conditions, but with a laser pulse duration of 100 ns, and reported that the extended concentration of Bi did not

Table 2 Estimated Invariant Points of the Si-Bi System

Monotectic transformation			Eutectic transformation		
Temperature, °C	Composition, at.% Bi		Temperature, °C	Composition, at.% Bi	Reference
	Si-rich liquid	Bi-rich liquid			
1400	3.3	96.7	~271.4	~100.0	This work
1393	4.0	96.0	~271	~100.0	[60Thu]

Fig. 2 Solid Solubilities of Bi in Si



R. W. Olesinski and G. J. Abbaschian, 1985.

Table 3 Crystal Structure and Lattice Parameter Data of Si and Bi at 25 °C

Phase	Homogeneity range, at.% Bi	Pearson symbol	Space group	Strukturbericht designation	Prototype	Lattice parameters, nm a	c	Reference
(Si)	0.0 to 0.0018	*cF*8	$Fd\bar{3}m$	*A*4	C (diamond)	0.54306(a)	···	[King1]
(Bi)	100	*hR*2	$R\bar{3}m$	*A*7	As	0.4546(a)	1.1862	[Pearson2]

(a) For the pure metals.

exceed 0.2 at.%. The concentration was also shown to be dependent on crystal orientation, with somewhat higher values for (100) substrates than for (111). Both investigators measured the Bi concentration by the backscattering and ion channeling techniques.

Crystal Structure

At normal pressure Si has the diamond-type cubic structure, whereas at high pressures it has a tetragonal βSn-type structure. The structure of Bi is rhombohedral, of the αAs-type. The structural and crystallographic data of both metals are listed in Table 3.

Bi forms a substitutional solid solution in (Si) [81Bae]. [33Jet] performed an X-ray study of Si-Bi phases by alloying 99.79% pure Si and 99.96% pure Bi in equimolar proportion and annealing at 240 °C. They were not able to measure the composition dependence of lattice parameters. Therefore, it may be assumed that due to the negligible solubility in the solid state, the lattice parameters of the Si-Bi alloy phases are almost identical with those of the pure components.

Thermodynamics

Both [60Thu] and [77Gir] assumed that the enthalpy and excess entropy of mixing of the liquid are given by the following functions:

$$\Delta_{mix}H = A(1 - X_{Bi})X_{Bi}$$

$$S^{ex} = B(1 - X_{Bi})X_{Bi}$$

where X_{Bi} is the mole fraction of Bi and A and B are constants independent of composition and temperature. Values of the coefficients A and B estimated by [60Thu] are given in Table 4. Also listed in Table 4 are the coefficients calculated by the present evaluators, who used the data of [60Thu] and [77Gir]. Gibbs energies of fusion for pure Si and Bi used in these calculations are as follows:

$$\Delta_{fus}G(Si) = 48531 + 0.5298\,T + 1.9288 \times 10^{-3}\,T^2 - 4.3723\,T \ln T - 1.77 \times 10^{5}\,T^{-1} \quad J/mol$$

$$\Delta_{fus}G(Bi) = 4198 + 108.96\,T + 15.234 \times 10^{-3}\,T^2 - 19.9493\,T \ln T + 2.05 \times 10^{5}\,T^{-1} \quad J/mol$$

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

Table 4 Thermodynamic Parameters of Si-Bi Liquid

Constants A J/mol	B J/mol·K	Reference
46 370	−2.26	This work
62 090	8.62	[60Thu]

The Si-Bi liquid solution is endothermic and indicates positive deviation from Raoultian behavior.

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*Indicates key paper.
#Indicates presence of a phase diagram.

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