The Al-Bi (Aluminum-Bismuth) System

26.98154 208.9804

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Equilibrium Diagram

Al-Bi is a simple three-phase system. Immiscibility is observed in the liquid, L, below a critical temperature. Solid solubilities in the terminal solid solutions, fcc (Al) and rhombohedral (Bi), are extremely limited. Two reactions occur: the L $\rightleftharpoons$ (Al) + L monotectic at ~657 °C and the L $\rightleftharpoons$ (Al) + (Bi) eutectic at ~270 °C. The assessed phase diagram shown in Fig. 1 is the result of a nonlinear, least-squares optimization by the method of [77Luk] of parametrized model free energy functions to selected phase diagram and thermodynamic data. In the immediate vicinity of the critical point, correction was made by the method of [83Mur] to account for the failure of classical free energy functions to predict correct critical exponents. Reactions are listed in Table 1.

This review supersedes an earlier evaluation [80Ell] in the *Bulletin,* which covered the literature only through 1966.

Reactions and Solid Solubilities. Data on the reaction temperatures and compositions are sparse. From the thermal analysis studies of [31Han], [39Kem], and [69Pre], the monotectic temperature is placed at 657.0 ± 0.5 °C. Combining melt analysis with thermal analysis, [39Kem] placed the monotectic composition at 0.45 at.% Bi, and, on the basis of chemical analysis and resistivity studies of heat treated and quenched samples, they concluded that less than 0.03 at.% Bi dissolves in Al at the monotectic temperature. The liquid terminus of the monotectic is placed at 84.0 ± 0.5 at.% Bi by the electrochemical studies of [66Mar] and the calorimetric work of [63Wit]. Differential thermal analysis work by [69Pre] and electrochemical studies of [66Mar] placed the eutectic temperature at 270.0 ± 0.5 °C. The eutectic composition is given by [66Mar] as 99.44 at.% Bi and by [65Wee], who carried out melt analysis, as 99.56 at.% Bi. An attempt to determine the solubility of Al in Bi was not mentioned in the literature, but the small melting point depression and the proximity of the eutectic composition to pure Bi suggest it to be virtually nil.

Because the terminal solubilities appear to be near zero, (Al) and (Bi) have been treated as line compounds in the fitting carried out in the present evaluation. This fit has yielded a monotectic temperature of 656.8 °C, composition of 0.42 at.% Bi, and a liquid terminus of 84.1 at.% Bi. The eutectic has been calculated to fall at 270.4 °C, with the eutectic composition 99.51 at.% Bi.

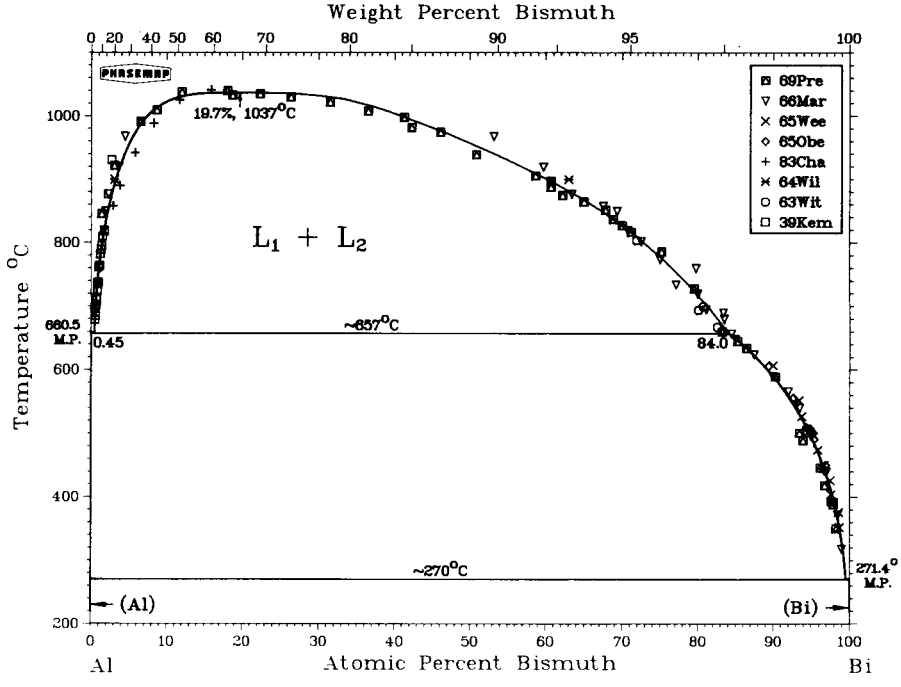
Liquid Miscibility Gap. The existence of liquid immiscibility and the monotectic reaction was established by early workers [1892Wri, 1894Wri, 02Cam 04Pec, 06Pec, 06Gwy]. This evaluation has focused on the data of [39Kem] (melt analysis and thermal analysis of Al-rich

Al-Bi Crystal Structure Data

Phase	Composition range(a), at.% Bi	Pearson symbol	Space group	Prototype
(Al)	0 to ~0.03	*cF*4	$Fm\bar{3}m$	Cu
(Bi)	100	*hR*2	$R\bar{3}m$	As

(a) From the phase diagram.

Fig. 1 Assessed Al-Bi Phase Diagram



A. J. McAlister, 1984.

alloys), [63Wit] (calorimetry and thermal analysis), [64Wil] (melt analysis), [66Mar] (melt analysis and electrochemical cell measurements), and [69Pre] and [83Cha] (both differential thermal analysis).

The gap data obtained by [63Cam] are in strong disagreement with the overall body of data. It is believed that their samples were allowed to cool significantly below equilibration temperatures before quenching, causing further phase separation. Therefore, they have not been used in this evaluation. The fitted critical point, T_C, occurs at 1037 °C, with a critical composition of 19.75 at.% Bi.

The selected data are listed in Table 2 and compared to the fitted diagrams in Fig. 1.

[L + (Al)]/L Phase Boundary. The data selected for this evaluation were those of [66Mar] (electrochemical cell), [69Pre] (differential thermal analysis), and [65Obe] and [65Wee] (both melt analysis). The melt analysis data of [66Dav] were omitted from consideration because it was judged that the reported time course of these measurements made attainment of equilibrium doubtful.

The selected data are listed in Table 3 and compared with the fitted boundary in Fig. 1.

Thermodynamic Measurements

Calorimetric measurements of the heat of mixing in the liquid were reported by [69Pre] (reaction temperature not given) and by [63Wit] (at several temperatures). Data selected for this work are listed in Table 4.

Liquid-Al partial free energies were obtained by the electrochemical cell method by [63Wit] at 900 °C, from 65 to 100 at.% Bi, and by [66Mar] over the temperature range 690 to 1000 °C, from 69.5 to 99.0 at.% Bi. Both sets of data have been employed in the fitting and are listed in Table 5.

Table 1 Reactions in the Al-Bi System

Reaction	Composition, at.% Bi			Temperature, °C	Type
L ⇄ (Al) + L	0.45 ± 0.02	0.02 ± 0.01	84.0 ± 0.5	657 ± 0.5	Monotectic
L ⇄ (Al) + Bi	99.5 ± 0.1	0.0	100	270 ± 0.5	Eutectic
Al		···		660.452	Melting point
Bi		···		271.442	Melting point

Table 2 Liquid Miscibility Gap Boundaries in Al-Bi

Reference	Temperature, °C	Compositions, at.% Bi		Method	Reference	Temperature, °C	Compositions, at.% Bi		Method
[63Wit]	667	···	82.6	Thermal analysis, calorimetry		720	···	80.00	
	694	···	80.1			774	···	75.00	
	700	···	80.7			802	···	72.50	
	804	···	71.9			858	···	67.50	
[39Kem]	685	0.59	···	Thermal analysis	[83Cha]	858	2.9	···	Differential thermal analysis
	702	0.70	···			890	3.8	···	
	725	0.85	···			942	5.8	···	
	735	0.91	···			988	8.3	···	
	738	0.94	···			1025	11.7	···	
	762	1.01	···			1041	15.9	···	
	782	1.23	···		[69Pre]	660	···	83.26	Differential thermal analysis
	789	1.32	···			728	···	79.53	
	795	1.38	···			786	···	75.28	
	810	1.53	···			817	···	71.26	
[39Kem]	679	0.53	···	Melt analysis		827	···	70.01	
	690	0.59	···			837	···	68.75	
	710	0.72	···			852	···	67.76	
	714	0.74	···			865	···	64.98	
	737	0.88	···			875	···	62.21	
	764	1.14	···			888	···	60.73	
	818	1.78	···			898	···	60.71	
	877	2.26	···			906	···	58.70	
	931	2.71	···			939	···	50.88	
[64Wil]	900	3.08	3.00	Melt analysis		975	···	46.11	
[66Mar]	690	0.46	83.38	Melt analysis		982	···	42.32	
	695	0.69	81.10			998	···	41.32	
	734	0.79	77.07			1008	···	36.52	
	760	1.13	79.72			1022	···	31.47	
	820	1.69	70.69			1030	···	26.42	
	850	1.89	69.34			1035	22.37	···	
	877	2.27	63.42			1033	19.84	···	
	920	3.65	59.74			1040	18.07	···	
	968	4.48	53.17			1038	12.00	···	
	982	4.53	47.24			1009	08.68	···	
	1008	4.33	43.02			991	6.63	···	
[66Mar]	657	···	84.50	Electrochemical cell		922	3.16	···	
	680	···	83.50			846	1.42	···	

Thermodynamic Calculations

The Gibbs free energy of the i^{th} phase was taken to be of the form:

$$ {}^0G^i_{Al}(1-x) + {}^0G^i_{Bi}x + RT[x \ln x + (1-x)\ln(1-x)] + x(1-x)[A_i + B_i(1-2x) + C_i(1-6x+6x^2) + D_i(1-12x+30x^2-20x^3)] $$

where x is the atomic fraction of Bi. The ${}^0G^i_j$ are lattice stability terms taken from [Hultgren, Elements] and have not been varied during fitting. (Al) and (Bi) have been treated as line compounds with free energies taken from [Hultgren, Elements]. Both lattice stability terms and interaction parameters have been considered to be linear in temperature. Final values of the parameters are listed in Table 6.

The present fit yields good agreement with the experimental thermodynamic data of Tables 4 and 5. The measured values of the liquid heat of mixing of Table 4 show strong scatter. The standard deviation of the data from the fit is 630 J/mol. Comparison of the fitted Al partial free energy with the measured results reveals a maximum difference of 700 J/mol at 85 at.% Bi. In this region, the curvature of the fitted result differs somewhat from experiment. Elsewhere, the agreement is very close.

Table 3 L/[L + (Al)] Phase Boundary in Al-Bi

Reference	Temperature, °C	Composition, at.% Bi	Method
[66Mar]	648	85	Electrochemical cell
	624	87.5	
	590	90	
	566	92	
	540	93.5	
	496	95	
	440	97	
	392	98	
	372	98.5	
	318	99	
[69Pre]	645	85.3	Differential thermal analysis
	635	86.5	
	589	90.3	
	501	93.5	
	489	94.0	
	446	96.2	
	418	96.8	
	393	97.7	
	388	97.9	
	350	98.3	
[65Obe]	606	89.4	Melt analysis
	556	92.7	
	549	93.2	
	510	94.4	
	508	94.9	
	501	95.3	
	491	95.4	
	441	96.8	
	450	96.9	
[65Wee]	607	90.0	Melt analysis
	552	93.4	
	527	93.8	
	503	94.7	
	474	95.9	
	450	96.7	
	426	97.5	
	404	97.6	
	376	98.6	
	352	98.7	

Table 4 Enthalpy of Mixing in Liquid Al-Bi Alloys

Reference	Temperature, °C	Composition, at.% Bi	Enthalpy of mixing ($\Delta_{mix}H$), J/mol	Method
[69Pre]	(a)	10	3766	Calorimetry
		30	6278	
		30	6800	
		40	7952	
		49	7323	
		60	6319	
		60	5859	
		70	4520	
		80	4101	
[63Wit]	804	2	433	Calorimetry
	702	85	2561	
	702	90	1962	
	702	91	1750	
	702	96	832	

(a) Not specified by authors.

Table 5 Partial Gibbs Free Energy of Mixing of Liquid Al

Reference	Temperature, °C	Composition, at.% Bi	Partial Gibbs free energy of mixing(a) ($\Delta_{mix}G_{Al}$), J/mol	Method
[63Wit]	900	65 to 80	$(x^2)(52178 - 61377x + 25397x^2) + 8.314\,T\ln(1-x)$	Electrochemical cell
	900	80 to 100	$(x^2)(32384 - 15564x) + 8.314\,T\ln(1-x)$	Electrochemical cell
[66Mar]	900 to 1173	72.5	$12702 - 11.927T$	···
		75	$12250 - 11.844T$	···
		80	$15204 - 15.443T$	···
		83.5	$17380 - 18.247T$	···
		84.5	$18134 - 19.335T$	···
		85	$17451 - 19.042T$	···
		87.5	$18125 - 20.590T$	···
		90	$18606 - 22.599T$	···
		92	$19339 - 24.440T$	···
		93.5	$21030 - 27.621T$	···
		95	$22666 - 31.555T$	···
		97	$21109 - 34.024T$	···
		98	$21963 - 38.460T$	···
		98.5	$23662 - 41.724T$	···
		99	$23051 - 44.654T$	···

(a) T is in kelvin; x is atomic fraction Bi.

Table 6 Fitted Thermodynamic Parameters for the Al-Bi System

Lattice stability terms

$^0G^L_{Al} = 0$
$^0G^L_{Bi} = 0$
$^0G^{(Al)}_{Al} = -10\,792 + 11.56\,T$(a, b)
$^0G^{(Bi)}_{Bi} = -11\,297 + 20.744\,T$(a, b)

Interactions

$A^L = 30\,972.9 - 6.878\,T$(a)
$B^L = 17\,612.5 - 7.514\,T$(a)
$C^L = 13\,121.5 - 8.642\,T$(a)
$D^L = 2\,629.5 - 0.723\,T$(a)

(a) T is in kelvin. (b) Treated as line compounds.

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*Indicates key paper.

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The Co-Fe (Cobalt-Iron) System

58.9332 55.847

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Equilibrium Phase Diagram

A number of investigations have been made that are relevant to the phase equilibria and phase transformations in the Co-Fe system. The constitution of the Co-Fe alloys is reproduced in Fig. 1 by adding the available information to the phase diagram of [Hansen, Elliott, Shunk, 81Riv].

Solidus and Liquidus. The liquidus and solidus relationships are well established. The liquidus curve falls from the melting point of Fe (1538 °C) to the temperature of the γ(fcc)/δ(bcc) peritectic reaction, which was found as 1499 °C [53Har] and 1494 °C [70Pre]. The liquidus continues to a minimum point at 1476 °C at 33.2 at.% Fe and then rises to a melting point of Co at 1495 °C [70Pre]. Experimental data are plotted in Fig. 2.

Solid Equilibrium. The δ/γ equilibrium is determined by thermal analysis [53Har] and magnetic susceptibility measurements [70Fis1], as illustrated in Fig. 2. The temperature of the γ/δ transformation of pure Fe is raised by the solution of Co. The temperature of the α(bcc)/γ(fcc) transformation is also raised by Co, which indicates that Co stabilizes austenite near the A_4 point, and it stabilizes ferrite near the A_3 point. The α/γ equilibrium is shown in Fig. 3 together with the data obtained from current