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Liquid miscibility gap in the Al–Pb–Sn system

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Abstract

The liquid miscibility gap boundary of two immiscible liquids, Al- and Pb-rich, has been measured in a temperature range between 1073 and 1293 K and a ternary liquid thermodynamic parameter has been evaluated based on experimental data measured in the present work together with phase equilibrium data available in the literature. From these, the phase diagram of the Al–Pb–Sn system including the liquid miscibility gap has been calculated using the CALPHAD method. The calculated results are in good agreement with the experimental data. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Alloys; Liquid alloys; Phase diagram; Thermodynamic modeling

1. Introduction

Al–Sn alloys have been used as commercial sleeve-bearing materials for automotive engines [1]. Recently, a number of attempts have been made to replace much of the Sn with Pb in these alloys, as Pb offers a considerable advantage over Sn for material costs [1–4]. Moreover, it is desirable that Pb-rich particles dispersed in bearing materials could act as more effective solid lubricant during sliding motion [2].

The Al–Pb system is characterized by an exceptionally large liquid miscibility gap that reaches up to about 1700 K [5]. The monotectic reaction of this system takes place at 933 K. In the Al–Pb–Sn system, the presence of a ternary liquid miscibility gap has been known to be still distinct up to a high Sn content [6]. The uniform dispersion of Pb-rich particles in the Al matrix plays a key role in producing Al–Pb–Sn sleeve-bearing alloys. Pb-rich particles in Al–Pb–Sn alloys are formed from Pb-rich liquid droplets separated in the miscibility gap during solidification. Thus, the dispersion of Pb-rich particles might be strongly influenced by the liquid phase equilibria of the Al–Pb–Sn system including the liquid miscibility gap at elevated temperatures as well as the process parameters such as solidification rate and fluid flow.

The aim of the present work is to investigate the ternary

liquid miscibility gap in the Al–Pb–Sn system employing both experimental and theoretical approaches. The liquid miscibility gap has been determined by holding Al–Pb–Sn alloys at selected temperatures, then quenching them and analyzing the two phases. The phase equilibria of this system have been calculated using the calculation-of-phase-diagram (CALPHAD) method [7]. The ternary Gibbs energy parameter describing the liquid phase has been evaluated based on the phase equilibrium data given in the present work together with literature data [6,8].

2. Experimental procedure

The alloy specimens were prepared from pure Al, Pb and Sn whose purities are all above 99.9%. The amounts of Al, Pb and Sn were determined in such proportions as to give approximately equal volumes of the two immiscible liquids, Al- and Pb-rich liquids. The specimens were melted in graphite crucibles, 4 mm in inner diameter and 60 mm in height, between 1073 and 1293 K and held for 12 h under Ar atmosphere so that thermodynamic equilibrium at each temperature could be attained. The graphite crucibles were suspended with a steel wire between heat elements and the crucible temperature was controlled using a K-type thermocouple. A schematic illustration of the experimental apparatus is given in Fig. 1. After holding for 12 h, the specimens with crucibles were dropped into water. Each composition of the Al- and Pb-rich portions in

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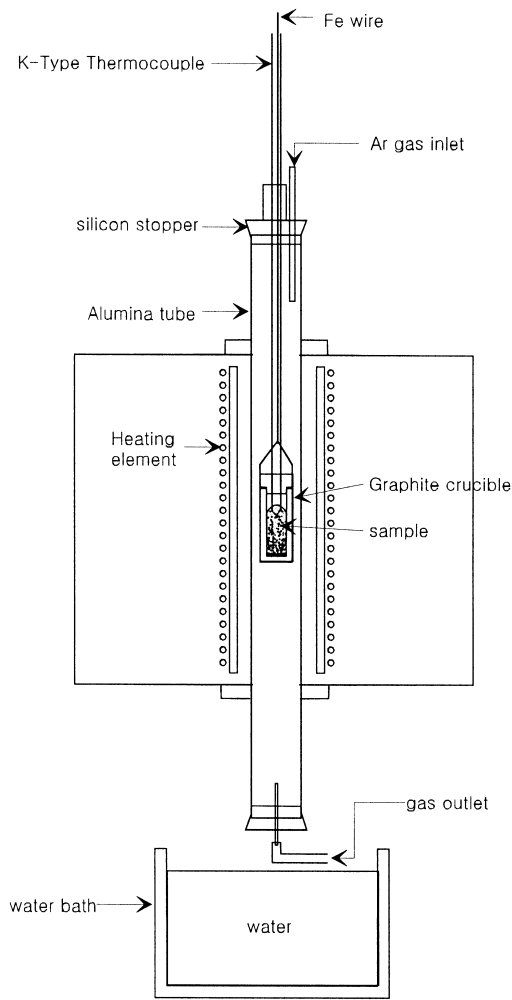


Fig. 1. Schematic illustration of the experimental apparatus.

the specimens was analyzed using atomic absorption (AA) and inductively coupled plasma (ICP) spectrometries.

3. Thermodynamic calculation

The Al–Pb–Sn system includes three phases: liquid, fcc (Al and Pb) and bct (Sn). The existence of any ternary compound has not yet been reported.

A regular solution model employed to describe the molar Gibbs energies of these phases is as follows:

$$G_m = x_{Al} \circ G_{Al} + x_{Pb} \circ G_{Pb} + x_{Sn} \circ G_{Sn} + RT(x_{Al} \ln x_{Al} + x_{Pb} \ln x_{Pb} + x_{Sn} \ln x_{Sn}) + {}^{ex}G_m \quad (1)$$

where

$${}^{ex}G_m = x_{Al}x_{Pb}L_{Al,Pb} + x_{Al}x_{Sn}L_{Al,Sn} + x_{Pb}x_{Sn}L_{Pb,Sn} + x_{Al}x_{Pb}x_{Sn}L_{Al,Pb,Sn} \quad (2)$$

The parameters $\circ G_i$ and x_i denote the Gibbs energy and mole fraction of pure component i ($i=Al, Pb, Sn$),

respectively. $L_{i,j}$ and $L_{i,j,k}$ denote the binary interaction parameter between components i and j and the ternary interaction parameter, respectively. They are usually expressed as the Redlich–Kister polynomials [9], which are functions of temperature and composition.

The $\circ G_i$ values of pure components have been critically reviewed and reported by Scientific Group ThermoData Europe (SGTE) [10]. These values have been accepted without modification in the present work. The binary interaction parameters $L_{i,j}$ have been taken from the recent assessments of the Al–Pb [5], Pb–Sn [11] and Al–Sn systems [12]. The ternary interaction parameter $L_{i,j,k}$ is to be evaluated in the present work.

Phase equilibrium data on the Al–Pb–Sn system have been reported in the literature. Based on the chemical analysis of two immiscible liquids, Davies [6] proposed liquid miscibility gap boundaries at three different temperatures 923, 1003 and 1073 K. Campbell and Kartzmark [8] reported two isothermal sections of the Al–Pb–Sn phase diagram at 773 and 873 K using chemical analysis. No thermochemical property of the Al–Pb–Sn system has been reported so far.

We have evaluated the ternary liquid interaction parameter based on the experimental results of the present work in combination with the above mentioned literature information. Subsequently, the phase equilibria of the Al–Pb–Sn system have been calculated using the evaluated parameter. The evaluation of the thermodynamic parameter and the calculation of phase equilibria have been carried out using computer softwares PARROT and POLY-3, respectively, both of which are part of a Thermo-Calc software package [13].

4. Results and discussion

Table 1 summarizes the liquid miscibility gap boundary in the Al–Pb binary system measured in the present work.

Table 1
Measured liquid miscibility gap boundary in the Al–Pb system

Temperature (K)	Al-rich (wt.% Pb)	Pb-rich (wt.% Pb)
953	1.76	99.82
971	2.22	99.80
993	2.36	99.82
1012	2.68	99.76
1042	3.56	99.69
1061	4.22	99.70
1072	4.43	99.65
1093	4.77	99.61
1115	5.92	99.61
1136	5.93	99.52
1147	6.72	99.41
1153	6.94	99.53
1168	7.43	99.43
1186	9.19	99.37

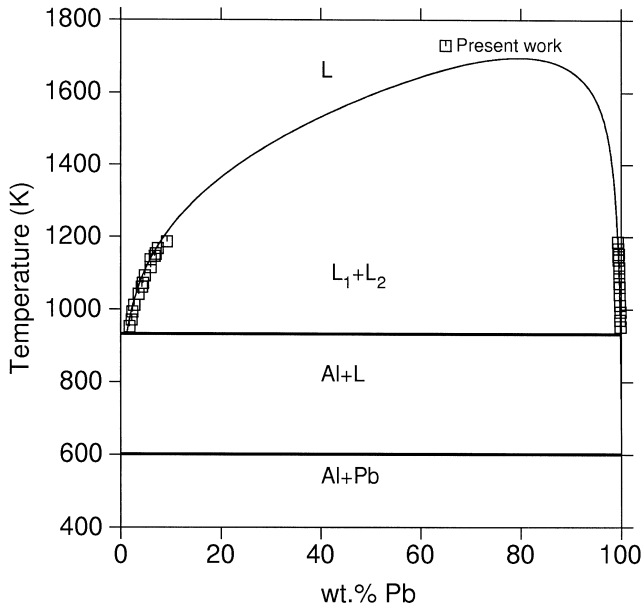


Fig. 2. Calculated phase diagram of the Al–Pb system together with experimental data.

Fig. 2 compares the measured data with the calculated phase diagram of the Al–Pb system that has been accurately defined in the previous assessment [5]. The measured data in both Al- and Pb-rich regions show excellent agreement with the calculated results [5], implying that the experimental method in the present work is indeed valid.

Table 2 summarizes the liquid miscibility gap boundary in the Al–Pb–Sn ternary system at temperatures ranging

Table 2
Measured liquid miscibility gap boundary in the Al–Pb–Sn system

Temperature (K)	Al-rich		Pb-rich	
	Wt.% Pb	Wt.% Sn	Wt.% Pb	Wt.% Sn
1073	6.01	10.10	95.35	4.17
	8.00	16.60	91.48	7.72
	7.97	27.20	83.25	15.50
	10.40	34.40	77.77	20.70
	15.60	37.70	69.23	27.10
1115	7.77	7.68	96.08	3.44
	9.14	17.50	91.60	7.51
	9.77	22.40	86.64	12.30
	10.80	29.50	81.85	16.70
	12.80	35.40	77.39	21.10
1168	6.40	8.97	96.57	2.74
	11.38	17.20	94.64	4.63
	11.57	30.10	87.11	12.10
1223	9.29	10.20	95.89	3.31
	14.49	16.20	91.32	7.72
	13.92	24.20	86.11	12.40
	24.83	36.29	77.83	19.0
1293	14.60	9.00	96.10	3.32
	12.95	17.30	92.46	6.53
	16.98	25.60	88.44	10.30
	20.57	31.94	84.38	14.50

Table 3
Evaluated thermodynamic parameter in the present work

$$L_{\text{Al,Pb,Sn}}^{\text{liquid}} = (-100\,000 + 57.7T)x_{\text{Al}} - 3286x_{\text{Pb}} - 364x_{\text{Sn}}$$

from 1073 to 1293 K measured in the present work. The ternary liquid interaction parameter evaluated in the present work is given in Table 3.

The calculated isothermal sections of the Al–Pb–Sn phase diagram at 773 and 873 K are presented in Fig. 3a and b, respectively. It is found that the liquid solubility

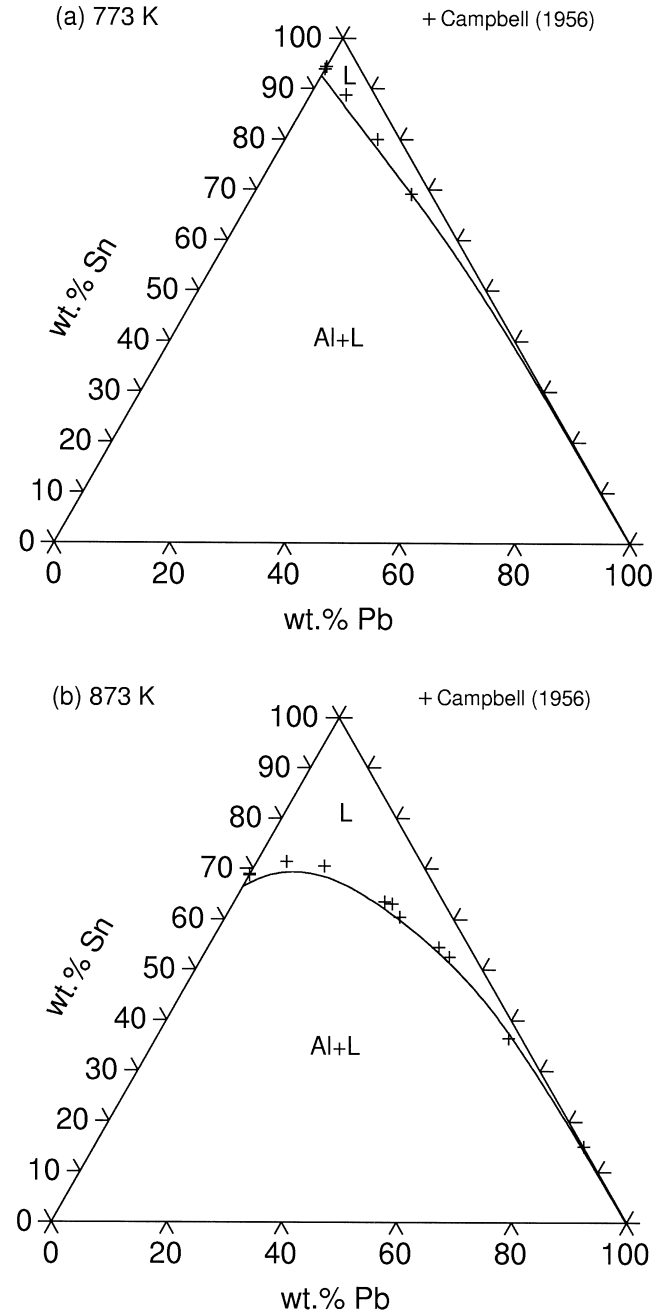


Fig. 3. Calculated isothermal sections of the Al–Pb–Sn phase diagram at (a) 773 and (b) 873 K together with experimental data.

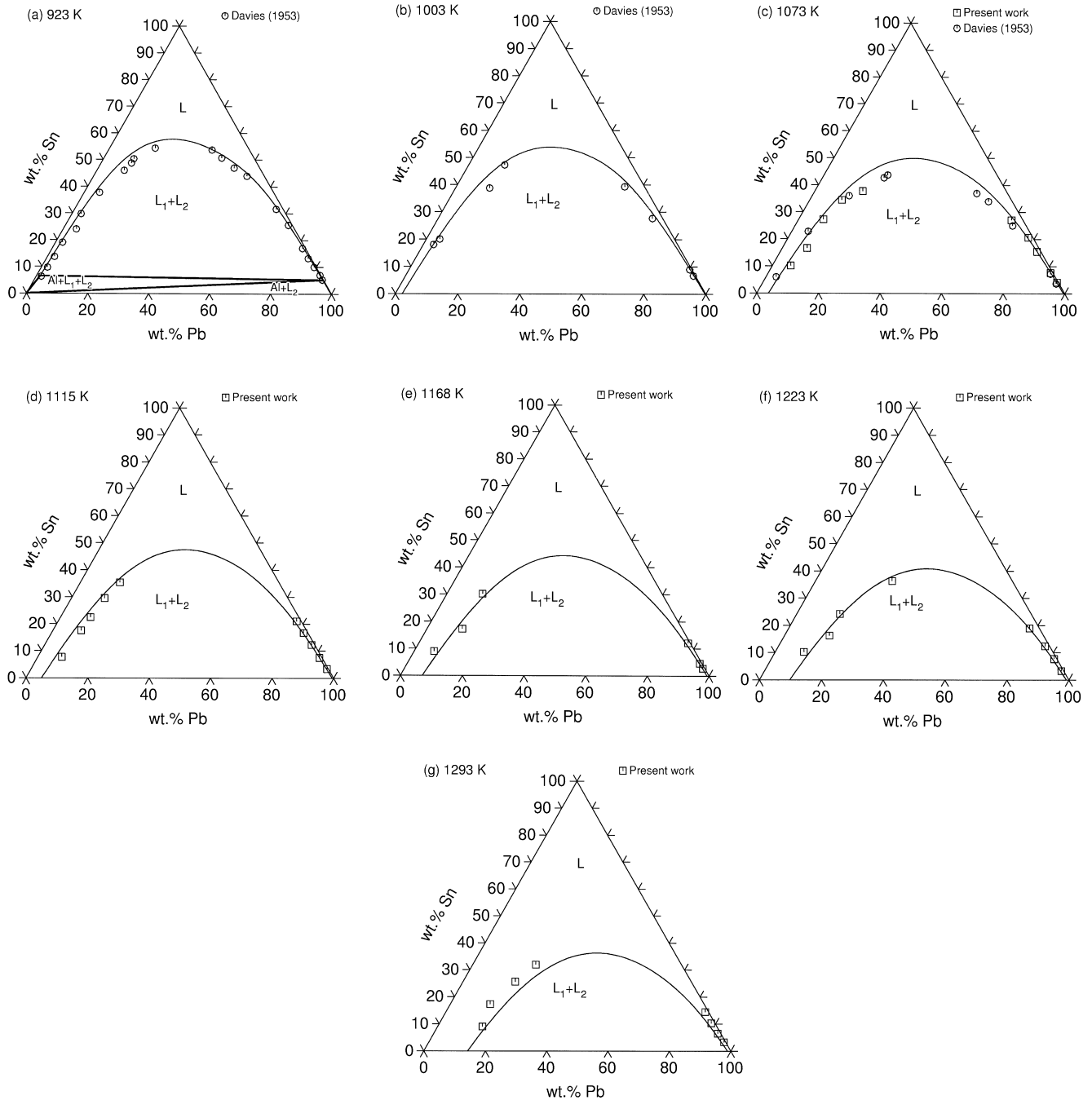


Fig. 4. Calculated isothermal sections of the Al–Pb–Sn phase diagram at (a) 923, (b) 1003, (c) 1073, (d) 1115, (e) 1168, (f) 1223 and (g) 1293 K together with experimental data.

decreases significantly as temperature decreases from 873 to 773 K. The calculated liquid solubility at both temperatures is in good agreement with the experimental data reported by Campbell and Kartzmark [8].

Fig. 4a–g show the calculated isothermal sections of the Al–Pb–Sn phase diagram at 923, 1003, 1073, 1115, 1168, 1223 and 1293 K, respectively, in comparison with the experimental data reported in the present work and by

Davies [6]. The comparison is generally satisfactory, though the calculated liquid miscibility gap at 1293 K shows a small discrepancy from the experimental data. The liquid miscibility gap boundary data at 1073 K independently measured in the present work and by Davies [6] show good agreement (Fig. 4c). It is found that the liquid miscibility gap is reduced significantly, particularly in the Al-rich region with increasing temperature.

References

- [1] S. Mohan, V. Agarwala, S. Ray, *Z. Metallkd.* 80 (1989) 439.
- [2] S. Mohan, V. Agarwala, S. Ray, *Wear* 140 (1990) 83.
- [3] V.O. Abramov, O.V. Abramov, F. Sommer, D. Orlov, *Mater. Lett.* 23 (1995) 17.
- [4] D.P. Howe, M. Mee, A.A. Torrance, J.D. Williams, *Mater. Sci. Technol.* 7 (1991) 330.
- [5] S.-K. Yu, F. Sommer, B. Predel, *Z. Metallkd.* 87 (1996) 574.
- [6] M.H. Davies, *J. Inst. Metals* 81 (1953) 415.
- [7] L. Kaufman, H. Bernstein, *Computer Calculation of Phase Diagrams*, Academic Press, New York, 1970.
- [8] A.N. Campbell, R. Katzmark, *Can. J. Chem.* 34 (1956) 1428.
- [9] O. Redlich, A.T. Kister, *Ind. Eng. Chem.* 40 (1948) 345.
- [10] A.T. Dinsdale, *Calphad* 15 (1991) 317.
- [11] H. Ohtani, K. Okuda, K. Ishida, *J. Phase Equilibria* 16 (1995) 416.
- [12] I. Ansara, J.P. Bros, M. Gambino, *Calphad* 3 (1979) 225.
- [13] B. Sundman, B. Jansson, J.-O. Andersson, *Calphad* 9 (1985) 153.