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Structure and Stability of Pb–Sb Liquid Alloys

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This investigation reports the structure and stability of liquid lead-antimony alloys determined with the help of the Kumar-Samarin technique of centrifuging liquid metals. It shows that liquid lead-antimony alloys in the composition ranges 0 to 35 and 65 to 100 at. % antimony are stable and can be regarded as a colloidal dispersion of lead- and antimony-rich clusters in monatomic matrices; the cluster size is minimum at the eutectic composition. The paper suggests that solutions in the intermediate composition range corresponding to the inflection in the liquidus curve are incipiently immiscible and shows that they can be separated into conjugate phases.

1. Introduction

In the preceding paper [1], it was shown that in certain eutectic systems, typified by Pb–Cd, the essential immiscibility existing in the solid state is extended in very rudimentary form to the liquid state since the atoms of the solvent (A) and solute (B), instead of randomly dispersing in solution, show a preference for spatial aggregation of their own kind. The existence of stronger bonds between similar (A–A or B–B) atoms than between dissimilar (A–B) atoms is reflected in the enthalpy of mixing acquiring a positive value. In extreme cases of marked preferential interaction, macroscopic immiscibility results in the liquid state, as in the Pb–Zn system. In terms of the same logic, a random distribution of atoms in the melt occurs when there is no interaction between the solute and solvent atoms, the enthalpy of mixing then being practically zero, a negative value of the enthalpy of mixing arises when there is a preponderance of unlike atom bonds and is indicative of the formation of intermediate phases, intermetallic compounds or superlattice structures in solid state as the solute-solvent interaction becomes more profound with drop in temperature. Certain simple eutectic systems, Pb–Sb for example, also show negative enthalpy of mixing with no known electron or intermetallic compounds or order/disorder change. However, if the negative enthalpy of mixing is regarded as a reflection of the increase in the co-ordination number and volume contraction of one of the constituent metals on melting (antimony), their liquid state can also be regarded as one exhibiting clustering of like atoms. It is significant that, despite the negative enthalpy of mixing in the liquid state and formation of stable beta-intermediate-phase through a peritectic reaction, the X-ray diffraction pattern of liquid Pb–Bi of eutectic composition shows [2, 3] the presence of two distinguishable peaks corresponding to the $\sin\theta/\lambda$ values of the main peaks of the pure solid components. This has been generally regarded as good evidence for the existence of lead- and bismuth-rich clusters in the liquid. Randomisation of atoms in the clusters of liquids of both types of eutectic systems occurs at higher temperatures and is marked by the appearance of a single peak in the X-ray diffraction pattern. But the interaction between lead and antimony atoms is not simple because the volume change on mixing is strongly dependent on temperature and composition [4]. It is noteworthy that in some alloys the volume change may vary from a decrease to an increase as the temperature of mixing is raised. The corresponding effect on the enthalpy of mixing is not yet known experimentally.

Against this background, it was decided to investigate the structure and stability of liquid lead-antimony alloys by the Kumar-Samarin [5, 6] technique of centrifuging liquid metals.

TABLE I Statistics of experimental data of Pb–Sb system

Composition at. % Sb	Centrifugal force ×g	Temp. ° C	Concentration gradient	Correlation coefficient	No. of observation	Probability level	Confidence range (±) on concentration gradient at 80%	90%
10	32	300	0.0380	1.0000	12	100	—	†
		400	0.0190	0.2197	12	< 90	—	0.0070
		500	0.0022	0.9776	12	99-100	—	†
		600	0.0031	0.2756	12	< 90	0.002	—
	63.5	300	0.0559	0.5483	7	90	—	0.0500
		400	0.0288	0.7779	10	88-100	—	0.0011
		500	0.0035	0.3324	11	< 90	—	0.0025
17	32	300	0.0063	0.7019	9	95-98	—	0.0036
		400	0.0035	0.2278	8	< 90	—	†
		500	0.0030	0.5968	10	90-95	—	†
		600	0.0023	0.3335	11	< 90	—	*0.0020
	63.5	300	0.0057	0.4200	11	< 90	—	*0.0056
		400	0.0090	0.1849	10	< 90	—	0.0014
		500	0.0040	0.7910	12	99-100	—	†
	94	400	0.0178	0.3116	6	< 90	0.0170	—
		500	0.0525	0.3572	8	< 90	—	0.0360
		600	0.0172	0.7570	6	90-95	—	0.0130
77	63.5	570	0.0430	0.7236	6	90	—	0.0340
		700	0.0115	0.7624	9	99-100	0.0099	—
87	63.5	650	0.0265	0.6019	6	< 90	0.0230	—

*50% confidence.
†100% confidence.

Details of the experimental technique and of statistical analysis of the result have been described in the preceding paper [1].

2. Experimental

Alloys containing 10, 17, 45, 77 and 87 at. % antimony were investigated in the temperature range 300 to 700° C, always above the liquidus. Samples of about 120 g of each alloy were individually made and centrifuged in stainless steel crucibles at various speeds of rotation at different temperatures for various times as summarised in tables I and II.

During centrifuging, the heavier lead-rich clusters migrated to the outer end of the crucible. Concentration gradients were set up in each of the alloys except in the one containing 45 at. % antimony. In all cases, the results of the chemical analysis were plotted on a logarithmic scale against the distance from the farther end of the crucible, as shown in figs. 1 to 3 in which the best fitting lines are also drawn on the basis of least squares analyses. The statistical correlation coefficients and the probability levels were calculated in each case and are recorded in table I. These calculations show that, in general, a finite concentration gradient is set up during centrifuging but the correlation between the logarithm of concentration (y) and distance (x) is not very reliable when centrifuging is done at high superheat, e.g. at 600° C in the Pb–10 at. % and Pb–17 at. % Sb alloys.

TABLE II Experimental conditions of centrifuging Pb–45 at.% Sb alloy

Time h	400° C			500° C			600° C			700° C		
	32 g	63.5 g	94 g	32 g	63.5 g	94 g	32 g	63.5 g	94 g	32 g	63.5 g	94 g
1	*	*	*	*	*	*	*	*	*	*	*	*
3	*	*	*	*	*	*	*	*	*	—	*	*
5	*	*	*	*	*	*	*	*	*	—	*	*
7	*	—	—	*	—	—	*	—	—	—	—	—
25	—	—	—	—	*	—	—	—	—	—	—	—

*Indicates that the experiment was performed.

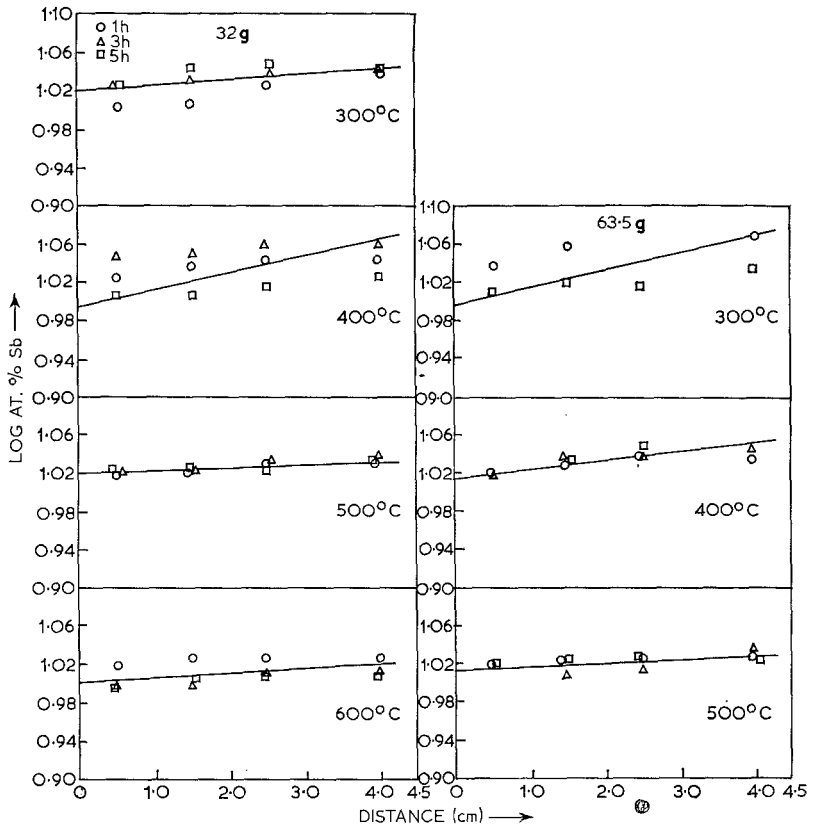

Figure 1 Logarithm of atomic concentration in Pb–10 at. % Sb alloys vs. distance from the farther end of the crucible.

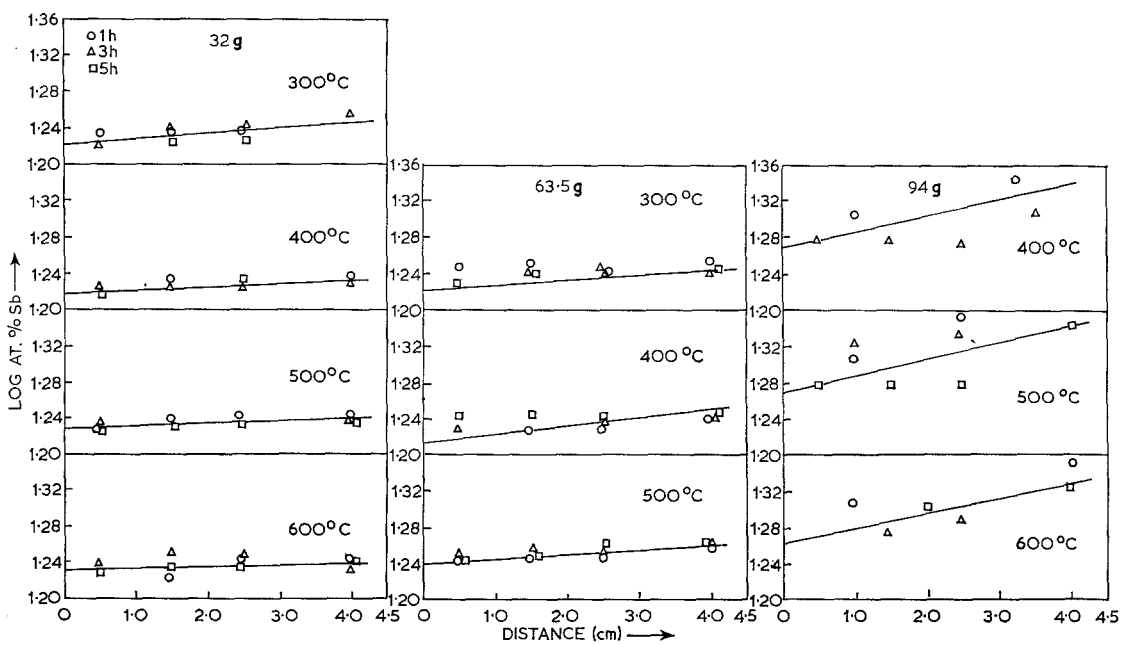

Figure 2 Logarithm of atomic concentration of Sb in Pb–17 at. % Sb alloys vs. distance from the farther end of the crucible.

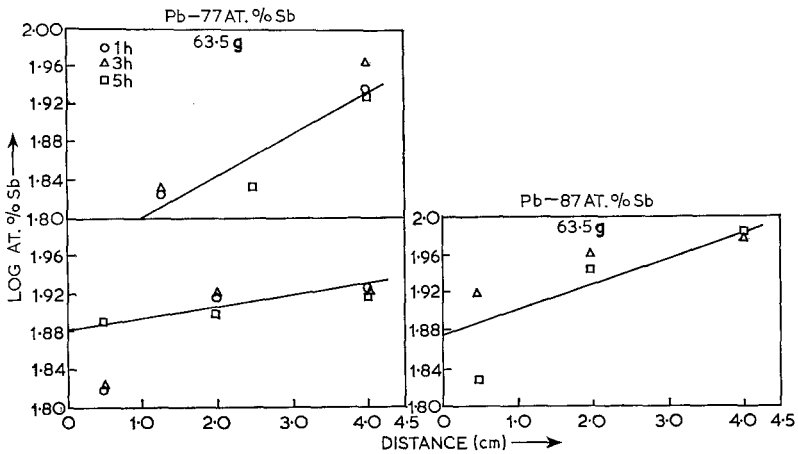

Figure 3 Logarithm of atomic concentration of Sb in Pb–Sb alloys vs. distance from the farther end of the crucible.

The cluster radii were calculated as earlier [1], by the sedimentation equilibrium equation, using published values of the densities of lead and antimony, as summarised in table III; the densities of the alloys were calculated on the assumption of ideal mixing, table IV.

A perusal of table I shows that the cluster size (a) depends upon composition but (b) neither changes with temperature up to 600° C nor with increasing centrifugal force. The temperature-dependence of the cluster size in Pb–87 at. % Sb alloy was not investigated.

When the computed cluster sizes are plotted along with their error band in fig. 4, the following conclusions can be drawn: (a) the size of *either* lead *or* antimony clusters decreases as the eutectic composition is approached in the hypo- and hyper-eutectic alloys respectively; (b) once the minimum size is reached at the eutectic composition there is no appreciable change thereafter.

TABLE III Cluster sizes in Pb–Sb system

Composition at. % Sb	Centrifugal force ×g	Temperature ° C	Cluster radius Å Calculated		Mean	
			Pb	Sb	Pb	Sb
10	32	300	58	23		
		400	47	20	40 ± 13	17 ± 5
		500	28	11		
		600	28	12		
	63.5	300	47	21		
		400	43	19	39 ± 9	17 ± 5
		500	26	10		
	32	300	18	10		
		400	21	12		
		500	23	12	21 ± 2	12 ± 1
		600	20	12		
17	63.5	300	17	10		
		400	23	13	20 ± 3	11 ± 1
		500	20	11		
	94	400	25	15		
		500	41	22	31 ± 7	18 ± 3
		600	28	16		
77	63.5	570	22	32		
		700	15	21	19 ± 4	26 ± 8
87	63.5	650	19	43	19	43

TABLE IV Densities of liquid Pb–Sb and alloys

Temp. °C	Density g/ml Pb	Sb	Pb–10 at. % Sb	Pb–17 at. % Sb	Pb–45 at. % Sb	Pb–77 at. % Sb	Pb–87 at. % Sb
300	11.34	6.68	10.96	10.52	—	—	—
400	10.51	6.68	10.22	9.87	9.189	—	—
500	10.30	6.68	10.11	9.81	9.109	—	—
570	10.30	6.50	—	—	—	7.459	—
600	10.27	6.50	9.94	9.69	8.869	—	—
650	10.20	6.47	—	—	—	—	7.008
700	10.15	6.45	—	—	—	7.393	—

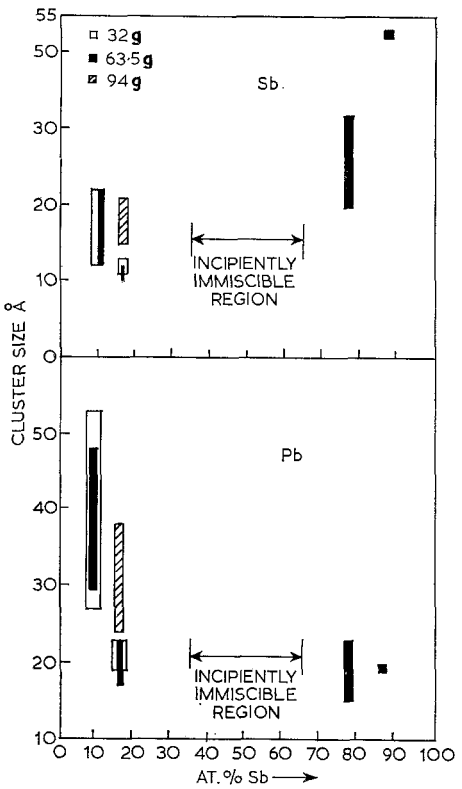

Figure 4 Composition dependence of cluster size in a Pb–Sb system.

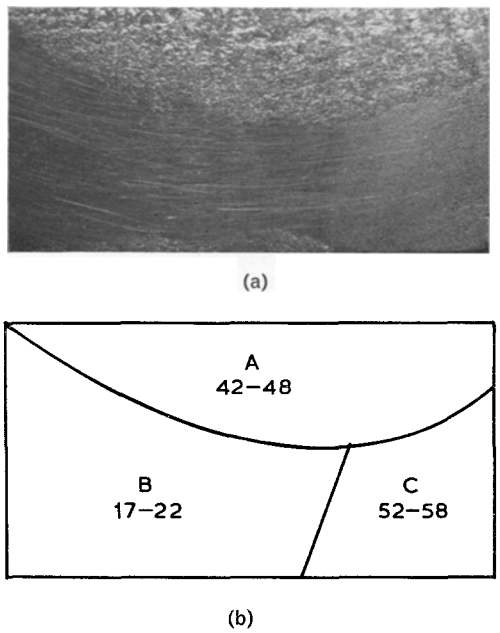

Figure 5(a) Macrophotograph of Pb–45 at. % Sb alloys. (b) Profile of the three regions with the range of Sb contents.

2.1. Stability of the Pb–45 at. % Sb Alloy

The behaviour of the lead-45 at. % antimony alloy, was consistently, uniquely different from the other four alloys on centrifuging between 400 and 700° C under the conditions listed in table II. Instead of a smooth concentration gradient being obtained in the solidified ingots, the liquid divided itself into three regions as shown in fig. 5a. The nature of separation was similar in all the specimens and fig. 5b sketches the profile of the three regions which have been marked as A, B and C. Samples were analysed chemically from each of the regions and the range of antimony contents is also indicated in the figure.

It has been suggested that an inflexion in the liquidus curve foreshadows immiscibility, which arises from an inflexion in the free energy vs. composition curve [7] and is associated with a special facility of close packing of dissimilar atoms near certain compositions. These observations show that (a) the solutions in the terminal composition ranges 0 to 35 and 65 to 100 at. % antimony are stable and (b) in the composition range 35 to 65 at. % antimony, corresponding to the inflection in the liquidus curve, the solutions are unstable or only incipiently immiscible. They break into conjugate liquid phases under suitable conditions. The decomposition of the

alloy into conjugate phases was not complete under the experimental conditions as the composition in region A corresponded to the original composition. Thus the liquid lead-antimony system does not enjoy undisputed solubility over the entire range of composition as hitherto believed. Similar results have been obtained in the Pb–Cd system [1].

3. Conclusion

This investigation shows that (a) liquid-antimony alloys in the composition ranges 0 to 35 and 65 to 100 at. % antimony are stable and can be regarded as colloidal dispersions, of lead- and antimony-rich clusters in monatomic matrices and (b) the cluster size is minimum at the eutectic composition. This paper suggests that solutions in the intermediate composition range, corresponding to the inflection, until now regarded as homogeneous, are in fact incipiently immiscible and can separate into the conjugate lead-rich and antimony-rich liquids on centrifuging.

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