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Structure of Liquid Cadmium-Antimony Alloys

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The structure of liquid Cd–Sb alloys was determined with the help of the Kumar-Samarin technique of centrifuging liquid metals. Alloys containing 7, 29, 50, 57 and 79 at. % Sb were examined in the range 350 to 650° C. It shows that (i) all alloys except in the vicinity of equi-atomic composition, consist of a colloidal dispersion of compound clusters in a random monatomic matrix, and (ii) the cluster size depends on composition with minima occurring at the two eutectic compositions. The volume fraction of clusters and their heat of formation were determined. The composition of the compound cluster was deduced as $Cd_{40}Sb_{30}$. Concentration gradient was not established in the equi-atomic alloy during centrifuging. The investigation shows that residual structure can exist far into the liquid state and is not confined to liquids of stoichiometric compound compositions.

1. Introduction

In a number of binary metallic liquid systems of the simple eutectic type, Kumar and Sivaramakrishnan [1–4] have demonstrated that a dispersion of clusters of like atoms (solute-solute or solvent-solvent) exists colloidally in random, monatomic environment of solute and solvent atoms. The formation of clusters in liquid alloys indicates that, despite the mutual solubility in the liquid state, the preferential interaction between like atoms in a solid solution is not entirely destroyed on melting. In binary alloy systems involving intermetallic compounds in the solid state, the strong interaction between unlike atoms, which results in compound formation in the solid state, is again not suddenly destroyed on melting, but clusters of short range order persist significantly in the liquid state. X-ray, electrical resistivity and thermodynamic observations relative to the liquid state indicate that the degree of short range order varies with composition, with a maximum usually occurring in the liquid alloy of intermetallic compound composition. As the temperature is raised in the liquid state in both types of systems, the extent of clusters of either like or unlike atoms decreases and randomisation of solute and solvent atoms is promoted.

The existence of clusters of short-range order in Al–Cu liquid alloys up to 25% Cu was demonstrated by Kumar and Singh [5], by the Kumar-Samarin technique which established concentration gradients on centrifuging liquid alloys due to the difference in the densities of clusters and monatomic liquid atoms. They deduced the composition of the clusters from thermodynamic arguments involving their size and volume fraction and the viscosity of the liquid and found them to be copper rich [6]. In their centrifuge, Kumar and Singh could not study the behaviour of the copper-rich Al–Cu alloys because of the corrosive action of the liquids on the stainless steel crucibles at temperatures above the liquidus line. If the concept of short range order is valid, centrifuging the alloys corresponding to the composition of the cluster in liquid state would not establish any concentration gradient.

The Cd-Sb system was chosen because it has strong interaction between Cd and Sb atoms and has been extensively investigated in the liquid state by conventional techniques. It forms both stable and metastable compounds [7] when liquid alloys are cooled at normal rates. In addition to the stable CdSb compound melting at 456 to 459° C, the formation of another compound Cd_4Sb_3 melting at about the same temperature is also reported, but CdSb is only ordinarily shown in their binary equilibrium diagram. The metastable Cd–Sb system, however, shows the formation of an additional intermetallic compound Cd_3Sb_2 melting at 420°C.

Geffken *et al* [8] concluded that the inflections in the plots of partial molar entropy versus composition in the temperature range 420 to 500° C at about 57 at. % Cd (Cd_4Sb_3) are due to the existence of strong short-range order in the liquid state, which decreases as the temperature is raised and the solution simultaneously tends towards randomisation. The resistivity composition curves of liquid alloys also show two maxima at compositions corresponding to the formation of CdSb and Cd_3Sb_2 in the solid state. Since the electrical resistivity of liquid metals provides information regarding interatomic interactions and their effects upon structures these results were interpreted in terms of complex short range ordering behaviour which changes rapidly with increasing temperature [9]. Similarly, the alloy CdSb has maximum viscosity in liquid state [10]. It, therefore, appears that strong interaction between Cd and Sb atoms persists in the liquid state in the composition range 40 to 50 at. % Sb.

2. Experimental

Details of the experimental techniques and methods of statistical analysis of the results have been described earlier [1, 2]. Alloys containing 7, 29, 50, 57 and 79 at. % Sb were investigated in the temperature range 350 to 650° C at two centrifugal speeds which developed forces 40 and 70 times gravitational acceleration. Samples of about 60 g each of the alloys were centrifuged in graphite crucibles for various times and at different temperatures. The experimental conditions are summarised in table I. If the preferential solid state interaction between Cd and Sb atoms persists in the liquid state as well, Cd–Sb compound clusters will migrate to the inner end of the crucible and this will result in the setting up of concentration gradients.

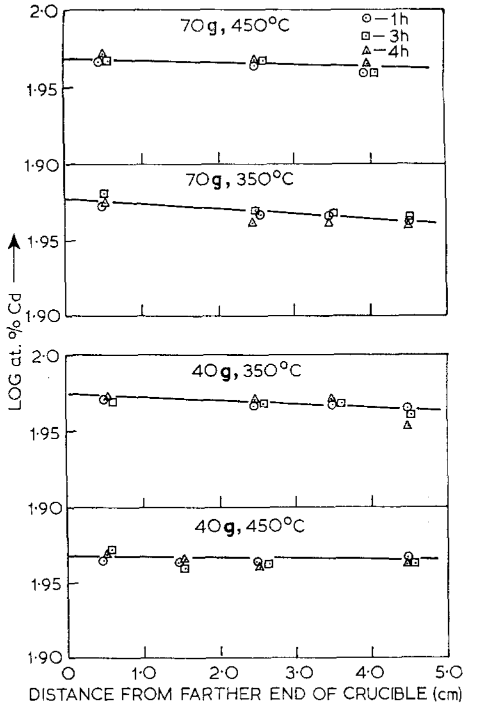

Figure 1 Chemical analysis data of Cd–7 at. % Sb alloys.

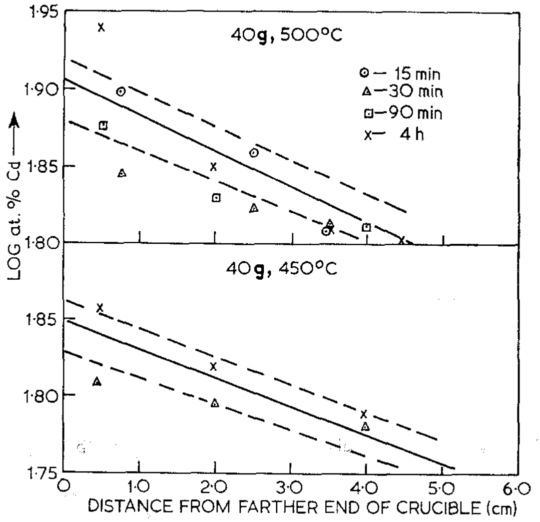

Figure 2 Chemical analysis of Cd–29 at. % Sb alloys.

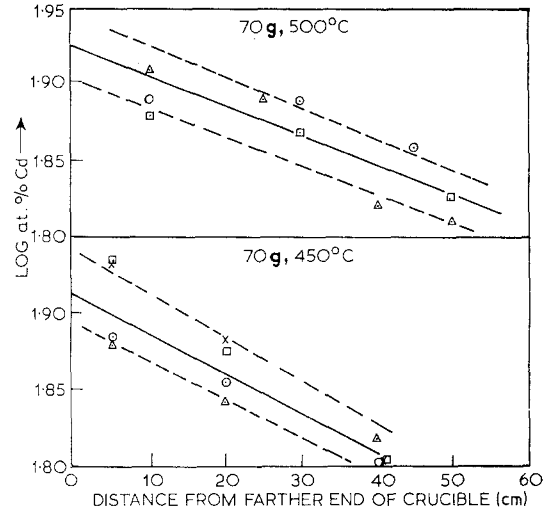

Figure 3 Chemical analysis of Cd–29 at. % Sb alloys.

2.1. Cluster Size

In figs. 1–5 best fitting lines are drawn on the basis of a least square analysis in each case. The

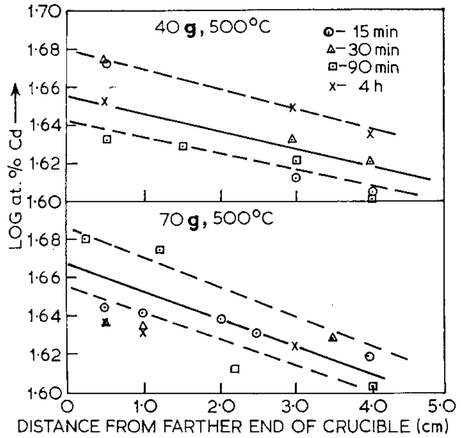

Figure 4 Chemical analysis data of Cd–57 at. % Sb alloys.

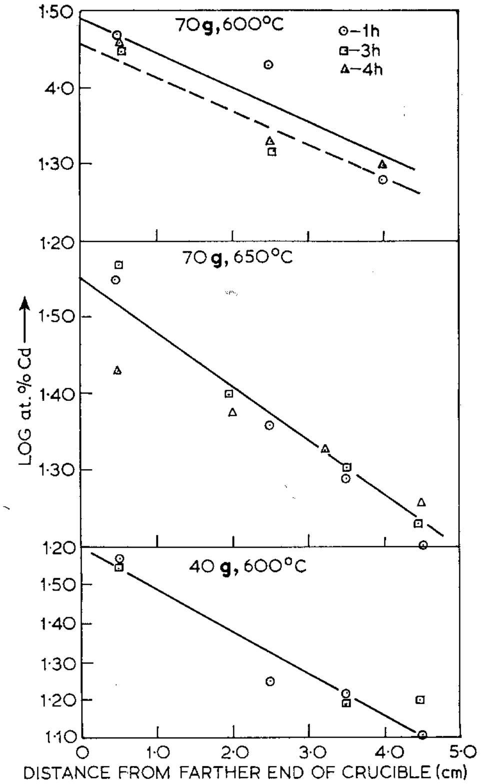

Figure 5 Chemical analysis data of Cd–79 at. % Sb alloys.

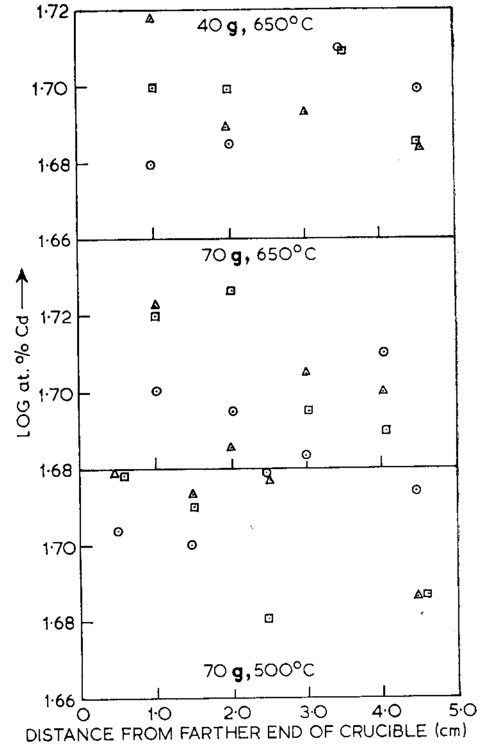

Figure 6 Chemical analysis of Cd–50 at. % Sb alloy showing no correlation.

statistical parameters are also recorded in table I along with their confidence ranges on the concentration gradients for 80 to 95% probability. These calculations show that, in general, the correlation between the logarithm of concentration and the distance is justified by rigorous statistical analysis. Table I also shows that correlation could not be established in the 50 at. % Sb alloy; the data are plotted in fig. 6. It can, therefore, be concluded that the liquid alloy of equi-atomic composition consists essentially of Cd_xSb_y molecules.

The cluster radii recorded in table II were calculated as was done earlier by the sedimentation equilibrium equation, using published values [10] of densities of Cd–Sb alloys. Values of the cluster radii are reproduced in table III.

These results show that the liquids corresponding to the two eutectic compositions have clusters of smaller sizes. The cluster size increases on the antimony-rich sides of both the eutectics. When the composition dependences of viscosity and cluster size are relatively evaluated, see fig. 7, it is noted that the viscosity plateau is in the region where short range order predominates in the liquid state and is not confined to the stoichiometric (equiatomic) compound composition. Increasing centrifugal force has practically no effect on the cluster size.

3. Volume Fraction of Clusters

If the deviation of the plot of viscosity against temperature from the usual Arrhenius type of expression,

TABLE I Statistics of the experimental data of Cadmium-Antimony system

Composition at. % Sb	Centrifugal force × g	Temperature °C	Concentration gradient	Correlation coefficient	No. of observations	Probability level %	% Confidence range on concentration gradient (±)		
							80	90	95
7	40	350	0.00241	1.0000	12	100	—	—	*
		450	0.00021	1.0000	12	100	—	—	*
	70	350	0.00317	1.0000	12	100	—	—	*
		450	0.00055	1.0000	9	100	—	—	*
29	40	450	0.01651	0.8170	6	95	—	0.006	—
		500	0.08037	1.0000	13	100	—	—	*
	70	450	0.02987	0.8900	12	99	—	—	0.005
		500	0.01740	0.7620	10	98	—	—	0.004
50	40	650	0.00023	0.0129	12	90	Correlation is very poor indicating that no Cd–Cd, Sb–Sb clusters are possible.		
		500	0.00002	0.0022	12	90			
	70	650	0.00096	0.2500	12	90			
57	40	500	0.00887	1.0000	13	100	—	—	*
	70	500	0.00741	0.1095	16	90	0.004	—	—
79	40	650	0.06398	0.3129	7	90	—	—	0.054
	70	600	0.06136	0.9070	9	99	—	—	0.011
		650	0.06065	0.9101	16	99	—	—	0.306

*100% confidence.

TABLE II Cluster size in Cadmium-Antimony alloys

Composition at. % Sb	Centrifugal force × g	Temperature °C	Statistical slope	Calculated values of cluster size Å, at mean minimum and maximum slopes					
				Cd		Sb		CdSb	
7	40	350	0.00241	20		—		18	
		450	0.00021	10		—		8	
	70	350	0.00317	18		—		16	
		450	0.00051	12		—		9	
29	40	450	0.01651	35	48 9	—		45	44 10
		500	0.08037	58		—		65	
	70	450	0.02897	35	42 30	—		54	58 41
		500	0.01740	29	31 27	—		39	36 32
50	40	500	0.00002	—		—		—	
		650	0.00023	—		—		—	
	70	650	0.00096	—		—		—	
57	40	500	0.00887	—		50	60 32	60	56 32
	70	500	0.00741	—		35		48	
79	40	650	0.06398	—		98	118 61	156	167 102
	70	600	0.06136	—		74	88 58	144	172 80
		650	0.06065	—		76	82 71	130	160 110

TABLE III Densities of Liquid Cadmium-Antimony and their Binary Alloys

Temperature °C	Density g/cc						
	Cd	Sb	7% Sb	29% Sb	50% Sb	57% Sb	79% Sb
350	8.22	6.68	7.80	—	7.25	—	—
450	7.85	6.68	7.62	7.30	6.95	—	—
500	7.82	6.68	—	7.18	6.88	6.80	—
600	7.72	6.50	—	—	6.64	—	6.62
650	7.67	6.41	—	—	6.52	—	6.55

TABLE IV Heat of formation of cluster in Cd–80 at.% Sb alloy

Temperature °K	Viscosity (millipoise)		% volume fraction of clusters	$ln Kx$	Heat of formation cal/g mole	Heat of formation Kcal/g atom $Cd_{40}Sb_{30}$
	η_i	η_{si}				
873	19.23	18.03	2.0	4.7053		
923	15.28	14.93	0.9	3.6848	33	4.708

$$\eta = \eta_0 \exp(E/RT),$$

is attributed to the existence of clusters in liquid metals, their volume fraction can be calculated [11] from the Einstein equation relating the viscosity of a colloidal solution to the volume fraction of the clusters:

$$\eta_i/\eta_{si} = 1 + \alpha\phi_i + \beta\phi_i^2$$

where η_i = actual value of viscosity in millipoise, η_{si} = value the viscosity would have if the Arrhenius expression is extrapolated to temperature T_i, ϕ_i = volume fraction of suspended particle per millilitre at temperature T_i, and α, β = constants equal to 2.5 and 7 respectively. Values of actual and extrapolated viscosity of Cd–80 at. % Sb alloy from the experimental observations of Fisher and Phillips [10], recorded in table IV, were used to calculate the volume fraction of the clusters at 873 and 923° K.

Following Ubbelohde [11] and assuming that associations or dissociation of clusters obeys mass-action equations and involves no volume change, the equilibrium constant (K_X) between monomeric and clustered atoms may be calculated if the number of atoms, g, in the cluster is known from the following relationship:

$$K_X = \frac{[g(1-\phi_i)]^g}{\phi_i[\phi_i + g(1-\phi_i)]^{g-1}}$$

for the reaction

$$(Cd_4Sb_3)g \rightleftharpoons g[4Cd + 3Sb]\,.$$

Values of K_X are also recorded in table IV. The heat of cluster formation was calculated with the help of Van't Hoff's equation:

$$ln\frac{K_{X2}}{K_{X1}} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

where ΔH is the heat of dissociation or aggregation of the cluster per g mol; the data yield a value of 33 Kcal/g mol, or 4.86 Kcal/g atom of the alloy for ΔH. But the thermodynamically determined value of the heat of formation [12] of 1 g atom of the alloy having a composition near Cd_4Sb_3, is 0.47 Kcal. The derived value can be reconciled with the thermodynamic value if it is assumed that the chemical composition of the cluster is around the pseudo-molecule $Cd_{40}Sb_{30}$ (0.486 Kcal/g atom of the alloy). In view of the strong interaction between Cd and Sb atoms around Cd_4Sb_3 composition, a region of pronounced short range order is indicated in fig. 7.

4. Discussion

In order to appreciate the structure of liquid metallic solutions, Darken [13] introduced the concepts of *stability* and *excess stability* to define the properties of the system. *Stability* is defined as the second derivative of the molal free energy with mol fraction where the free energy change of any process by which the solution is broken down into two solutions is proportional to the stability function d^2F/dN_2^2 identical with d^2F/dN_1^2 where F represents the molal free energy of the system. The stability of an ideal solution is $RT/(N_1N_2)$ and the quantity

$$\frac{d^2F}{dN_2^2} - \frac{RT}{(N_1N_2)}$$

is designated as the *excess stability*. These

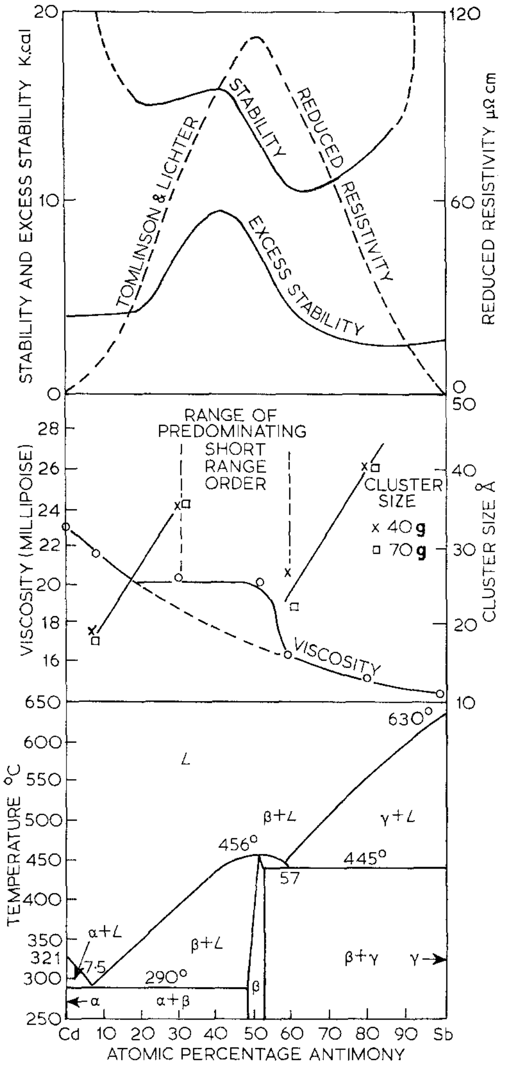

Figure 7 Viscosity, cluster size, reducing electrical resistivity and stabilities versus composition of Cd Sb liquid alloys.

functions are plotted in fig. 7 for the Cd–Sb system. The excess stability approaches a constant value in each terminal region, but exhibits a marked positive peak in the central region. Darken observed that such peaks usually occur at or near the composition(s) anticipated from a consideration of classical valencies of components, or at the composition of intermediate solid-state phases. Excess stability can be thought of as an indication of the extent to which the electrons are tied up in bonding. Tomlinson and Lichter [14] observed that the maximum in the reduced resistivity versus composition curve for the Cd–Sb system corresponds to the maximum in the excess stability. Reduced resistivity was defined as equal to ($\rho_{\text{exp}} - \rho_1 N_1 - \rho_2 N_2$) where ρ_{exp}, ρ_1 and ρ_2 are the resistivities of the alloy and of the pure components respectively. They attributed this correspondence between resistivity and excess stability to the lack of availability of electrons caused by the stabilisation of that particular composition by electron bonds.

5. Conclusion

The investigation has shown that the strong Cd–Sb interaction of solid state is retained in the liquid state and that liquid alloys of compositions other than around the equi-atomic, consist of a colloidal dispersion of pseudo-compound clusters amongst monatomic atoms. The size of the clusters is a function of composition and temperature.

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