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# Stability of Liquid Pb–Cd Systems

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Alloys containing 17, 30, 38 and 60 at. % cadmium were examined in the range 300 to 600° C by the Kumar-Samarin technique of centrifuging liquid metals. Whereas smooth concentration gradients were set up in the first three alloys, thus indicating stability, the 60 at. % cadmium alloy decomposed into two liquids. Regarding the solution as colloidal, the sizes of predominantly lead- and cadmium-rich clusters were determined in the first three alloys and found not to change appreciably with temperature.

## 1. Introduction

In many eutectic systems, the tendency to immiscibility existing in the solid state is extended to the liquid state and is reflected in the existence of an almost flat portion in the liquidus curve which is suggestive of imminent immiscibility in the liquid. In such cases, the atoms of the solvent (A) and solute (B) instead of atomistically dispersing in solution, show a preference for spatial aggregations of their own kind. Kumar [1] and Samarin *et al* [2] with the help of a technique of centrifuging liquid metals, independently developed by them, showed that liquid solutions of the Pb–Sn system in fact consist of colloidal dispersion of solute- and solvent-rich clusters in monatomic matrices [3] which behave like true liquids*, though it is conventional to regard the system as homogeneous liquid above the liquidus temperature. The concept of the existence of clusters in liquid metals [4] has found wide acceptance. Kumar *et al* [5] also showed that although there are clusters in the melt, most of it is made up of unclustered atoms. A similar conclusion [6, 7] about the structure in the liquid state is also drawn from X-ray diffraction patterns of liquid eutectics which show the existence of two peaks in the intensity versus ($\sin\theta/\lambda$) curves.

## 2. Experimental Procedure

In order to study the structure of a liquid Pb–Cd system in terms of the cluster size, and its variation with temperature and composition, it was decided to use the Kumar-Samarin [1, 2] technique which exploits the minute differences in the densities of clusters and those of randomised atoms to obtain a sedimentation equilibrium on the application of centrifugal force. Details of the experimental technique have been previously described; it consists essentially of (a) centrifuging about 120 g of liquid alloy at constant temperature in a stainless steel crucible which is swung horizontally at rotational speeds which develop centrifugal forces of 40 **g** or 141 **g** where **g** denotes acceleration due to gravity; (b) quenching the liquid alloy during centrifuging, by running cold water in the outer annular jacket of the stainless steel crucible, after centrifuging for predetermined times and (c) chemically analysing a longitudinal half of the ingot at several positions and metallographically examining the other. Four alloys containing respectively 17, 30, 38 and 60 nominal at. % of cadmium were prepared. Alloys for each experiment were prepared individually. Experimental conditions of centrifuging are recorded in table I. The liquid metals did not apppreciably corrode the stainless steel crucible in the temperature range of the investigation. The water quenching was sufficiently fast to prevent any mass transport during the solidification.

## 3. Results and Discussion

Results of chemical analysis indicated that the behaviour of the alloys fell in one of the following two categories: either a concentration

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*True liquids are monatomic assemblies in which the internal degrees of freedom are the same as in a gas and the viscosity is related to temperature through an Arrhenius relationship: $\eta = \eta_0 \exp(E_n/RT)$.

TABLE I Statistics of the experimental data of Pb–Cd systems

| Composition at. % Cd | Centrifugal force ×g | Temp. °C | Concentration gradient | Correlation coefficient | No. of observations | Probability level % | Confidence range (±) on concentration gradient at 70% | 80% | 90% |
|---|---|---|---|---|---|---|---|---|---|
| 17 | 40 | 300 | 0.0270 | 0.5757 | 9 | < 90 | — | 0.0220 | — |
| | | 400 | 0.0240 | 0.6299 | 10 | 95-98 | — | — | 0.0186 |
| | | 500 | 0.0056 | 0.1653 | 10 | — | * | — | — |
| | 141 | 300 | 0.0140 | 0.3618 | 8 | < 90 | — | — | 0.0120 |
| | | 400 | 0.0062 | 0.5388 | 7 | < 90 | * | — | — |
| | | 500 | 0.0096 | 0.5348 | 9 | < 90 | — | — | 0.0019 |
| 30 | 40 | 400 | 0.0060 | 0.4099 | 12 | < 90 | 0.006 | — | — |
| | 141 | 400 | 0.0209 | 0.1174 | 11 | — | — | 0.018 | — |
| | | 500 | 0.0024 | 1.000 | 10 | 100 | — | — | ‡ |
| | | 600 | 0.0098 | 0.4760 | 10 | < 90 | 0.009† | — | — |
| 38 | 40 | 300 | 0.0210 | 0.5132 | 10 | < 90 | — | — | 0.0130 |
| | | 400 | 0.0096 | 0.8712 | 10 | 99 | — | 0.008 | — |
| | | 500 | 0.0454 | 0.7481 | 7 | 95 | — | — | 0.0400 |
| | 141 | 300 | 0.0051 | 0.5590 | 11 | 90-95 | 0.005† | — | — |
| | | 400 | 0.0041 | 0.3928 | 10 | < 90 | 0.004 (at. 50%) | — | — |
| | | 500 | 0.0053 | 0.2727 | 12 | < 90 | * | — | — |

*Less than 50% confidence. †60% confidence. ‡100% confidence.

gradient was set up on centrifuging the alloys in liquid state or the normally homogeneous melt underwent decomposition into two conjugate liquids. The behaviour of the alloys containing 17, 30 and 38 at. % Cd fell in the first category, but the significance of the concentration gradient in the Pb–30 at. % Cd alloy at 300° C was not statistically authenticated. Typical results for each of the alloys are shown in figs. 1 to 3 where logarithm of atomic concentration of cadmium is plotted against the distance from the farther end of the ingot towards the axis of rotation. Best fitting lines are drawn in the figures on the basis of least square analyses of the experimental

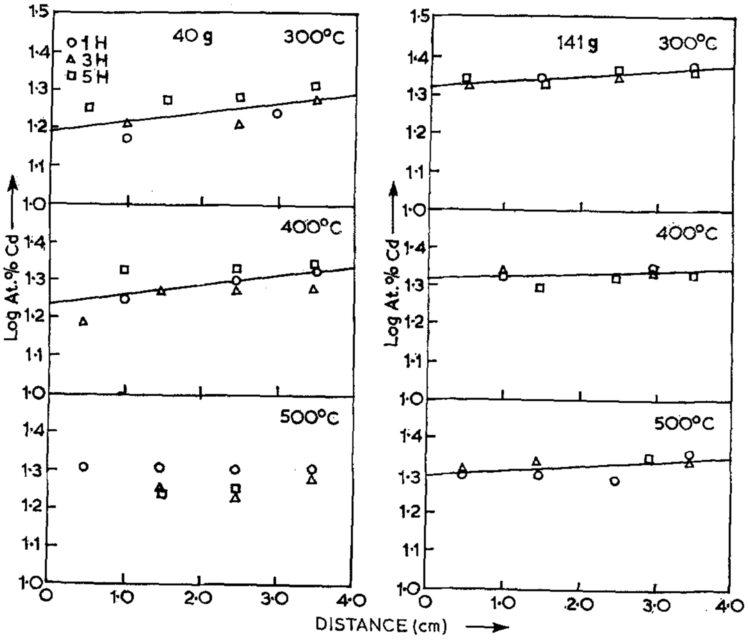

*Figure 1* Logarithm of at. % Cd vs. distance from farther end of crucible (cm) of Pb–17 Cd alloys.

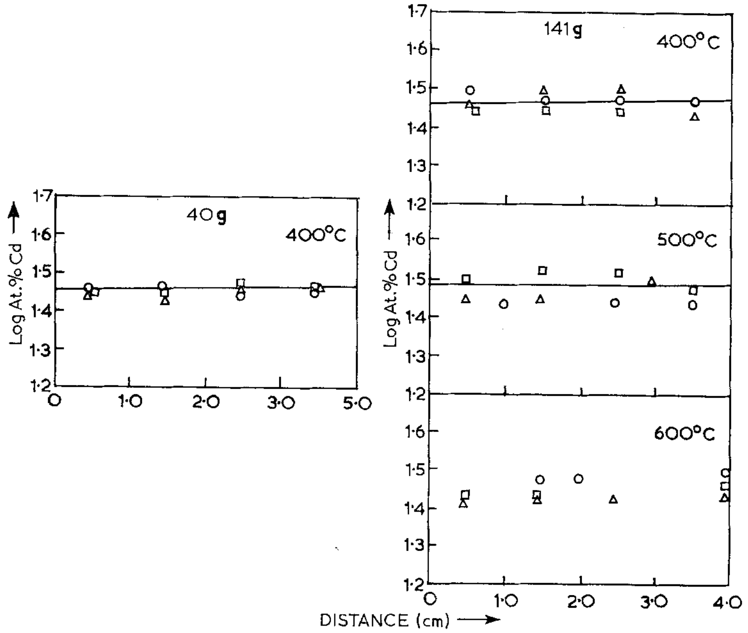

*Figure 2* Logarithm of at. % Cd vs. distance from farther end of crucible (cm) of Pb–30 Cd alloys.

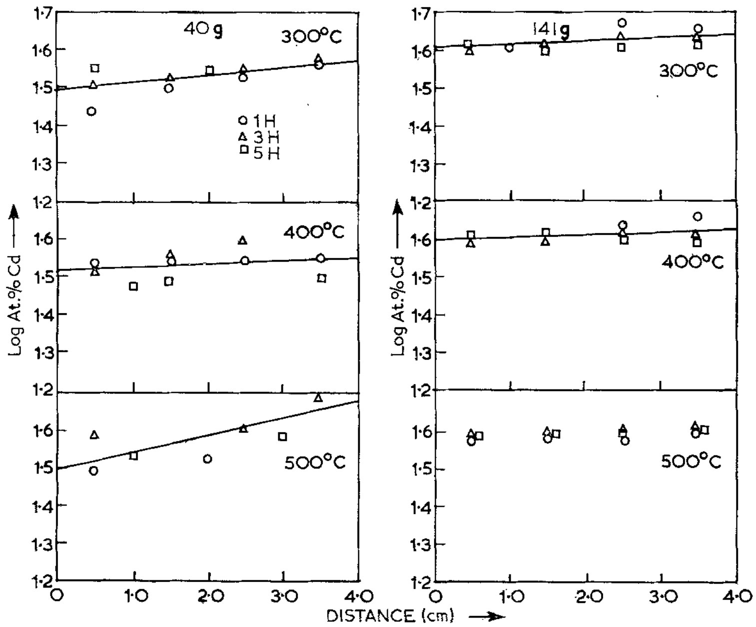

*Figure 3* Logarithm of at. % Cd vs. distance from farther end of crucible (cm) of Pb–38 Cd alloys.

data shown in table I. In order to establish whether the linear correlation between the logarithm of composition ($y$) and the distance along the crucible ($x$) is significant, or not, the criterion [8] of the statistician's correlation coefficient, $r$, was adopted:

$$r = \frac{\Sigma^1 xy}{[\Sigma^1 x^2 \, \Sigma^1 y^2]^{\frac{1}{2}}},$$

where $\Sigma^1 xy = \Sigma xy - \bar{x}\Sigma y$

$$\Sigma^1 x^2 = \Sigma x^2 - \frac{(\Sigma x)^2}{N}$$

$$\Sigma^1 y^2 = \Sigma y^2 - \frac{(\Sigma y)^2}{N},$$

where $\bar{x}$ is the arithmetic mean.

In general, correlation coefficients range between ± 1 and zero, depending on the goodness of the fit of the lines; in a perfect case the correlation coefficient equals ± 1. The calculated values of the correlation coefficient in each case are shown in table I and the probability levels of the correlation coefficient were determined with the help of standard tables at the proper degrees of freedom ($N - 2$), where $N$ is number of observations. Confidence limits on the slope of the least squares line, defined as $\pm\, t_s(b)$, were determined from the variance of the estimate, $S^2(\hat{y})$; $t$ was selected at the proper degrees of freedom ($N - 2$) and the desired probability level obtained from standard tables:

$$S^2(\hat{y}) = \frac{(1 - r^2)\, \Sigma^1 y^2}{N - 2}$$

$$t_s(b) = \left[\frac{S^2(\hat{y})}{\Sigma^1 x^2}\right]^{\frac{1}{2}}.$$

These statistical calculations show that good correlation exists in most cases, particularly at lower temperatures of centrifuging when confidence can be placed in calculations based on concentration gradient. Owing to randomisation of clusters at higher temperature ($\geqslant$ 500° C), no concentration gradient was established in the Pb–30 at. % Cd alloy at 600° C (40 g). For the same reason, no great confidence could be placed in the existence of concentration gradients in the following cases: Pb–17 at. % Cd at 500° C (40 g); Pb–30 at. % Cd at 600° C (141 g); Pb–38 at. % Cd at 500° C (141 g). In such cases of poor correlation the least square lines are not drawn in the figures but the concentration gradients and other statistical parameters are recorded in table I.

The cluster size was calculated in each case and is included in table II on the assumption of a distribution of uniform, spherical clusters with the help of the following sedimentation equilibrium expression [9] relating the cluster radius ($\theta$) to the logarithm of the concentration gradient ($K$).

$$K = \frac{4}{3}\pi \left[\frac{\mathrm{N}\,(D - \delta) f}{2.3\,\mathrm{R}T}\right]\theta^3$$

where $\delta$ = density of the liquid;
$D$ = density of the cluster;
R = 8.314 × $10^7$ ergs/° C g.mol;
$f$ = centrifugal force;
N = Avogadro's number.

The densities [10] of liquid lead, cadmium and their alloys are given in table III, those of the alloys were calculated on the assumption of ideality. A perusal of table II shows that: (a) the

TABLE II Cluster size in Pb–Cd systems

| Composition at. % Cd | Centrifugal force ×g | Temperature °C | Cluster radius Å Calculated Pb | Calculated Cd | Mean observed Pb | Mean observed Cd |
|---|---|---|---|---|---|---|
| 17 | 40 | 300 | 45 | 23 | | |
| | | 400 | 45 | 24 | 40 ± 7 | 21 ± 3 |
| | | 500 | 30 | 16 | | |
| | 141 | 300 | 24 | 12 | | |
| | | 400 | 19 | 10 | 22 ± 2 | 11 ± 1 |
| | | 500 | 23 | 12 | | |
| 30 | 40 | 400 | 24 | 16 | 24 | 16 |
| | 141 | 400 | 24 | 7 | | |
| | | 500 | 13 | 8 | 19 ± 4 | 9 ± 2 |
| | | 600 | 20 | 13 | | |
| 38 | 40 | 300 | 31 | 23 | | |
| | | 400 | 25 | 19 | 37 ± 9 | 25 ± 6 |
| | | 500 | 46 | 34 | | |
| | 141 | 300 | 27 | 10 | | |
| | | 400 | 9 | 9 | 19 ± 8 | 10 ± 1 |
| | | 500 | 22 | 11 | | |

TABLE III Densities of Pb, Cd and their alloys

| Temperature °C | Density g/ml Pb | Cd | Pb–17 at.% Cd | Pb–30 at.% Cd | Pb–38 at.% Cd |
|---|---|---|---|---|---|
| 300 | 11.34 | 8.64 | 11.00 | 10.04 | 10.52 |
| 400 | 10.51 | 7.93 | 10.16 | 9.94 | 9.72 |
| 500 | 10.31 | 7.82 | 9.99 | 9.83 | 9.60 |
| 600 | 10.27 | 7.72 | — | 9.71 | — |

cluster size is minimum at the eutectic composition; similar results were previously observed in Pb–Sn and Al–Cu systems [1, 11]; (b) generally the sizes of the lead or cadmium clusters do not change significantly with temperature at least up to 600° C. The cluster size appears to decrease as the centrifugal force is increased and this is suggestive of the presence of clusters of varying sizes. This may be due to the fact that smaller clusters require longer times at lower centrifugal forces or shorter times at higher centrifugal forces to attain sedimentation equilibrium. The computed cluster size at any centrifuging speed is thus a mean of the distribution of different sizes. The liquid state of these alloys can, therefore, be regarded as a stable colloidal dispersion of clusters in a monatomic (randomised) matrix. The existence of finite clusters in liquid Pb–Cd system explains the fact that the system does not belong to the class of regular solutions.

In sharp contrast to the behaviour of these alloys, the Pb–60 at. % Cd liquid melt decomposed into two conjugate liquids on centrifuging at 500°C (63.5g) for periods up to 16 h. Although the demarcation between the two liquids could be observed on visual examination of the ingot, the contrast could not be reproduced with clarity in photographs. However, it was also supported by chemical analyses and the two regions shared respectively approximately 50 and 65 at. % Cd. Thus a region of micro-immiscibility or incipient immiscibility exists immediately above the liquidus and a single-phase melt is likely to form at a much higher temperature. Such micro-immiscibility is well known in ceramic systems [12] but has not so far been shown in metallic systems.

The formation or otherwise of a solution is determined by the two mutually opposing factors of enthalpy and entropy:

$$\Delta G_\mathrm{M} = \Delta H_\mathrm{M} - T\Delta S_\mathrm{M},$$

where $\Delta G_\mathrm{M}$ = free energy of mixing; $\Delta H_\mathrm{M}$ = enthalpy of interaction between solvent and solute atoms on mixing, a measure of the departure from ideality; $\Delta S_\mathrm{M}$ = the entropy change on mixing the solvent and solute atoms.

Since the condition for equilibrium in any system is that the total free energy be minimised, it is obvious that a single-phase solution is stable when $T\Delta S_\mathrm{M} > \Delta H_\mathrm{M}$ and that immiscibility develops when $\Delta H_\mathrm{M} > T\Delta S_\mathrm{M}$. Hume-Rothery and Anderson [13] suggested that immiscibility in the former type of solutions can arise because of geometrical packing considerations which lead to a sharp valley, and consequent inflexions in the free energy versus composition curve and the liquidus curve. An inflexion in the liquidus curve, therefore, foreshadows immiscibility, but none had so far been reported in the Pb–Cd system which has a pronounced inflection in the liquidus curve. However, the potential immiscibility in systems with inflected liquidus was experimentally revealed below liquidus temperatures in the Cu–Fe and Cu–Co systems by Nakagawa [14].

Centrifugal force has thus merely promoted the separation of conjugate, incipiently immiscible phases. Whereas such decomposition in the solid state is a fairly widespread phenonemon in physical metallurgy, that occurring in the liquid state has only been shown in this investigation.

## 4. Conclusions

This investigation shows that (a) the lead-rich liquid solutions are colloidal suspensions of clusters, approximately 20 to 80 Å diameter, and are essentially stable, (b) the cluster size is minimum at eutectic composition and that (c) an otherwise homogeneous solution in the composition range corresponding to the inflection in the liquidus curve may decompose into conjugate phases, when the tendency for phase separation is accentuated by centrifugal force.

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