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Structure and Stability of Liquid Aluminium-Zinc Alloys

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The structure of liquid aluminium-zinc alloys was investigated by the Kumar-Samarin centrifuging technique, and it was found that liquid alloys falling outside the composition range in which there is solidus inflection are stable and consist of a colloidal dispersion of clusters, while those within that range are incipiently immiscible.

1. Introduction

Investigating the structure of liquid eutectic-type alloy systems with the help of the Kumar-Samarin technique of centrifuging liquid metals, Kumar and Sivaramakrishnan [1, 2] showed that the liquid solution, over the entire range of composition in binary eutectic systems, may not be homogeneous and stable in the presence of a characteristic inflection in the form of the liquidus. They showed that in liquid lead-cadmium and lead-antimony alloys, (i) liquids outside the composition range of the liquidus inflection on either end of the binary phase diagram are stable and consist of colloidal dispersions of solute- and solvent-rich clusters; (ii) the essential immiscibility existing in the solid state is extended in rudimentary form in the liquid state in the composition range of the inflection, and a region of incipient immiscibility exists above the liquidus on melting; (iii) the incipiently immiscible liquid can be separated into its two conjugate phases by centrifuging in the liquid state. The region of incipient immiscibility was not found to exist in the simple eutectic system Pb-Sn in which the liquidus was not inflected [3].

To study the structure and stability of the liquid in systems which show more pronounced inflection in the solidus than in the liquidus, it was decided to extend the work to the Al-Zn system in which the solidus exhibits an inflection in the composition range 20 to 60 at. % zinc. Just as an inflection in the liquidus is often considered to foreshadow immiscibility in the liquid state, so a region of two solid solutions exists at lower temperatures below the region of the inflected solidus. The existence of two solid solutions is deduced from discontinuities in the lattice parameter versus composition curve at elevated temperatures [4].

2. Experimental

Details of the experimental techniques and of the statistical analysis of the results have been described earlier [1]. Alloys containing 16, 40, 50 and 90 at. % Zn respectively were investigated in the temperature range 450 to 750° C, always above the liquidus. Only the alloys with 16 and 90 at. % Zn fell outside the region of solidus inflection. Samples of about 60 g each of the alloys were centrifuged in graphite crucibles at two speeds of rotation for various times and at different temperatures. The experimental conditions are summarised in table I. During centrifuging the heavier zinc-rich clusters migrated to the outer end of the crucible, resulting in the setting up of concentration gradients in alloys with 16 and 90 at. % zinc as shown in figs. 1 and 2. But the two alloys with 40 and 55 at. % Zn did not behave in this manner.

2.1. Cluster Size

In figs. 1 and 2, best-fitting lines are drawn on the basis of a least square analysis. The statistical correlation coefficient and the probability levels were also calculated in each case and are recorded in table I along with their confidence ranges on the concentration gradient for 80 to 95% probability. These calculations show that in general, the correlation between the logarithm

TABLE I Statistics of experimental data of Al-Zn systems

Composition at.% Zn	Centrifugal force ×g	Temperature °C	Concentration gradient	Correlation coefficient	No. of observations	Probability level %	Confidence range (±) as concentration gradient at 80%	90%	95%
16.0	40	650	0.0075	0.8658	9	>95	—	—	0.0038
		750	0.0164	1.0000	9	100	—	—	*
	70	650	0.0080	0.6530	9	>80	0.0056	—	—
		750	0.0145	0.7616	9	>95	—	—	0.0118
90.0	40	450	0.0189	0.7048	9	>90	—	0.0152	—
		550	0.0478	0.5349	9	>60	†0.0475	—	—
	70	450	0.0232	0.8038	8	>95	—	—	0.0073
		550	0.0583	0.4592	9	>70	‡0.0470	—	—

*100% confidence range; †value at 60% confidence range; ‡value at 70% confidence range

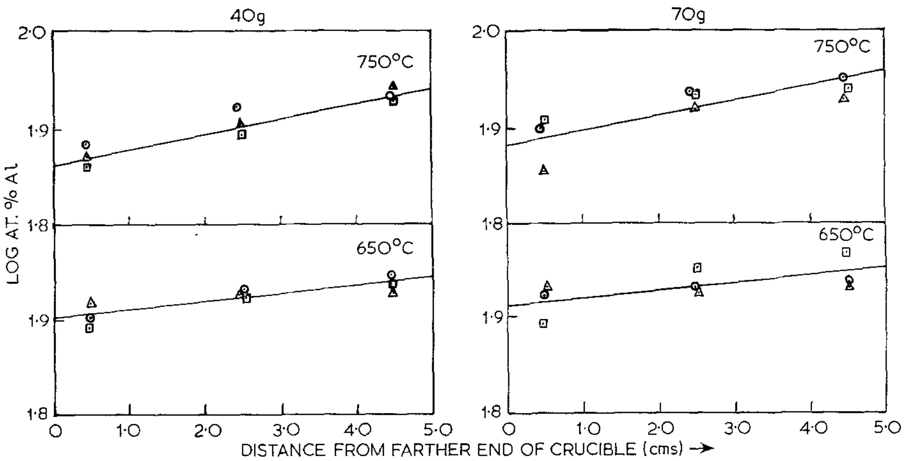

Figure 1 Chemical analysis of Al-16 at. % Zn alloys.

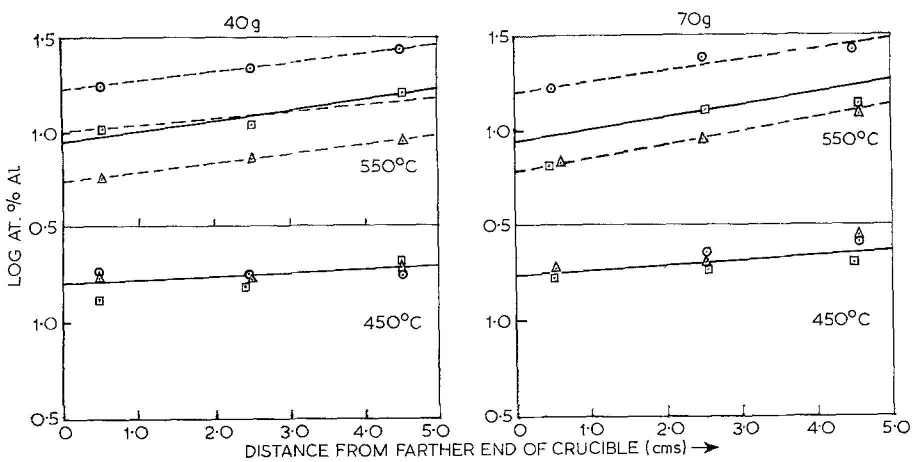

Figure 2 Chemical analysis of Al-90 at. % Zn alloys.

of concentration and the distance, is justified by rigorous statistical analysis, but the correlation is poor when centrifuging is done at high super-heat, as in the case with the eutectic aluminium-zinc alloys (90 at. % Zn) at 550° C. The high volatility of zinc contributes to the

TABLE II Densities of Al, Zn and their liquid alloys

	Density g/ml			
Temperature	Al	Zn	Al-16Zn	Al-90Zn
450	2.37*	6.66	—	2.827
550	2.37	6.55	—	2.808
650	2.37	6.50	2.965	—
750	2.31	6.40	2.894	—

*Indicates density in the solid state.

relatively poor correlation; better correlation would, however, result if observations of individual runs are considered singly as shown by dashed lines in fig. 2.

The cluster radii were calculated, as was done earlier [1], by the sedimentation equilibrium equation using published values [5] of the density of aluminium and zinc, as summarised in table II. The calculated cluster size in the two aluminium-zinc liquid alloys with 16 and 90 at. % Zn respectively is recorded in table III. The extremes of cluster size within the confidence range of the concentration gradient are also indicated by super- and subscripts in the table. It is noted that the cluster size depends on composition and temperature.

2.2. Region of Incipient Immiscibility

Alloys with 40 and 50 at. % Zn decomposed into two conjugate phases on centrifuging between 550 and 750° C. The results of the chemical analysis in the two phases are given in figs. 3 and 4. It is noted that instead of a gradual concentration gradient being obtained in the solidified ingot, the liquid divided itself into two predominant liquids having their compositions near the two limits of the inflection.

3. Conclusion

The investigation shows that (i) liquid aluminium-zinc alloys are stable in the composition ranges 0 to 20 and 60 to 100 at. % Zn, and consist of

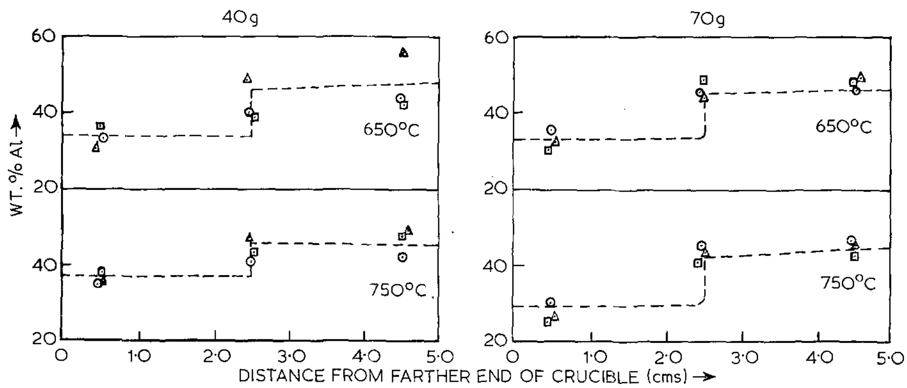

Figure 3 Chemical analysis of Al-40 at. % Zn alloys.

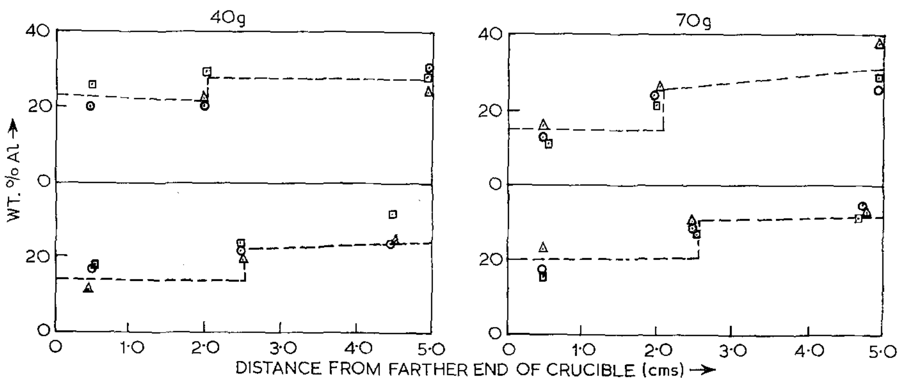

Figure 4 Chemical analysis of Al-50 at. % Zn alloys.

TABLE III Cluster size in Al-Zn systems

Composition at.% Zn	Centrifugal force ×g	Temperature °C	Calculated values of cluster, Å, size at mean, minimum and maximum slopes: Al (mean)	Al (min)	Al (max)	Zn (mean)	Zn (min)	Zn (max)
16	40	650	28	22	32	16	12	18
		750	38			21		
	70	650	24	16	29	13	9	16
		750	30	17	37	17	10	20
90	40	450	40	22	47	19	11	23
		550	56	10	70	27	5	34
	70	450	34	30	38	17	15	19
		550	50	29	60	24	14	30

colloidal dispersion of aluminium- and zinc-rich clusters and, (ii) the liquid in the composition range of the inflection in the solidus consists of an incipiently immiscible solution of two conjugate liquid phases which can be separated by centrifuging.

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