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Structure of liquid aluminium-silicon alloys

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The Kumar-Samarin technique of centrifuging was adopted to study the structure of aluminium-silicon alloys in terms of the concept of the existence of clusters in liquid state. The investigation shows that in hypo-eutectic alloys the clusters are denser than the monatomic matrix whilst in hyper-eutectic alloys they are lighter. It is suggested that this difference in the distribution of silicon in liquid state could account for the difference in the solidification behaviour of hypo- and hyper-eutectic alloys.

1. Introduction

Although metallurgical interest in the aluminium-silicon system dates back to the early 1920s, the solidification behaviour of its commercially important alloys, both in the hypo- and hyper-eutectic regions, has yet defied a basic understanding. Thus, despite the well-known fact that *modification* (i.e. refinement) of the cast eutectic structure in hypo- and hyper-eutectic alloys improves their mechanical properties, the precise mechanism of modification is not understood; whilst the modification in hypo-eutectic alloys is achieved through inoculation by sodium in the liquid state, that of the hyper-eutectic alloys is achieved by phosphorus. The present status of the knowledge is best expressed through the statement that in hyper-eutectic alloys "the effects of sodium and phosphorus are the same as far as the eutectic solidification and eutectic structure are concerned, but that sodium decreases, while phosphorus increases, the number of primary silicon grains in the structure; phosphorus promotes nucleation of the primary silicon phase by providing nuclei which have been reported as having the composition of a compound AlP. For this reason, phosphorus is normally added to the hyper-eutectic alloys as a grain-refining element for primary silicon. Thus, an apparent anomaly exists in the eutectic alloy; sodium refines and phosphorus coarsens the silicon phase, while in the hyper-eutectic alloys, exactly the opposite happens with the primary silicon". [1]. It will thus be appreciated that no universally acceptable theory is yet available to explain the modification of cast structures in the entire range of aluminium-silicon alloys. One important drawback of the existing theories [2] is that they have been developed without any consideration of the nature of the distribution of silicon in the liquid alloys. This investigation was specifically undertaken to study the structure of aluminium-silicon alloys in liquid state with the Kumar-Samarin technique [3, 4] in terms of the existence of clusters.

2. Experimental

Details of the experimental technique and the statistical evaluation of the results have been discussed in earlier publications [5].

Aluminium-silicon alloys containing 1, 4, 7, 12, 14 and 19 nominal per cent of silicon were prepared in an electric furnace, using conventional flux and degasser, and were cast into metallic moulds. All the alloys were centrifuged at 700° C and 500 rpm which developed a centrifugal force of 63 *g*. In addition, the 7% silicon alloy was also centrifuged at 750° C and the eutectic alloy (12% silicon) at 600 and 650° C as well. After centrifuging for different periods from 15 to 180 min at each temperature level, the samples were solidified rapidly *in situ*. The details of the experimental conditions are summarized in Table I. A large number of centrifuged ingots were obtained for each experimental condition of time and temperature for statistical evaluation of the results.

3. Experimental results

The results of the chemical analysis for all the alloys are shown in Figs. 1 to 6. Concentration

TABLE I Experimental conditions and statistical analysis

Composition (wt % Si)	Centrifuging temperature (°C)	Concentration gradient	Correlation coefficient	No. of observations	Probability level (%)	% confidence range on concentration gradient (±) 80	95
1	700	−0.0573 ± 0.0129	0.70	30	99		0.0129
4	700	−0.0680 ± 0.046	0.46	50	99		0.046
7	700	−0.0820	1.00	45	100		*
	750	−0.0739 ± 0.0173	0.904	63	95		0.0173
12	600	−0.0547	1.00	33	100		*
	650	−0.0530	1.00	32	100		*
	700	−0.0312 ± 0.0269	0.575	19	98		0.0269
14	700	0.0055 ± 0.0027	0.052	101	90	0.0027	
19	700	0.0178 ± 0.0175	0.475	30	95	0.0175	

* 100% confidence.

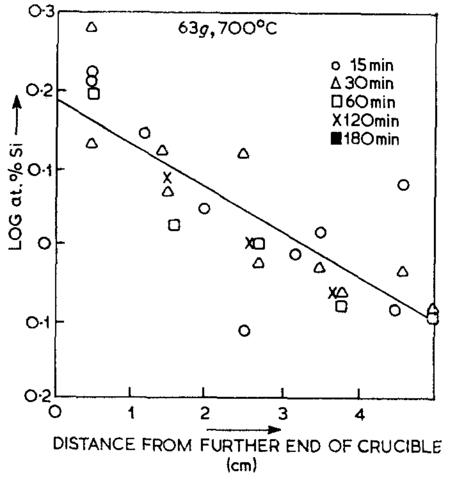

Figure 1 Chemical analysis data of Al-1% (wt) Si alloy.

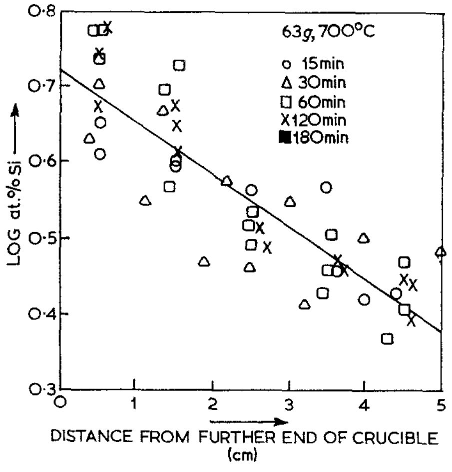

Figure 2 Chemical analysis data of Al-4% (wt) Si alloy.

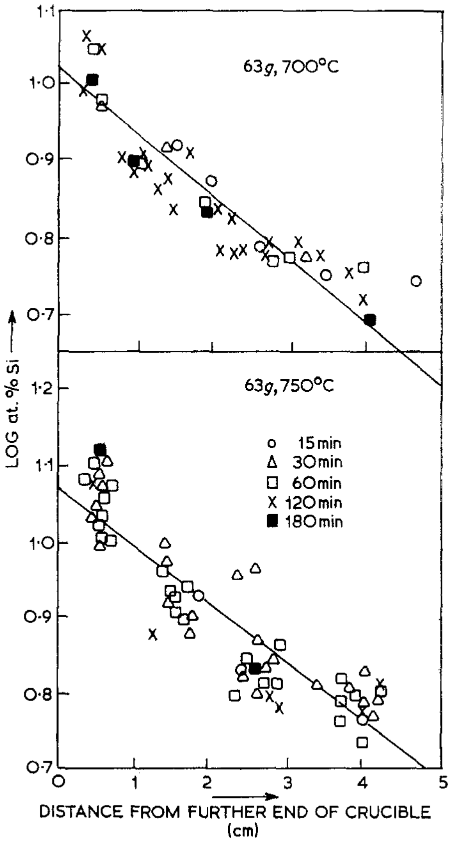

Figure 3 Chemical analysis data of Al-7% (wt) Si alloy.

gradients are set up in all cases as a result of centrifuging. The concentration gradient was calculated statistically on the basis of least square analysis in all cases and the best fitting lines are drawn in each case. The other statistical para-

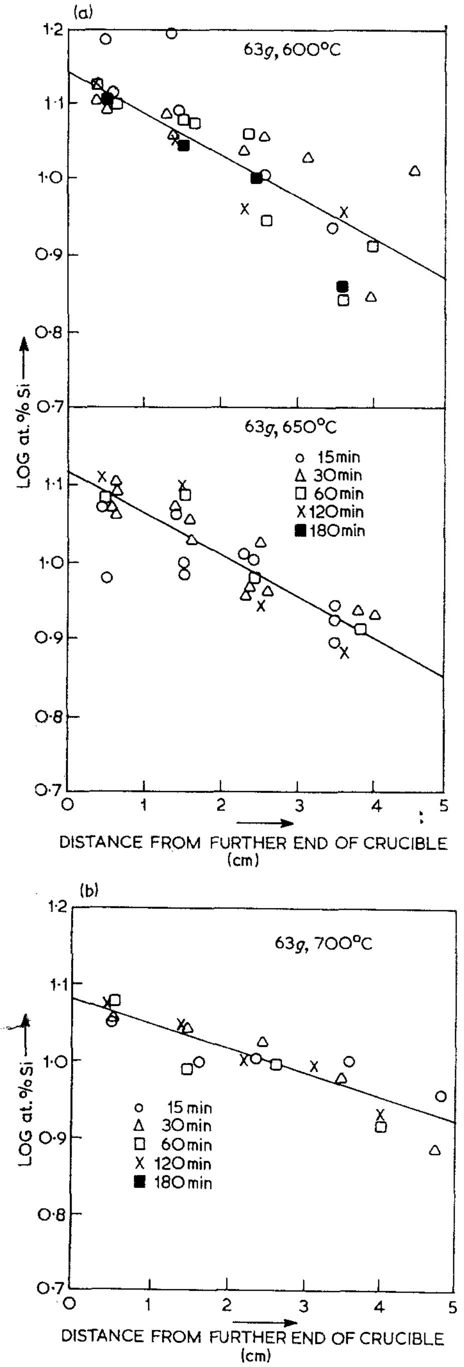

Figure 4 (a) and (b) Chemical analysis data of Al-12% (wt) Si alloy.

meters are also recorded in Table I along with their confidence ranges on the concentration gradients for 80 and 95% probability. These calculations show that, in general, the correlation between the log of concentration and the distance is justified by rigorous statistical analysis.

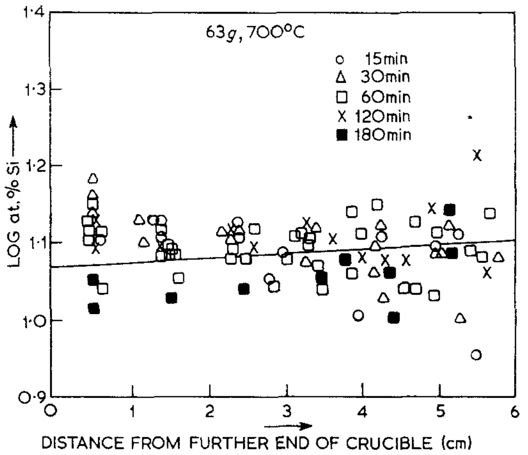

Figure 5 Chemical analysis data of Al-14% (wt) Si alloy.

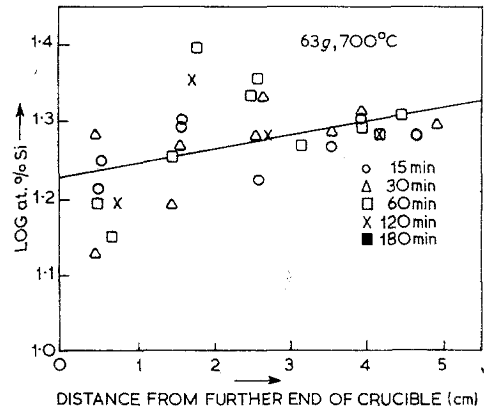

Figure 6 Chemical analysis data of Al-19% Si alloy.

The nature of the concentration gradient in hypo-eutectic and eutectic alloys is different from that in the hyper-eutectic alloys. In the hypo-eutectic alloys silicon is preferentially sedimented at the further end of the ingot, thus behaving as if its clusters were heavier than the matrix. In the hyper-eutectic alloys, on the other hand, it is segregated at the top end of the ingot as if its clusters were less dense than the matrix. This observation is also confirmed by metallographic examination of a large number of specimens. Typical microstructures of the hypo- and hyper-eutectic alloys from the bottom, middle and top portions of the centrifuged ingots are shown in Fig. 7. It may be noted that the distribution of silicon in the hyper-eutectic alloys is not only idiomorphic but also extremely coarse.

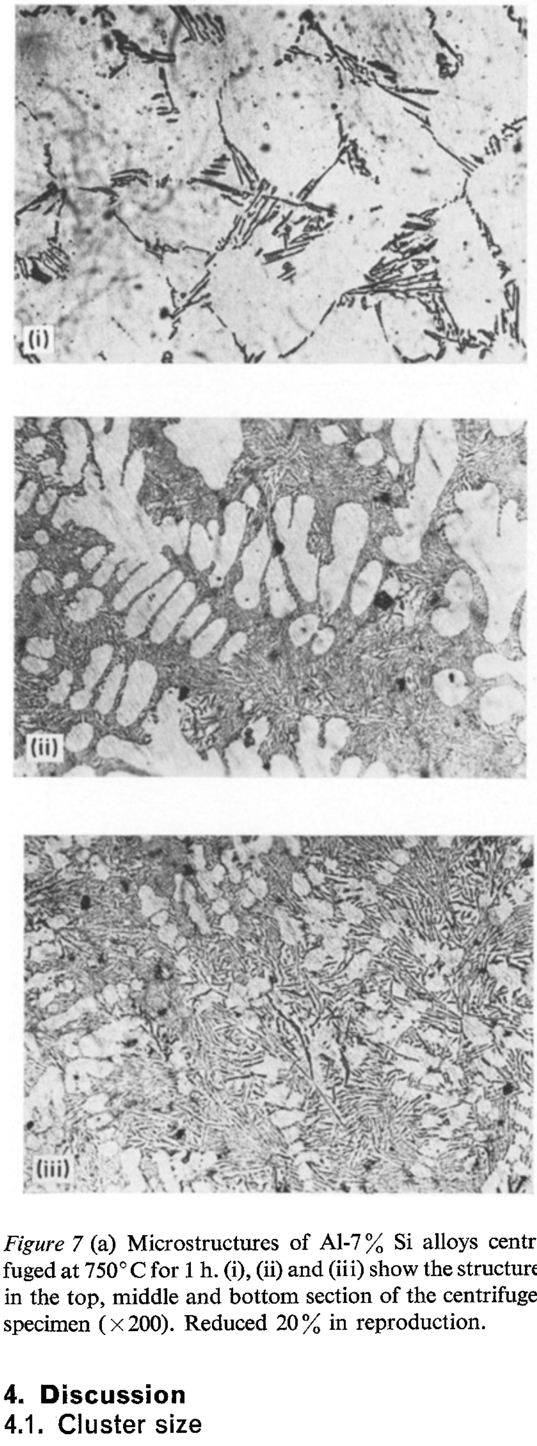

Figure 7 (a) Microstructures of Al-7% Si alloys centrifuged at 750° C for 1 h. (i), (ii) and (iii) show the structures in the top, middle and bottom section of the centrifuged specimen (×200). Reduced 20% in reproduction.

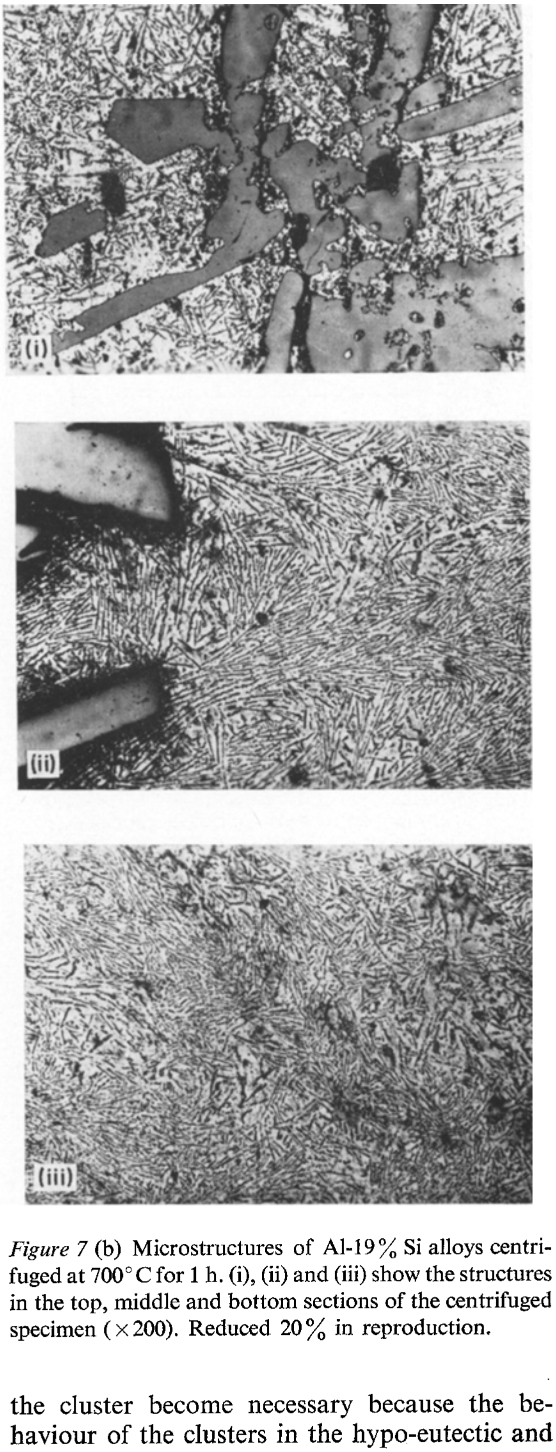

Figure 7 (b) Microstructures of Al-19% Si alloys centrifuged at 700° C for 1 h. (i), (ii) and (iii) show the structures in the top, middle and bottom sections of the centrifuged specimen (×200). Reduced 20% in reproduction.

4. Discussion

4.1. Cluster size

Kumar and co-workers had earlier shown that the cluster size can be calculated with the help of Perrin's equation [6]. In order to calculate the cluster size in the aluminium-silicon system, certain assumptions with regard to the nature of the cluster become necessary because the behaviour of the clusters in the hypo-eutectic and eutectic alloys is different from that in the hyper-eutectic alloys. If the behaviour of the aluminium-silicon system were identical with that of the other eutectic systems, silicon should have preferentially segregated at the top of the ingots in all alloys irrespective of the silicon concentration, because the density of silicon is less than that of aluminium at corresponding temperatures. It is known that the addition of silicon to aluminium initially increases its density in the liquid state [7]; silicon, therefore, appears initially to consolidate the short-range order in aluminium-silicon alloys. The heat of formation of aluminium-silicon alloys is negatively maximum at the equiatomic composition and thus it was assumed that the clusters could correspond to the composition AlSi. In order to calculate the cluster size with the help of Perrin's equation, further assumptions with regard to the density of the equiatomic alloy become necessary. Data on the temperature-dependence of density of silicon are not available. If its temperature dependence is taken to be similar to that of the other metals of the same group (bismuth, antimony and gallium) a density of 2.7 g/ml is deduced for AlSi clusters on the basis of the additivity rule. There is no doubt that these are rather arbitrary assumptions but they are necessary to obtain an idea of the cluster size. It may be mentioned that even if the deduced density of the calculated AlSi cluster is in error by as much as 25% it would affect the cluster size only to a limited extent. For the hyper-eutectic aluminium-silicon alloys, silicon is present essentially as silicon clusters for which a density of 2.34 g/ml has been taken. The calculated cluster sizes for all the aluminium-silicon alloys are incorporated in Table II. The values of the densities of the alloys in the liquid state have been taken from published values [8, 9] which are recorded in Table III.

TABLE III Densities of liquid aluminium-silicon alloys.

Alloy (wt % Si)	Centrifuging temperature (°C)	Density (g/ml)
1	700	2.36
4	700	2.38
7	700	2.40
	750	2.39
12	600	2.43
	650	2.42
	700	2.41
14	700	2.42
19	700	2.47

4.2. Volume fraction of clusters

The deviation of the plot of viscosity against temperature from the usual Arrhenius type of expression $\eta = \eta_0 \exp(E/RT)$ is plotted in Fig. 8. If this deviation is attributed to the existence of

TABLE II Cluster size in aluminium-silicon alloys

Composition (wt % Si) (nominal)	Centrifuging temperature (°C)	Statistical slope	Calculated values of cluster size in Å, at maximum mean and minimum slopes
1	700	−0.0573 ± 0.0129	69
			59
			53
4	700	−0.0680 ± 0.046	76
			63
			44
7	700	−0.0820	70
	750	−0.0739 ± 0.0173	72
			67
			61
12	600	−0.0547	60
	650	−0.0530	60
	700	−0.0312 ± 0.0269	63
			51
			27
14	700	0.0055 ± 0.0027	50
			44
			35
19	700	0.0178 ± 0.0175	69
			55
			15

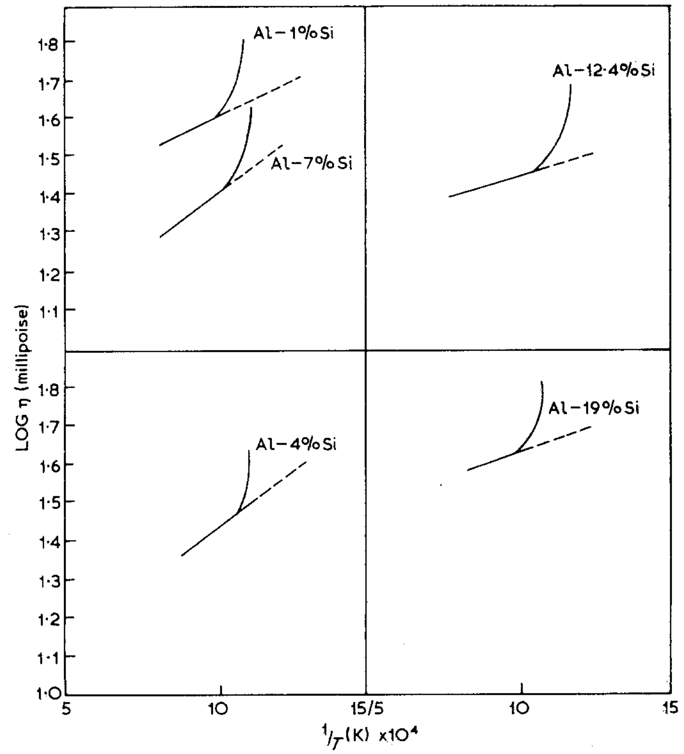

Figure 8 Viscosity of Al-Si alloys.

TABLE IV Percentage volume fraction of clusters in aluminium-silicon alloys

Alloy	Temperature (K)	η_i	η_{Si}	ϕ_i (%)
Al-1.0% Si	973	43.0	41	< 1
Al-7.0% Si	973	26.0	25.5	< 1
Al-12% Si	873	35.5	30.2	6
	923	30.2	29.5	1
	973	29.0	28.50	< 1
Al-19% Si	973	45	43.50	1

clusters in liquid metals, the volume fraction of clusters can be calculated using Einstein's equation relating viscosity of a colloidal solution to the volume fraction of the clusters according to the procedure outlined earlier [10]. Values of actual and extrapolated viscosity of aluminium-silicon alloys from the experimental observations of Gebhardt [8] and Jones and Bartlett [9], recorded in Table IV, were used to calculate the volume fraction of the clusters at 973K for 1, 7 and 19% silicon and 873, 923 and 973K for the eutectic aluminium-silicon alloys respectively. The values of the volume fraction are also summarized in Table IV, and show that the volume fraction of the clusters is 6% near the melting point and decreases to less than 1% as the temperature is raised in the liquid state.

In accordance with the procedure outlined in earlier papers [10, 11], the heat of formation of the AlSi clusters in the eutectic alloy was found to yield a value of 1.16 kcal/g. atom at 923K and 0.295 kcal/g. atom at 973K respectively.

5. Conclusion

This investigation, therefore, establishes beyond any shadow of doubt that the distribution of silicon in the hypo-eutectic alloys is significantly different from that in the hyper-eutectic alloys. Whilst no experiments have been done to study the effects of sodium or phosphorus on the distribution of silicon in liquid state, the present results seem to offer a possible explanation for the divergent effects of sodium and phosphorus on the modification behaviour of the hypo- and hyper-eutectic alloys.

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