Structure of Liquid Aluminium-Copper Alloys

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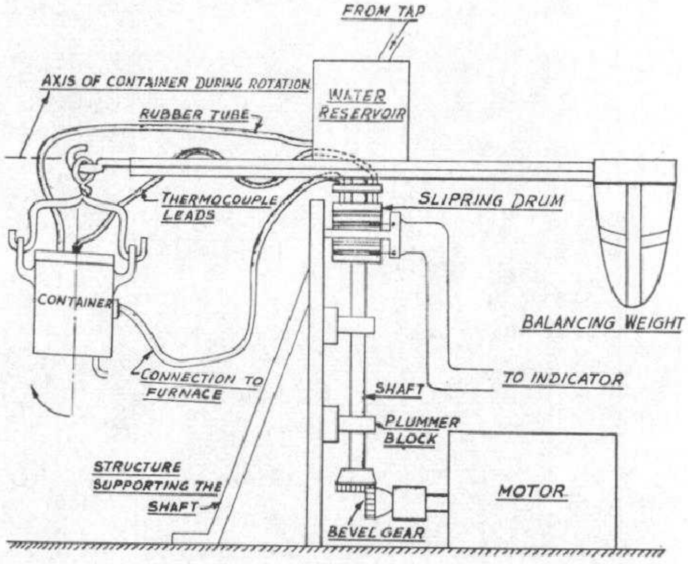
EARLIER work[1] done in these laboratories has established the existence of copper-rich clusters in tne liquid aluminium copper alloys. It was decided to investigate the behaviour of these clusters at various temperatures in aluminium-copper alloys because of the great commercial and scientific interest, in age-hardening alloys. Such an understanding would be of help in forming a physical picture of the early stages of the precipitation processes. The existence of the clusters is thermodynamically possible as it lowers the free energy of the system by increasing the entropy of mixing. The aluminium-rich or copper-rich clusters in liquid aluminium-copper alloys arise because of the negative heat of solution. The density of the copper-rich clusters is greater than that of the parent liquid and the difference in the density could be magnified several times by centrifuging the molten alloy, thus causing the heavier copper-rich clusters to move away from the radius of rotation. Conditions are thus created which divide the liquid into aluminium-rich and copper-rich portions.

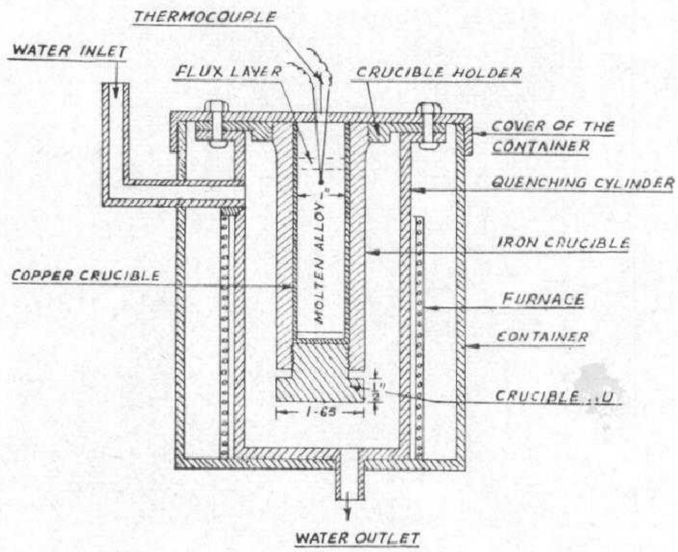
Experimental technique

An apparatus described elsewhere[1] was used with the modification that the aluminium-4·0% copper alloy was kept in a thin walled copper crucible. This crucible was kept inside a close fitting double walled steel crucible, the copper crucible served to avoid the contamination of the aluminium copper alloys with iron. It was, however, found that some of the copper of the crucible was taken into solution in the molten alloy, thereby increasing its average copper content up to about 8 to 12·0% depending on the time of centrifuging. A flux of sodium and calcium fluorides was used to prevent surface oxidation. The alloys were centrifuged at 700 and 800°C for different times varying from 1 to 8 hours at 120 r.p.m., the length of the radial arm carrying the crucible being 55 cm. At the end of the predetermined time water was allowed to rush through the annular space of the double walled crucible and this served to chill the distribution of copper atoms existing in the liquid state at that instant of centrifuging. The solidified ingot was recovered and



APPARATUS FOR CENTRIFUGING.

Fig. A.



SECTION THROUGH CONTAINER ASSEMBLY.

Fig. B.

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Plate 1.
Showing distribution of two phases near the top of the ingot.
Magnification—84X.

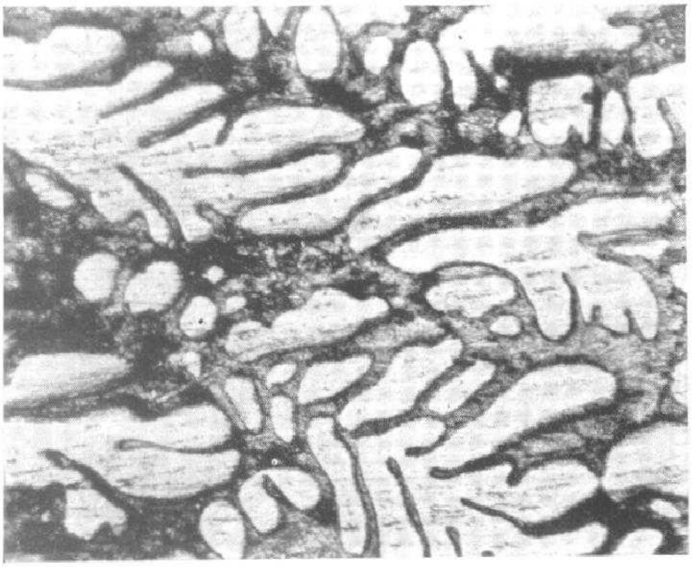

Plate 2.
Showing distribution of two phases near the centre of the ingot.
Magnification—84X.

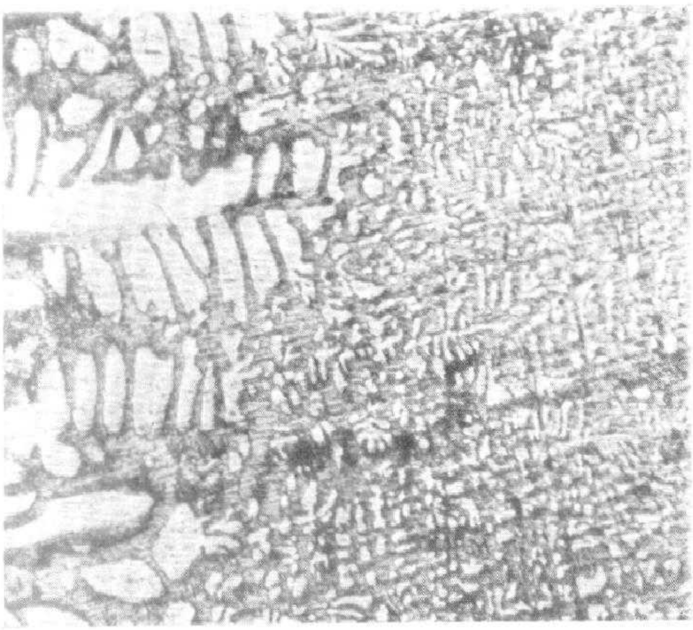

Plate 3.
Showing the demarcation in the coarse and the fine structure.
Magnification—84X.

Plate 4.
Showing distribution of two phases near the bottom of the ingot.
Magnification—84X.

samples were taken for metallographic and chemical analysis.

Results and discussion

Metallographic examination revealed :

(*i*) The presence of a second phase at the grain boundaries near the top of the ingot (aluminium rich end) plate 1.

(*ii*) The quantity of the second phase progressively increases towards the bottom of the ingot. Plate 2 shows the coarse cast structure near the centre of the ingot.

(*iii*) The quantity of the second phase continues to increase, but the distribution suddenly becomes finer. The demarcation in the coarse and fine structure is shown in Plate 3. The demarcation corresponds to a sharp increase in the copper content of the alloy. The structure at the bottom of the crucible is shown in Plate 4.

Figs. 1 to 6 summarise the distribution of copper existing after centrifuging at 700 and 800°C for different times at 120 r.p.m. It would be seen that the separation is more effective at 800°C. In accordance with the generally accepted notions the size of the clusters should decrease as the temperature is raised. However, the observations can be explained if you bear in mind that the heat of solution is negatively greater at higher temperatures[2]. The effects of corresponding changes in viscosity have yet to be investigated. It would also be seen from the figures that the copper content at the aluminium-rich end does not fall below about 6·0% even for centrifuging up to 8 hours. It is obvious that the size of the clusters existing in Al–6·0% Cu alloy is such that the centrifugal force has not been able to overcome the forces responsible for the particular cluster distribution. Further the heat of solution is negatively greater for alloys of greater copper concentration, the clustering is therefore not very perfect.

Figs. 7, 8 and 9 show the variation in the concentration of copper at a particular position with time. The figures show that as a result of centrifuging, copper clusters are continuously moving from top to the

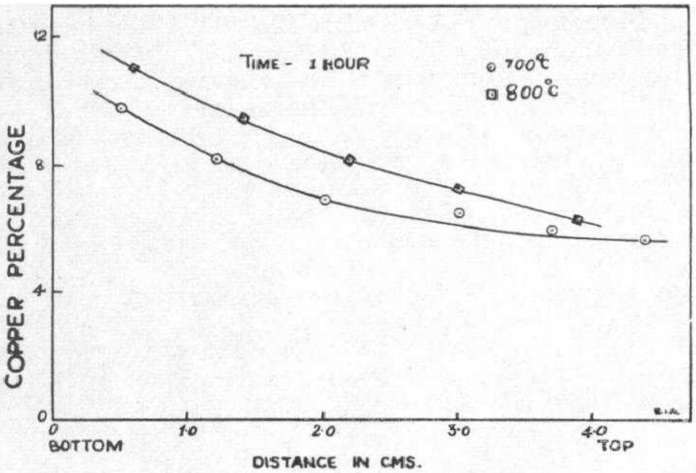

Fig. 1.
Distribution after 1 hour's centrifuging.

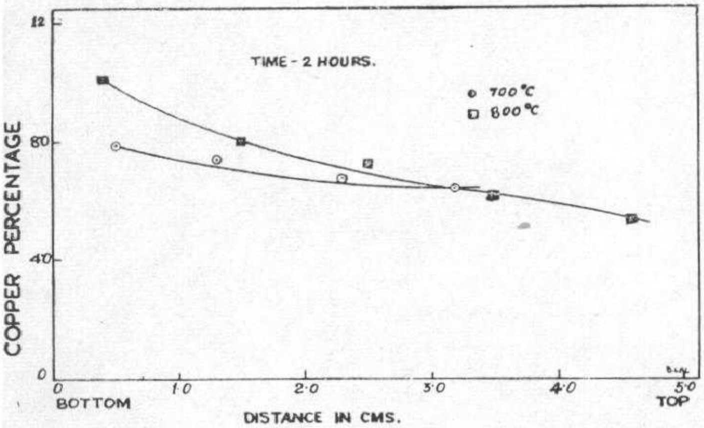

Fig. 2.
Distribution after 2 hours' centrifuging.

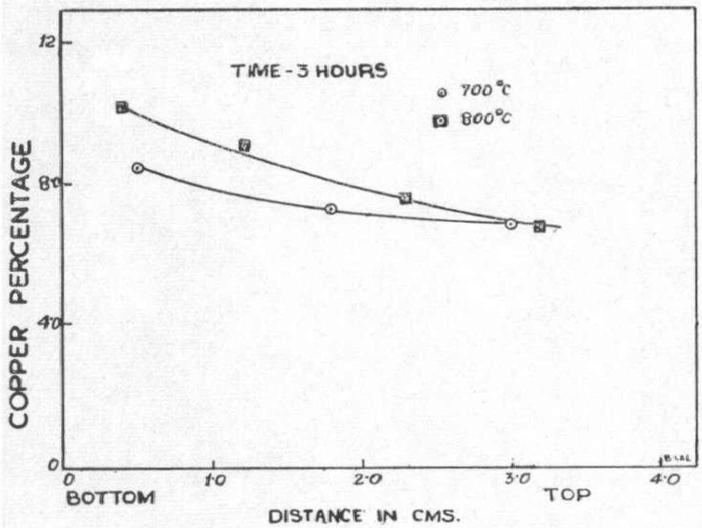

Fig. 3.
Distribution after 3 hours' centrifuging.

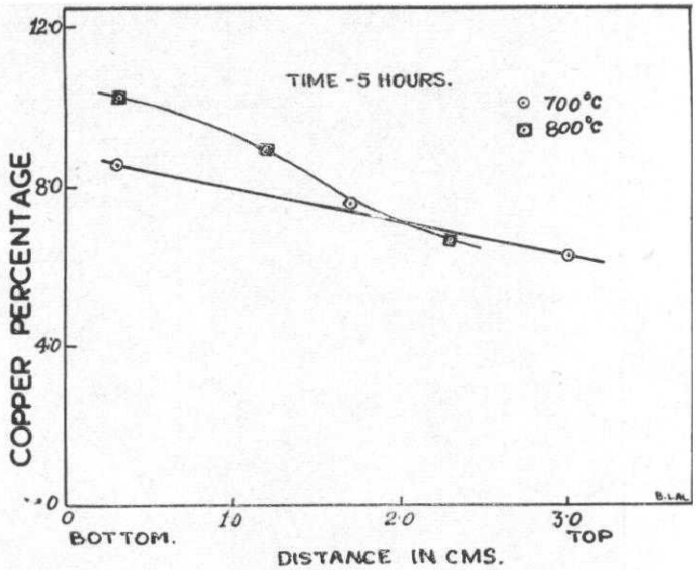

Fig. 4.
Distribution after 5 hours' centrifuging.

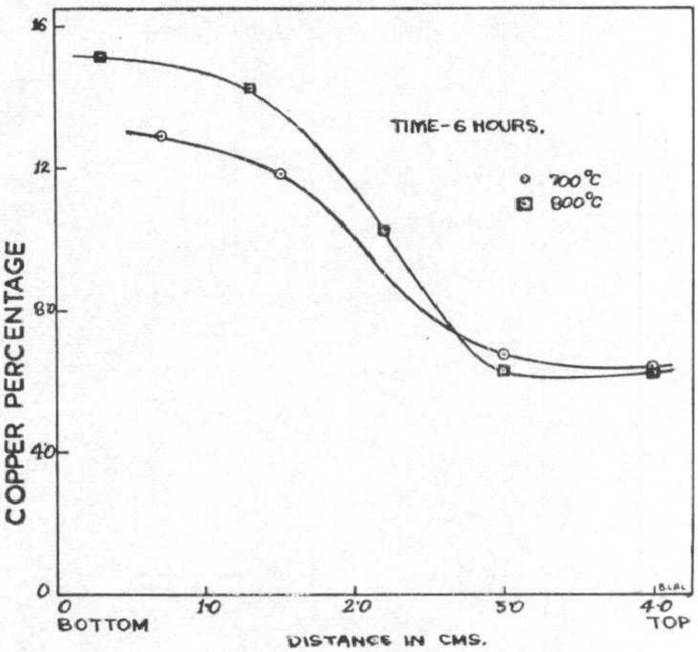

Fig. 5.
Distribution after 6 hours' centrifuging.

bottom of the ingot. As the concentration of copper drops in the liquid a longer time is required for causing a large scale movement of copper atoms. This can be appreciated from Fig. 9 which shows that a period of about 7 hours is required to grow the clusters to a critical size characteristic of the speed of rotation. When the critical size is attained the centrifugal force

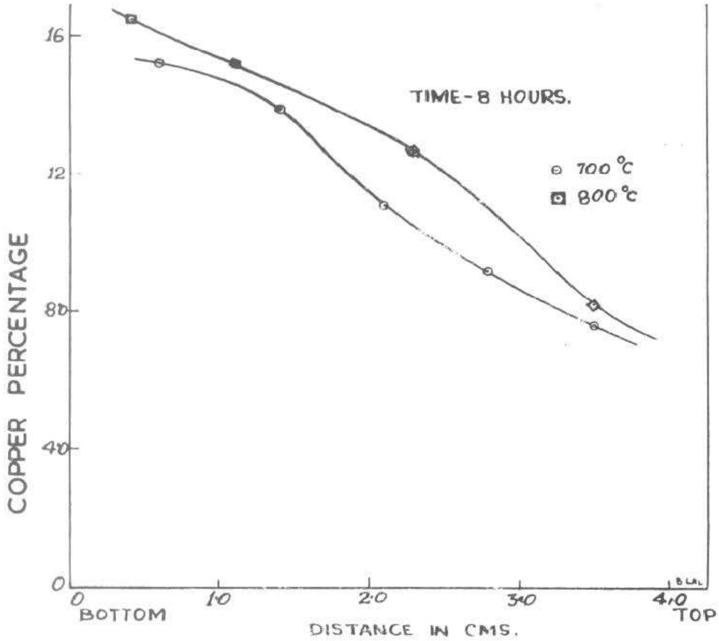

Fig. 6.
Distribution after 8 hours' centrifuging.

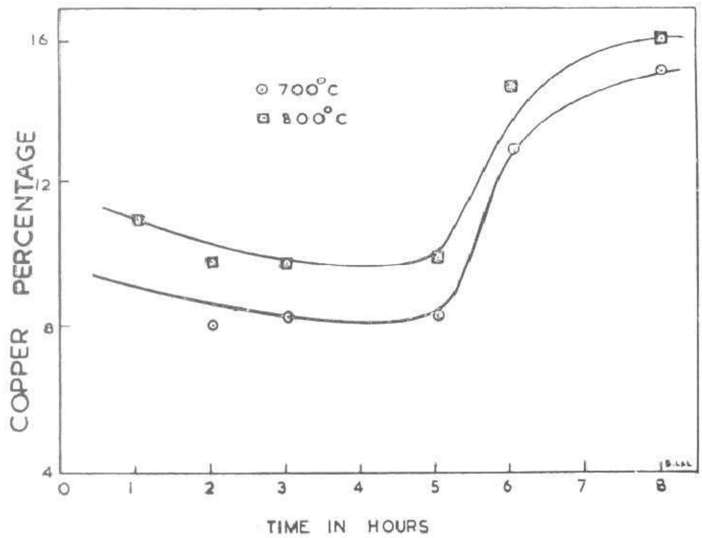

Fig. 7.
Copper content at 0·6 CM. from bottom.

overcomes the forces of viscosity, etc. and is centrifuged outward.

Guinier and Preston[3, 4, 5] in their classical studies on the precipitation processes in aluminium copper alloys suggested that the first step in the precipitation of a second phase consists of the preferential accumulation of the copper atoms along certain crystallographic planes. They are commonly known as G. P. zones and are copper rich platelets 100-500 A° in diameter and one to a few atoms distances thick and are about 100 A° apart from each other. However, Jagodzinkis and Laves[6] have criticised the existence of the G. P. zones as outlined above on the basis that such a large accumulation of copper atoms would require an extremely fast rate of diffusion which is practically impossible to attain. They have on the other hand suggested that the maximum copper content of these platelets is 10% and that the number of platelets is much greater than that visualised by Guinier.

This difference of opinion in the interpretation of X-ray data is perhaps due to the fact that whilst it is possible to calculate the X-ray scattering that would be caused by a given configuration of atoms, it is

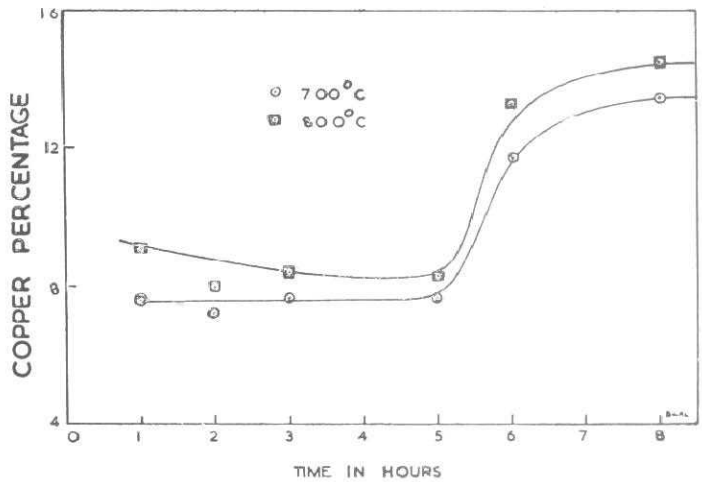

Fig. 8.
Copper content at 1·5 CM. from bottom.

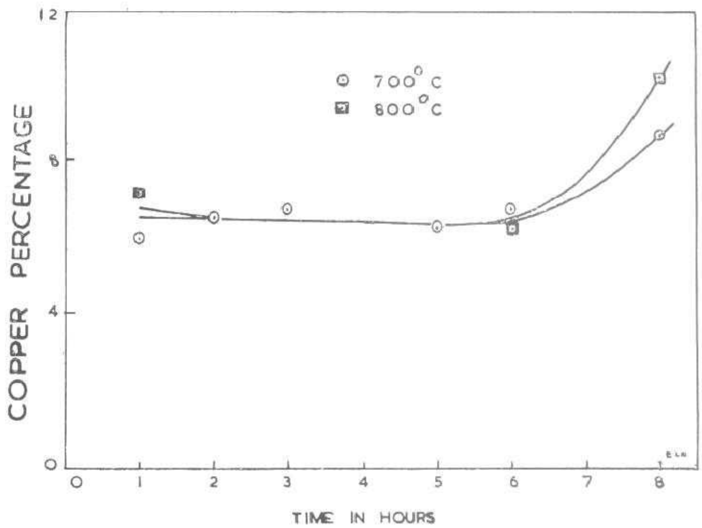

Fig. 9.
Copper content at 3·0 CM. from bottom.

not yet possible to deduce the actual atomic configuration from the observed X-ray scattering. The conclusions regarding the structure of clusters are thus only the best estimates of specialists and can seldom be regarded as conclusive[7].

The results obtained in this investigation have given a physical confirmation of the existence of the copper-rich clusters in the liquid state. As has been demonstrated earlier[1] these clusters arise because of the Cu-Al bond being stronger than either the Al-Al or the Cu-Cu bond. The strength of the bond would be even more stronger in the solid state where the temperatures are comparatively lower. The super-saturated solid solution of copper in aluminium, therefore, consists of copper-rich clusters of various sizes randomly distributed throughout the whole mass. These clusters are the potential G. P. zones and the larger of them initially nucleate the G. P. zones, the nucleation requiring slight, if any, diffusion of copper atoms.

Whilst it has not been possible to calculate the size of these clusters in the liquid state the observations have shown that copper-rich regions do exist in the lattice of aluminium. The criticism of Jogodzinkis and Laves[6] is, therefore, perhaps not valid. This also explains why the ageing process starts with very little incubation period.

Acknowledgement

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DISCUSSIONS

Dr. B. R. Nijhawan, NML : I must say that Dr. Kumar has presented his results lucidly which should provide an interesting discussion. I would like to ask Dr. Kumar as to what are the practical implications of this study in the sense of formulation of certain alloys which may be of practical use and application. Is it possible to derive any conclusions to the effect that by such liquid concentration of clusters of copper atoms, we can obtain from an overall composition by centrifuging, certain concentration of atoms that may give certain optimum beneficial practical properties?

Dr. Rajendra Kumar (Author) : I am thankful to Dr. Nijhawan for the kind remarks he has made on this paper and in reply I would like to say that it is rather premature at this stage to discuss the practical implications of this paper. In a previous paper, however, we have shown that it is possible to separate lead and tin from their liquid of eutectic composition; the concentration of Sn in the mass which was thus separated was sufficient to give a "tin cry". We believe similar studies can be done on other liquid systems and may be coupled with zone refining. The studies may also be useful in studying the mechanism of ageing, and we propose to investigate the effect of various minor additions such as magnesium in Al-Cu alloys.

Mr. D. V. Paranjpe, Tata Iron and Steel Co. Ltd., Jamshedpur : Could the principle of centrifuging be used for a practical application, viz. separation of lead and tin from the turning of bearings containing tin-rich babbit metal and lead-rich babbit metal? If this could be done, the resulting metal could be used for making tin-rich bearings or even for producing pure tin and pure lead from a mixture of the two metals in the bearing alloys.

Dr. Kumar (Author) : I think the suggestion is worth trying in view of our earlier results on the Pb-Sn system, where we were able to separate Pb and Sn from their eutectic mixture. I have got here some samples of the tin thus separated, which you can inspect, if you so desire.

Mr. R. Choubey, NML : Dr. Kumar has presented in one of his studies a curve which shows a rise in incubation period and a sort of concentration of Cu-rich nuclei which tend to concentrate towards the rim of the apparatus. I would like to know whether from this saturation state, one can guess the nature of nuclei that probably exist during the liquid state because near about 12% Cu, we find some sort of saturation. Dr. Kumar has mentioned earlier that due to the copper container there is some copper pick-up and copper concentration near the rim comes to that higher limit. So it might be due to this cause or due to the nature of nucleii formed during liquid state under those prevailing conditions which concentrate towards the rim and give rise to that saturation limit.

Dr. Kumar (Author): I would not like to say that there is a saturation in the liquid state because in the liquid state these alloys are known to be completely miscible subject to the departures I have enumerated in the paper. These departures relate to the existence of Cu in the form of Al–Cu clusters in the parent liquid. Top limit of the Cu-concentration at the farther end depends on the Cu-content of the liquid alloy with which we start initially. Since the submission of the paper we have done certain experiments with a view to avoid copper pick-up; we made a stainless steel crucible and found that even in an Al–4% Cu alloy the same type of distribution as described in the paper exists after centrifuging with the difference that maximum value of Cu-concentration was not 12% but slightly less about 8%.

Mr. H. P. S. Murthy, NML: I am interested in the experimental technique and would like to know from the author: (1) What was the speed of centrifuge? (2) Is the existence of clusters proved? and, (3) If Cu clusters are present, the liquid should deviate from a Newtonian fluid and should show a different coefficient of viscosity. It may even exhibit thixotropy. Hence viscosity determination may help to, at least partially, prove the existence of clusters.

Dr. Kumar (Author): The rotation was 120 r.m.p. and the incubation period was 5 hours. If the speed of rotation is increased, it will perhaps decrease the incubation period and the separation will be more effective. We have still to investigate the effect of speed on migration of Cu.

The existence of clusters is suggested by the negative departure from the Raoult's Law. The reason why we do not say that Cu alone is migrating is that if Cu-Cu bonds were stronger, the Cu will be present in the form of Cu clusters and in this case the departure from Raoult's Law will be positive as in the case with Pb and Sn.

Mr. R. Seshadri, Indian Smelting and Refining Co., Bombay: We have the problem of "inverse segregation" in the case of aluminium-copper alloys. Have the authors taken into consideration this problem? In order to be able to study the effect of this, it could have been better if a concurrent study of the ingot without centrifuging is made and the same is compared with the results obtained regardless of the ingot size.

Dr. Kumar (Author): We have not investigated the relation between "inverse segregation" and the present problem.

Dr. V. G. Paranjpe, Research and Control Labs., Tisco, Jamshedpur: I must compliment the author on this interesting set-up of experiments. I have only two suggestions to make:

(*i*) It would perhaps be advantageous if the crucible started out at the centre and went towards the periphery because by that you will get a variation in speeds from 0 to a very high value. This would be much higher than the 1·5–2·0 fold increases obtained by the authors. It would possibly be done by having the crucible spreading out on both sides so that the centre is not affected by any centrifugal action whatsoever, and the two sides are definitely under a centrifugal action.

(*ii*) Whether this phenomenon could not perhaps be explained rather by a simple approach from the point of view of gravitation? After all two substances which differ quite a lot in specific gravity are dealt with and even in a liquid one can have gravitational separation.

Dr. Kumar (Author): Thanks for the suggestions. Centrifuging merely helps to exaggerate the gravitational segregation and therefore separation is effected in a short period of time.

Dr. V. G. Paranjpe, Res. and Control Lab., Tisco, Jamshedpur: Normally we do not consider gravitation forces in discussing phase equilibria. But, if you really go through expositions of Gibbson on the heterogeneous equilibria, you will find the methods of dealing with influences of gravitation, centrifugal forces, etc. on chemical potentials. Normally we can neglect gravitational potential because the substances are under the same influence. But when one purposely sets out to create a different gravitational force in one part of system compared to other, one cannot overlook the contribution of gravitational or some of these complex centrifugal fields to thermodynamic potentials.

Dr. E. G. Ramachandran, NML: I would also like to express my appreciation to the very able presentation of Dr. Kumar and to the very interesting subject which has been expounded today. I am also interested to know how the movement of Cu-rich clusters actually takes place and how much of it is due to the centrifugal force and how much of it is due to simple gravity movement. I have also a small suggestion to make to Dr. Kumar, which he would perhaps examine for what it is worth. As the mould takes up a horizontal position when rotated, and the difference in radii between the top and bottom is of the order of 5 cms only, I would suggest using a mould of this shape.

In this mould, there would perhaps be no gravity effect, but only the centrifugal effect and the Cu-rich clusters may naturally be then thrown to the periphery. With a mould of this type and one with the bend opposite, it may be possible to explain the outward movement of Cu-rich clusters.

I also wish to comment on the implications of Dr. Kumar's statement that the existence of clusters is proved because of the departure from Raoult's Law. I think that the existence of clusters is a postulate. Clusters have been postulated to exist, to explain the deviations from the Raoult's Law. It is not a proof. For example, Guinier-Preston zones were postulated to explain age-hardening. But not till low-angle scattering photographs were taken, could their existence be taken as confirmed. In a similar fashion, I think Dr. Kumar should eliminate the effect of gravity or of erosion attack upon the copper crucible and by chemical analysis prove the existence of the clusters.

Mr. H. P. S. Murthy, NML : I think Dr. Ramachandran has partly raised my doubt. I would like to have a physical proof of their existence. Dr. Ramachandran suggested a chemical method. I am wondering whether viscosity determination would help in this regard. A Newtonian liquid has got a particular coefficient of viscosity and if there are certain discreet particles present in it, the liquid will deviate from the Newtonian Law and its viscosity also will deviate. If these Cu clusters are present or come into existence at a particular stage, then it is quite possible that the liquid may not behave like Newtonian liquid. Can any viscosity determinations at these temperatures help in proving or at least partially confirming the existence of clusters ?

Dr. Kumar (Author) : We are building up an apparatus to determine the viscosity of the Al-Cu alloys at these temperatures and after we have carried out experimental work, we shall be in a position to discuss these points in more details. In the literature there seems to be practically no experimental observations of the changes in viscosity with temperature of these alloys. We are also trying to study the problem from the point of view of specific heat. At this moment, we are building up that apparatus also. As you said, these clusters should have some bearing on viscosity and I fully agree with you.