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Rapid solidification and decomposition of a hypomonotectic Al-Cd alloy

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Rapid solidification of Al–1.5 at % Cd alloy can lead to a wide variety of morphologies. The sequence of the morphologies with increasing foil thickness is single phase → elongated cell → hexagonal cell → dendrite. Monotectic reaction ahead of the solid–liquid interface leads to a unique distribution of the cadmium particles. Models are proposed to explain the genesis of the distribution of these particles. The study of the decomposition behaviour confirms the existence of a preprecipitation stage. The G.P. zones are found to be spherical and lead to a precipitate-free zone near grain/cell boundaries. The coarsening of the precipitates at liquid temperatures takes place by the migration and coalescence of the droplets.

1. Introduction

Rapid solidification is known to produce a variety of morphologies in two-phase systems. Almost all the studies to date deal with either eutectics or peritectics and very little is known of the effect of rapid solidification on a monotectic alloy. Depending upon the freezing conditions and the interfacial energies of the phases, a wide range of morphologies can be observed in monotectic alloys [1]. These include co-operative growth as well as complete phase separation. Recently, Ojha and Chattopadhyay [2] reported the effect of rapid solidification on an Al–In monotectic alloy and established the possibility of obtaining unique morphologies and new metastable phases in such systems. The present investigation is in continuation of the same programme and we report here the results obtained when a slightly hypomonotectic aluminium–cadmium alloy is subjected to rapid solidification.

2. Experimental procedure

The melting of the alloy was done in a graphite crucible with the help of an acetylene torch to minimize the time of melting and hence the loss of cadmium due to vapourization. However, some loss of cadmium was always noticed. With the help of careful weight loss measurements, the nominal composition of the alloy was found to be Al–1.5 at % Cd (6.27 wt % Cd). Small quantities of the homogenized alloy were rapidly solidified by the "gun technique" [3] and the resultant foils were examined directly by X-ray diffraction and transmission electron microscopic techniques. The ageing behaviour of the rapidly solidified alloy was followed by hot-stage electron microscopy using a Philips EM300 microscope.

3. Results and discussion

3.1. The as-splatted structure and morphology

X-ray diffraction analysis of the as-splatted structure shows the existence of α aluminium solid solution and cadmium only. However, transmission electron microscopy has yielded valuable information on the morphology of the Al–1.5 at % Cd alloy developed under the influence of rapid solidification.

A featureless grain structure indicating a single-phase solid solution can occasionally be observed in some small and thin regions (Fig. 1). The frequency of such observation is, however, low. Generally, in thin areas, we observe a characteristic morphology where spherical cadmium particles are aligned in rows inside the α aluminium grains (Fig. 2a). A high magnification micrograph of the same region (Fig. 2b) reveals that fine particles are

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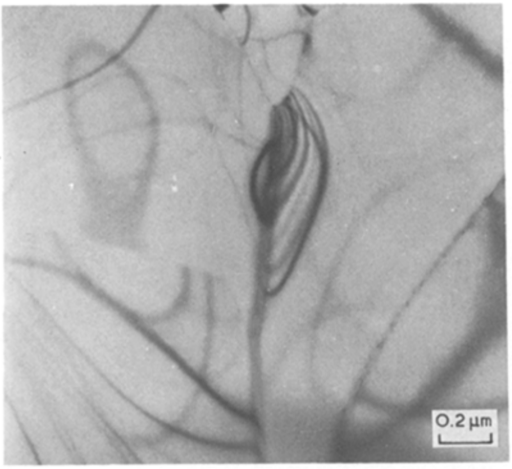

Figure 1 Electron micrograph of as-splatted Al–1.5 at% Cd showing single-phase solid solution.

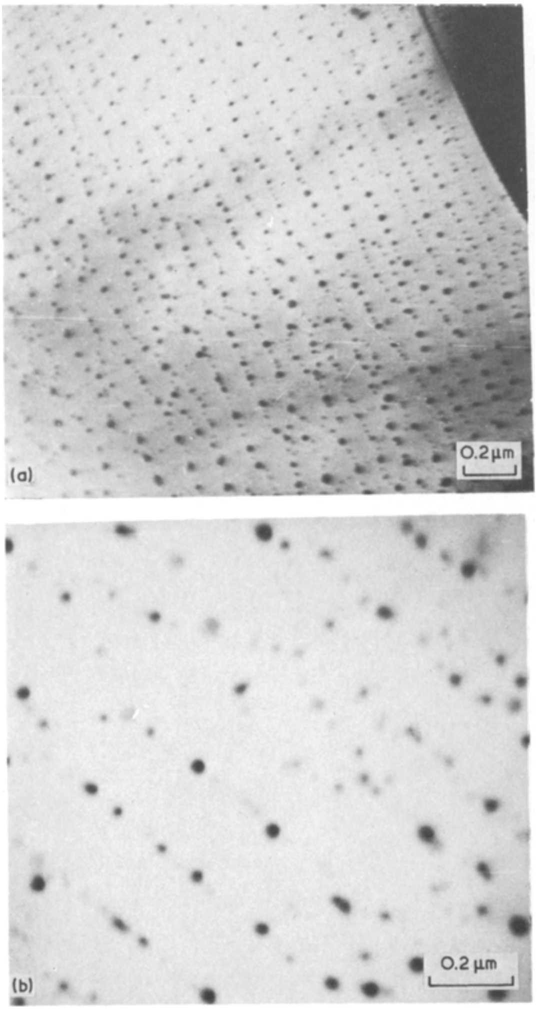

Figure 2 Regularly arranged cadmium particles in as-splatted Al–1.5 at% Cd alloy. (a) and (b) show two different magnifications.

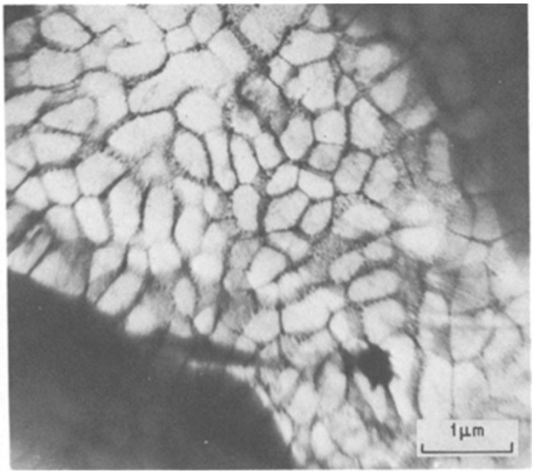

Figure 3 Hexagonal cells in the as-splatted Al–1.5 at% Cd alloy. Note the Cd particles at the cell boundaries.

actually segregated at the boundaries of the elongated cells. On the basis of the analysis of the diffraction patterns it was found that the plane of the foil is nearly perpendicular to the [0 1 1] zone axis in these regions.

The most common morphology observed in the thicker region of the foils consists of a well-developed regular hexagonal cell structure (Fig. 3). The intercellular regions in such cases reveal a drop structure indicating the monotectic reaction in the intercellular liquid. In still thicker regions, a dendritic morphology can frequently be observed (Fig. 4). Fig. 5a shows a region where the dendrites grew in the plane of the foil from all directions

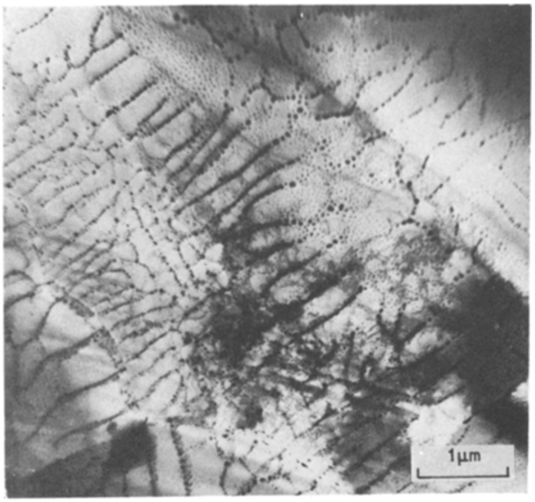

Figure 4 Dendritic morphology observed in the thicker regions of the foils.

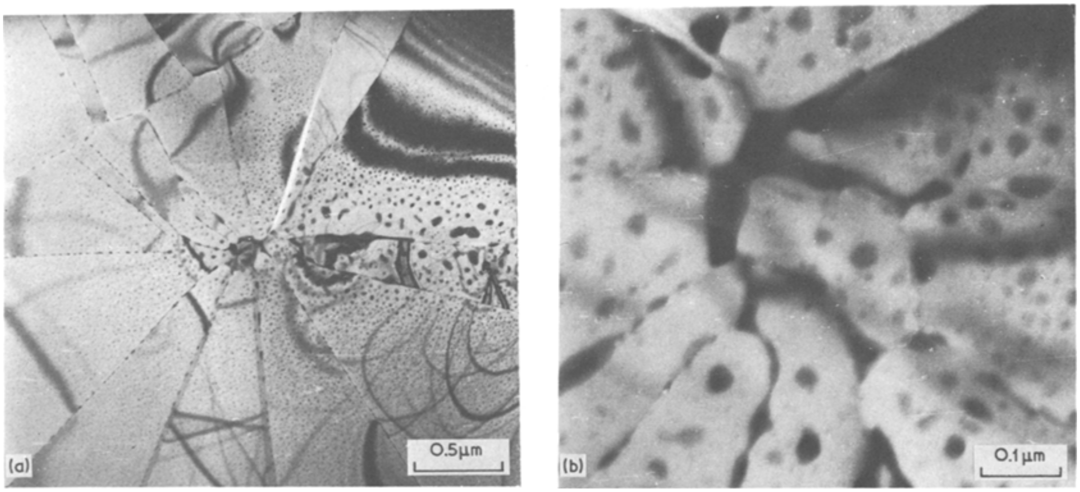

Figure 5 (a) Set of dendrites merging at the centre of the micrograph. (b) High magnification micrograph of the central region showing the nature of the cadmium at the colliding interfaces.

and merged at the centre of the micrograph. As the micrograph reveals, a large number of cadmium particles are trapped inside the dendrites as well as at the boundaries. The size of the particles increases towards the centre. Fig. 5b shows the central portion at a higher magnification. A continuous network of cadmium can be seen at the junction where the dendrites from different directions collided.

With the help of the above microstructural observations, it is possible to understand the growth mechanism of hypomonotectic Al–Cd alloy during rapid solidification. At extreme growth rates when the interface velocity is more than the rate of diffusion of the solute, the latter will be trapped in the growing matrix and it is possible to obtain a metastable solid solution. Such an extension of solid solubility has been observed in a large number of aluminium binary systems [4]. The shape of the interface in such a case will essentially be determined by the heat transfer conditions. However, as the growth rate decreases, solute will start diffusing at the interface. Physically the situation now will be analogous to that encountered in normal solidification when the plane front breaks down due to a solute boundary layer to give a cell structure [5, 6]. Thus when the solute build up is sufficient due to decrease in growth rate and hence increase in effective diffusion at the interface, we observe, predominantly, a cell structure. Morris and Winegard [7] carried out detailed investigation of the morphology of the normal cell structures. They found that crystallographic factors may play an important role in determining the morphology especially at the onset of cell formation. In the case of a ⟨1 1 0⟩ growth oriented crystal, the perturbation at the interface will be such that an elongated cell will result. The microstructures presented by the above researchers are very similar to those observed by us although the scale of microstructure is finer in our case. As the heat transfer in most of the regions of the gun-quenched foil can be expected to take place normal to the foil, the electron diffraction evidence of the ⟨1 1 0⟩ direction being normal to the foil in the regions where elongated cells are observed, further confirms the similarity. In normal solidification, an elongated cell is transitional in nature and gives way to more stable hexagonal cell configuration. The same is also true for the present case where in slightly thicker regions well-developed hexagonal cells are predominant. Fig. 6 illustrates the transformation from elongated cell to hexagonal cell as a function of increasing thickness of the foil and therefore, decreasing cooling rate. Several attempts have been made to correlate cell spacings with the solidification parameters [8, 9]. An empirical approach is to plot cell spacings as a function of $(GR)^{-1}$ where G is the temperature gradient and R is the growth rate. In many cases, a linear relation can be obtained. It is interesting to note that GR is dimensionally equivalent to the cooling rate. In a recent paper, Hunt [10] has developed a theoretical expression to correlate cell spacings with the solidification parameters. Although this treatment seems to explain the

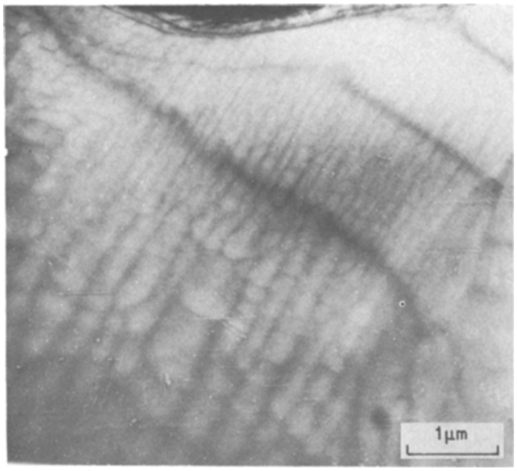

Figure 6 Formation of elongated cells and their transition to regular cells in as-splatted Al–1.5 at % Cd alloy.

experimental data, it cannot be applied directly in the present case. This is because the partition coefficient K is not constant in the present case. Rather it changes with growth rate due to the trapping of solute. Therefore, further development of Hunt's formulation is needed for any quantitative evaluation of the present situation though qualitatively the decreased cell spacing during rapid solidification can be understood in terms of high cooling rate and growth rate. Our results also indicate that with further decrease in cooling rate, i.e. in thicker regions, a cell-to-dendrite transformation takes place.

The uniqueness of the microstructure observed in the present investigation is due to the morphology of the intercellular regions. The genesis of the second-phase morphology shown in Fig. 2 lies in the monotectic reaction that has taken place in the intercellular regions. The high supersaturation of solute in these regions led to the nucleation of the second-phase liquid ahead of the interface. Uhlmann *et al.* [11] have shown that for the trapping of a second phase by a moving interface, a critical size is necessary for a given interfacial velocity. Below this size the particles will be pushed by the interface. Thus trapping will be preceded by: (a) attainment of the critical supersaturation for nucleation, (b) nucleation of the second liquid phase, and (c) growth of the nucleus to the critical size for trapping. In a steady state situation, therefore, a periodicity in the trapping event is expected provided that the critical size and intercellular regions are of similar dimensions. In such a situation only one particle can grow to the critical size at a time and become trapped. The situation has been schematically illustrated in Fig. 7, case I. This explains the characteristic rows of cadmium particles at the elongated cell boundaries

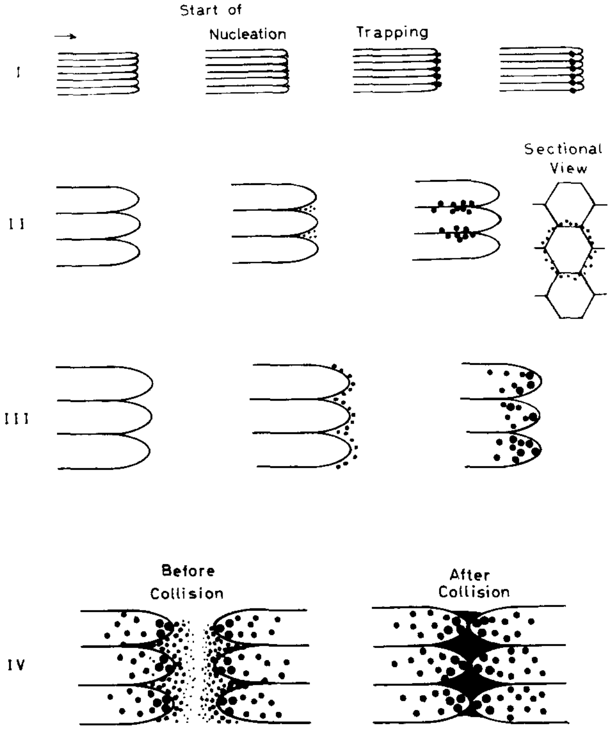

Figure 7 Schematic illustrations of the different mechanisms proposed to explain the morphologies observed in the as-splatted Al–1.5 at% Cd alloy.

of Fig. 2. The loss of exact periodicity in the rows indicate local fluctuations in the moving interfacial velocity.

However, when the intercellular regions are larger (which is associated with larger cell spacings), a number of nuclei can grow simultaneously and reach the critical size required for trapping. Fig, 7, case II shows schematically such a situation which will result in the morphology as shown in Fig. 3 where a large number of droplets of cadmium may be seen in the intercellular regions. In the two cases discussed so far, it is implicitly assumed that sufficient supersaturation for the nucleation of the second liquid is available only at the intercellular grooves. With the progressive fall in growth rate or cooling rate, the nucleation of the second liquid (cadmium) will take place at all points along the moving interface because of the accumulation of sufficient solute. When these droplets exceed the critical size for trapping, the interface will trap them inside the matrix and a randomly distributed second-phase morphology will result (Fig. 7, case III, Fig. 5). A cell-to-dendritic transition also takes place at this point in the present Al–Cd alloy (Fig. 4). As the dendrites from each side approach one another, their growth rates decrease due to the large accumulation of the latent heat from all the interfaces. This is reflected in the increasing size of the trapped cadmium particles, as the critical size will increase with decrease in the interfacial velocity. When the interfaces are about to collide with each other, the second liquid particles which have sub-critical size are pushed by each interface and coalesce rapidly to form a thin continuous layer separating the dendrites (Fig. 5b). This situation is schematically illustrated in Fig. 7, case IV.

3.2. The precipitation of cadmium from solid solution

In most of the cases, existence of very fine precipitates can be observed inside the cells or dendrites (Fig. 8). The coarser particles in the micrograph are due to the trapping of monotectic second liquid and fine particles are due to precipitation. In places where precipitates are barely resolvable, diffraction patterns reveal the existence of a diffuse halo around the fundamental reflections of aluminium solid solution (Fig. 9).

Studies on the effect of cadmium as a ternary

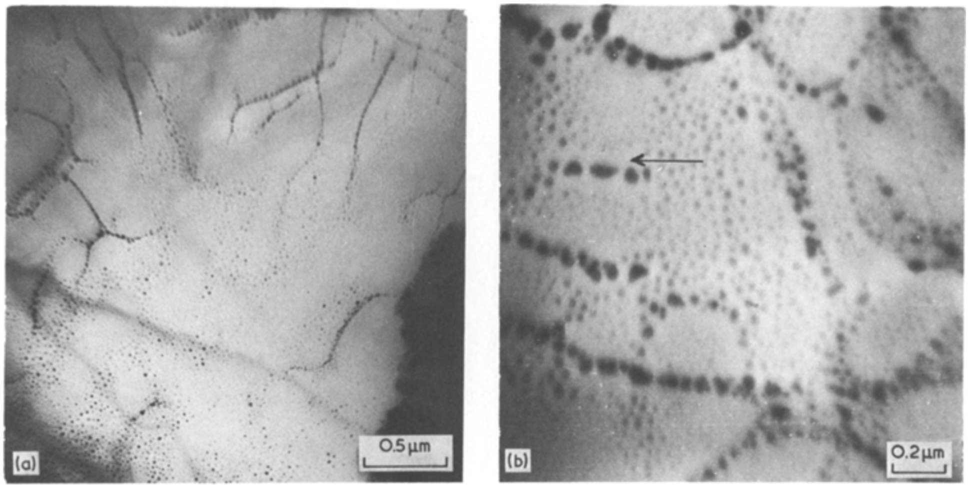

Figure 8 Precipitation of fine cadmium inside the aluminium matrix, (a) at lower magnification, and (b) at higher magnification showing the interior of the cell. The denuded zone is marked by the arrow.

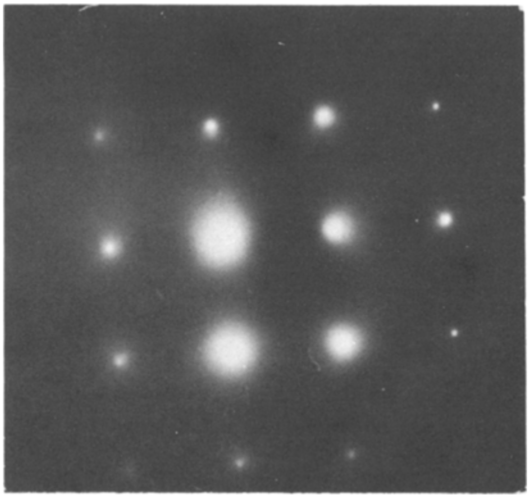

Figure 9 Electron diffraction pattern showing diffuse halo around the main spots due to GP zones.

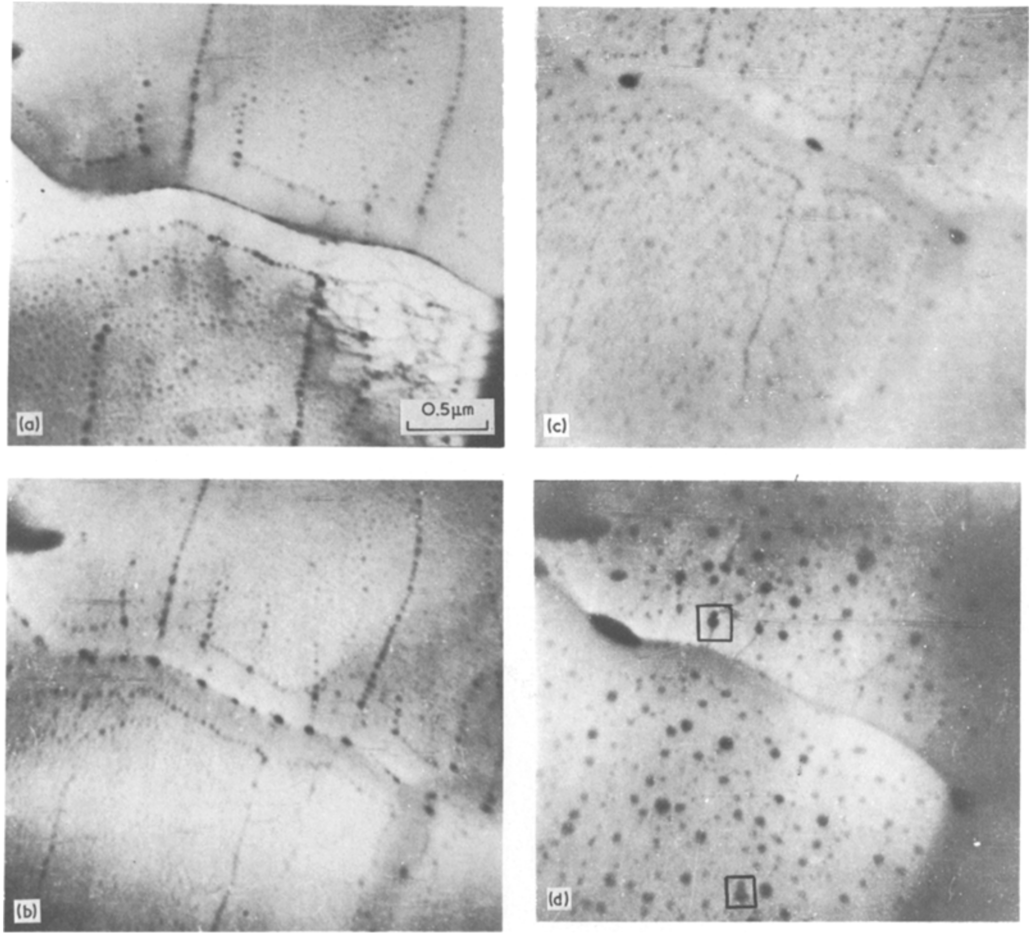

Figure 10 (a) Precipitate-free zone in as-splatted Al–1.5 at% Cd alloy. (b) Same area as in (a). Heated *in situ* at 300° C for 15 min. (c) Same as above, after ageing for 1 h at 300° C. (d) As (c) and heated to 350° C and held for 30 min. Note the coalescence of the migrating droplets.

addition to aluminium–copper binary precipitation hardening systems [12–14] indicate that cadmium exerts a strong influence on the kinetics of precipitation due to a strong vacancy–cadmium interaction. On the basis of hardness and resistivity measurements on aluminium–1 wt% cadmium, Ceresara and Fiorini [15], in addition to confirming the above, have concluded that a preprecipation stage exists in the dilute aluminium–cadmium alloys. The diffuse halo observed around the matrix spots in our work provides the metallographic evidence in support of their conclusion regarding the existence of spherical zones. The hexagonal cadmium nucleates on these growing zones. The transition seems to be continuous and we are unable to confirm or repudiate the existence of the transitional phase Cd′ observed by Silcock [16] owing to difficulties in obtaining an adequate number of good diffraction patterns.

Further evidence supporting our conclusion concerning the existence of zones can be found in the observation of the precipitate free zones (PFZs) in our foils in both cell and grain boundaries (Fig. 8b and 10a). These can be explained on the basis of the model proposed by Lorimer and Nicholson [17]. According to this model the size of the zones near the boundaries, which may act as vacancy sinks, will be smaller due to a smaller number of quenched-in excess vacancies present in these regions. As the heterogeneous nucleation of the precipitate particles on zones requires a critical size of the latter, a denuded zone may result in these regions. It must be pointed out, however, that the occurrence of a solute-depleted region due to the coarsening of segregates at the cell boundary in the solid state cannot be ruled out completely. In fact, Spalding *et al.* [18] have shown that considerable thickening of Al_2Cu

platelets in Al–Al_2Cu as-solidified eutectic occurs during solid state coarsening. However, observation of PFZs at the grain boundaries which are relatively free of precipitates (Fig. 10a) leads to the conclusion that, in the present case, zone formation is responsible for the observations of PFZs.

In order to study the decomposition behaviour further, *in situ* heating experiments were carried out in the electron microscope. Fig. 10b and c show the same area after 15 min and 1 h at 300° C. It can be seen that the heterogeneous nucleation of cadmium has taken place at the grain boundaries with very few precipitates nucleating and growing at PFZ. In these regions (PFZs) reversion of zones most probably took place at this temperature and thus nucleation sites are not available for cadmium. Prolonged ageing led to the coarsening of the previously nucleated and favourably oriented cadmium precipitates in the matrix as well as at the grain boundaries. Fig. 10d shows the resulting micrograph when the same area is heated to 350° C and held for 1 h. At this temperature, the precipitates undergo a solid-to-liquid transition as well. Hot-stage electron microscopy confirms that the coarsening observed is due to the thermal migration of the liquid phase inside the solid matrix and consequent coalescence (note the precipitates marked by squares). At the grain boundaries they migrate to those areas where it is easier to balance their surface energies (e.g. nodal points).

The observation of large amounts of cadmium precipitates in rapidly solidified foils indicates that the kinetics of nucleation of these particles on zones is fairly rapid and the critical size of the zones required is small. Even faster rates than normal are expected in the present case if an extension of solid solubility of cadmium in aluminium is conceded. The metastable solid solution that may be obtained will provide a greater chemical driving force for the cadmium to precipitate.

4. Conclusions

On the basis of the present investigation the following conclusions can be drawn:

(a) rapid solidification of a hypomonotectic alloy of Al–1.5 at % Cd leads to a wide variety of morphologies. They can be rationalized in terms of the occurrence of a single phase → cellular → dendritic transition with increasing thickness of the foil and hence with decreasing cooling rate;

(b) the transition can be explained qualitatively in terms of the relative magnitudes of growth velocity and diffusivity which will control the solute layer in front of the moving interface;

(c) both elongated and hexagonal cells can exist and their origin can be explained with the help of a normal solidification mechanism;

(d) the as-solidified microstructures are characterized by unique second-phase morphologies. It is shown that they can be related to the monotectic reaction ahead of the interface and prevailing local conditions for trapping of the monotectic liquid phase by the moving interface;

(e) decomposition of aluminium solid solution leads to the formation of spherical zones;

(f) equilibrium cadmium precipitates nucleate on the zones and as a result precipitate-free zones are observed near the boundaries;

(g) the precipitate coarsens at higher temperature. At the temperature where the precipitate is liquid, coarsening takes place by the coalescence of the migrating droplets.

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