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Solidification of undercooled cadmium–zinc eutectic melts

S. N. OJHA*, T. R. ANANTHARAMAN
Department of Metallurgical Engineering, Banaras Hindu University, Varanasi-221005, India

P. RAMACHANDRARAO
School of Materials Science and Technology, Banaras Hindu University, Varanasi-221 005, India

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Molten specimens of Cd–Zn eutectic alloy (26.50 at.% Zn) were undercooled by the glass-slag technique using glass-forming $ZnCl_2$ as the slag. The microstructure of the solidified samples, weighing about 20 g each, was found to be a function of the undercooling produced. At lower undercoolings the microstructure consisted of supersaturated primary cadmium dendrites co-existing with the eutectic, while at higher coolings duplex structures were observed. Possible causes for the differences in microstructure are discussed with due importance given to the recorded recalescence effects.

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1. Introduction

There have been several exceptions to the Hume–Rothery criteria for the formation of unbroken series of solid solutions in binary alloy systems, notable amongst them being Cd–Zn and Cu–Ag, both of which are characterized by eutectic reactions. The advent of rapid solidification techniques enabled the attainment of complete metastable solid solubility in the case of Cu–Ag [1] alloys, but Cd–Zn had continued to be exceptional [2]. Even solidification at cooling rates as high as 10^6–10^9 K sec^{-1} results in the formation of solid solutions only over a restricted range of compositions [3, 4]. The failure to obtain homogeneous solid solutions over the entire composition range has often been attributed [5] to an unfavourable composition dependence of T_0, where T_0 is the temperature where the liquid and solid of a given composition have equal free energies. Altman and Lohberg [6] suggested that in the case of techniques involving ejection of melt by a shockwave, the very process of ejection could induce nucleation of the melt by cavitation and limit the undercooling attained by rapid solidification. Perepezko *et al.* [7] have shown that the splat-cooling technique is not suitable for retaining metastable solid solutions in low-melting alloys. They argued that the presence of defects, surface impurities and small thickness of the foil obtained by these techniques enhance the kinetics of precipitation. On the other hand, undercooling in bulk is free from these defects. Thus in Sn–Bi alloys they could show evidence for formation of undecomposed metastable solid solution at room temperature and at compositions, where splat-cooled samples showed only a decomposed microstructure.

Experiments in our laboratories have shown that it is possible to reproduce results obtained by rapid solidification by conventional undercooling experiments [8]. The present communication reports results obtained on undercooling a Cd–Zn eutectic alloy by the glass-slag technique and compares them with data obtained by traditional rapid solidification techniques.

2. Experimental details

The eutectic alloy (26.50 at.% Zn) was prepared by melting and casting weighed quantities of high-purity (> 99.9999%) Cd and Zn in an evacuated

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*Present address: Research and Development Centre, Steel Authority of India Ltd., Ranchi-834 002, India.

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Pyrex glass tube. The tube was shaken thoroughly to ensure proper mixing of the constituents and then quenched in water for rapid chilling to obtain a homogeneous cast microstructure. The undercooling experiments were conducted by repeatedly melting and freezing the alloys in a Corning glass tube (1 cm diameter) under cover of $ZnCl_2$. The cooling rate was invariably maintained (in the range of 5 to $10\,K\,min^{-1}$). Each specimen weighed around 20 g.

A fine chromel–alumel thermocouple was used to measure the thermal changes associated with undercooling the melt. The hot junction of the thermocouple was tightly fitted to the inward projection at the bottom of the Corning glass tube (5 cm long and 1 cm diameter). The output of the thermocouple was fed to a sensitive strip-chart recorder which was connected in parallel to a high impedence microvoltmeter, which provided a visual secondary check on the output of the thermocouple. In each experiment the thermocouple was calibrated with reference to the melting point of pure tin. Thus the accuracy of measurements in temperature was ensured and estimated to be better than ± 2 K.

$ZnCl_2$ slag was found suitable for undercooling Cd–Zn alloys. It melts at 556 K which is greater than the melting point of Cd–Zn eutectic (539 K). However, it is well known that $ZnCl_2$ is a relatively easy glass former [9] and undercools drastically, the glass transition temperature being only 375 K. The maximum solubility of Zn in $ZnCl_2$ is 0.18 mol% of 773 K, but increases rapidly to 1.65 mol% at 943 K [10]. Therefore, superheating of the melt was limited to 50 to 60 K above the eutectic temperature to ensure that Zn from the alloy does not dissolve in $ZnCl_2$ to any appreciable extent. Further the slag was observed to be very effective in removing impurities from the melt. All surface contaminations in the cast alloy were removed by the slag even in the first melting under it. The glass formation characteristics of $ZnCl_2$ were thus fully exploited in undercooling the Cd–Zn eutectic alloys.

The quantity of slag was kept just sufficient to form a thin layer at the bottom of the crucible and a column of about 1 cm height above the melt. Care was taken to avoid the use of larger quantities of slag, since $ZnCl_2$ is known to crystallize (rather than undercool) on cooling in air when the quantity exceeds 10 g [11]. Since the molten metal sinks in the slag the crucible was first charged with $ZnCl_2$ and the metal was introduced after melting $ZnCl_2$. The undercooled alloys were either slowly cooled or quenched from a desired temperature. In either case, the samples were sectioned and studied under a Leitz optical metallograph.

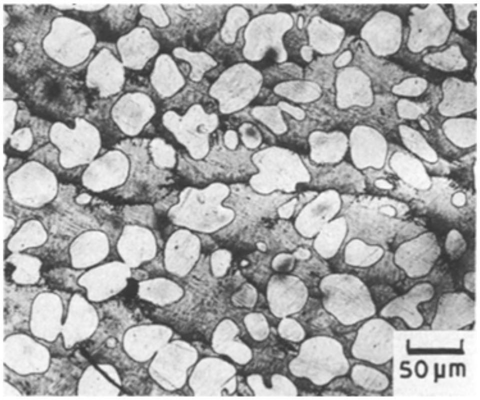

Figure 1 Micrograph of a Cd–Zn eutectic alloy solidified after undercooling by 22 K exhibiting primary dendrites co-existing with the eutectic.

3. Results and discussion

The maximum undercooling achieved as determined from time–temperature plots of the Cd–Zn eutectic alloy was 34 K. A rapid recalescence was observed in the melt due to release of latent heat of fusion during nucleation and subsequent growth of the crystals. When a 20 g melt undercooled by 34 K it showed 16 K recalescence, whereas recalescence to the extent of 5 K could be detected when the same melt nucleated from an undercooling of 22 K. The microstructural details of the alloys nucleated at two different temperatures also showed significant differences.

Fig. 1 shows the microstructure of the eutectic alloy quenched from an undercooling of 22 K. The most striking features of this micrograph is the existence of a large volume fraction of primary Cd-rich phase in comparison to the as-cast alloy (Fig. 2). Quantitative metallographic studies indicated that the primary phase accounts for 26% of the volume. Also this phase displays almost spherical morphology and rarely reveals any tendency to assume characteristic dendritic shapes. Even at a high magnification (× 1000) no internal structure is observed in them (Fig. 3a). On the other hand, when allowed to cool slowly after 22 K undercooling, the primary phase is fully decomposed. At higher magnification there is unmistakable evidence for precipitation inside the

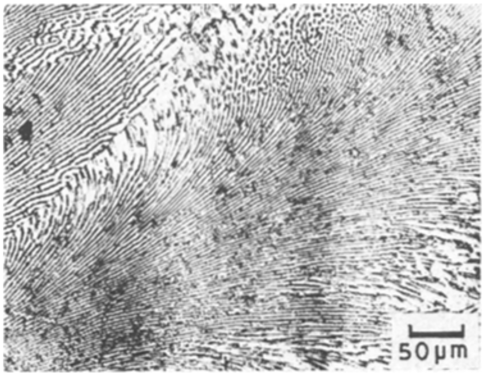

Figure 2 As-cast microstructure of a Cd–Zn eutectic alloy displaying typical lamellar morphology.

primary phase region (Fig. 3b). The Cd-rich phase boundary is decorated by the presence of closely spaced Zn rods. When the alloy was quenched after undercooling to 34 K, a particulate kind of microstructure was observed in certain regions (Fig. 4a), while similar regions co-existed with the eutectic in other parts of the specimen (Fig. 4b).

Micrographs obtained from alloys undercooled by 22 and 34 K (Figs 3 and 4), respectively, demonstrated significant differences on solidification from these two undercooled states. Whereas the alloy solidified at 517 K (22 K undercooling) revealed a well-delineated primary phase co-existing with the eutectic (Fig. 1), the bulk of the alloy solidifying at 505 K (34 K undercooling) showed a distinctly different particulate microstructure, which sometimes co-existed with that of the eutectic. Since X-ray diffraction experiments showed only the presence of Cd and Zn, it can be concluded that the particulate microstructure contains these two phases only.

The existence of primary dendrites in an alloy of eutectic composition is generally explained on the basis of a shift in eutectic composition due to undercooling of the melt. With reference to a binary equilibrium diagram, it is widely accepted that on undercooling, the solid which deposits will have its composition given by the extended metastable solidus line [13]. The change in composition of the primary phase then results in a significant change in the volume proportion of the phases. The first solid nucleated in the undercooled melt is supersaturated with respect to the solute. During recalescence rapid diffusion of the solute and partial remelting of the metastable phases formed at the beginning occurs, the remaining melt then approaching equilibrium freezing temperature and solidifying with near-normal equlibrium microstructure.

The process of recalescence is quasi-adiabatic and therefore it is not possible to suppress it completely. Attempts can only be made to minimize its impact by rapidly chilling the melt [14]. The specimens quenched in the present study immediately after nucleation do not therefore exhibit any signs of precipitation inside the primary phase (Fig. 3a), while those allowed to cool slowly after nucleation show precipitates (Fig. 3b). The extent of precipitation is too large to be associated with changes in equilibrium solid solubility of Zn in Cd with temperature. Hence, it follows that considerable metastable extension of Zn solute in Cd has occurred. Boswell and Chadwick [12] studied rapidly solidified Cd–Zn alloys by electron metallography. They contend that massive solidifi-

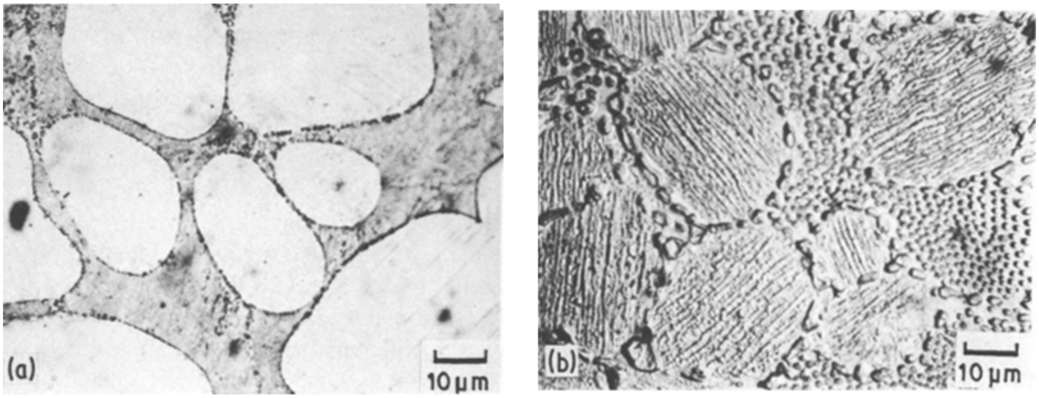

Figure 3 Micrograph of Cd–Zn eutectic alloy undercooled by 22 K and solidified by (a) quenching showing single-phase primary solid solution, and (b) slow cooling showing precipitation in the primary phase.

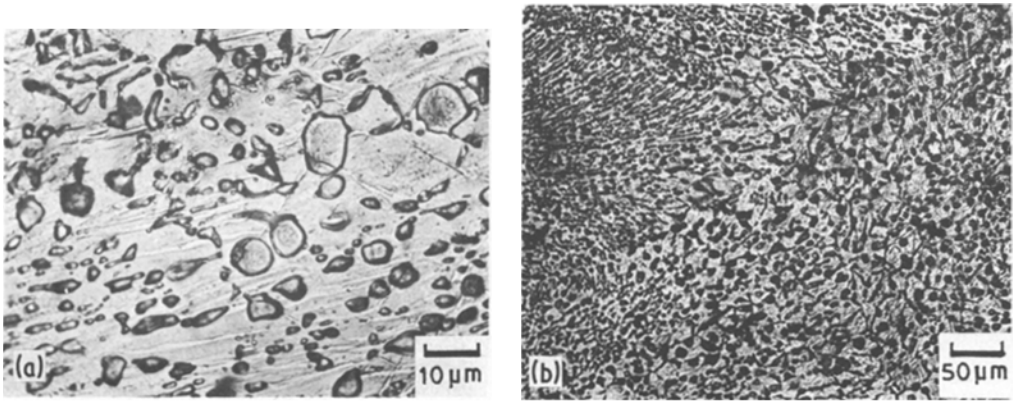

Figure 4 Micrograph of Cd–Zn eutectic alloy solidified by quenching after undercooling by 34 K (a) showing particulate morphology, and (b) exhibiting particulate morphology co-existing with normal eutectic morphology.

cation of the eutectic alloy without solute partitioning is possible at high cooling rates. However, they found that the single phase resulting from such experiments rapidly decomposed at room temperature and gave rise to two-phase grains with homogeneously distributed solute-rich precipitates in the solvent-rich matrix.

In an earlier investigation by Armstrong and Hellawel [13] also similar microstructures were observed in an Al–Ag eutectic alloy frozen at very high growth rates. These authors have provided convincing evidence for the discontinuous precipitation of Ag–Al on a coarse scale. In the background, traces of a dendritic structure could be seen, which they termed ghost dendrites. It was believed that in the Al–Ag system such lamellar precipitation is possible because primary Al and eutectic Al have the same orientation and also prefer the same highly stable configuration in both the eutectic and solid solution. According to these investigators, the whole solidification process is conditioned by the need for achieving equilibrium volume fractions and compositions of the constituent phases.

Precipitation within the Cd-rich phase observed in this work can also be associated with post-solidification changes. Evidence for solid-state precipitation stems from the fact that the inter-lamellar spacing of the eutectic is 2 to 5 μm in the matrix as against very fine spacing of 0.2 to 0.5 μm inside the primary phase. This excludes the possibility of migration of eutectic interface into the primary phase in the solid state, as suggested in case of the Al–Ag eutectic [13]. It is known that the orientation relationship between Cd and Zn in eutectic is $(0\,0\,0\,1)_{\mathrm{Cd}} \parallel (0\,0\,0\,1)_{\mathrm{Zn}}$ and $\langle 0\,1\,1\,0\rangle_{\mathrm{Cd}} \parallel \langle 0\,1\,1\,0\rangle_{\mathrm{Zn}}$ [15]. Boswell and Chadwick [12] found that there is a well-defined basal–basal orientation relationship when Zn precipitates from Cd, the relationship being $(0\,0\,0\,1)_{\mathrm{Cd}} \parallel (0\,0\,0\,1)_{\mathrm{Zn}}$ and $\langle 1\,1\,\bar{2}\,0\rangle_{\mathrm{Zn}} \parallel \langle 1\,1\,\bar{2}\,0\rangle_{\mathrm{Cd}}$. This close identity may be responsible for the similarity of the eutectic morphology and lamellar precipitation inside the primary phase. It is interesting to note the shape of the lamellae formed inside the Cd-rich phase (Fig. 3b). These have a tendency to break down and take on globular shape, possibly to minimize the interfacial energy and acquire a stable structural configuration during recalescence.

The particulate microstructure (Fig. 4) obtained in the alloy solidifying at 505 K could have arisen either due to formation and decomposition of a metastable solid solution or by independent nucleation of Cd and Zn. The first of these explanations has earlier been advanced by Kattamis [14], who studied undercooled Ni–Sn eutectic alloys. Boswell and Chadwick [12] have also argued, after considering several possible mechanisms to explain similar microstructures in rapidly solidified Cd–Zn alloys, that the massively solidified metastable solid solution decomposes rapidly at room temperature and results in a microstructure consisting of solute-rich, plate-like precipitates in a solvent-rich matrix. The microduplex structures observed by them in some of the areas of splat-quenched foils were considered to develop via interdendritic precipitation in thicker regions, whereas in thin regions these might have resulted from independent nucleation of both Cd and Zn solid solutions. The argument here is that the surface of the thin foils can catalyse independent nucleation at relatively low undercoolings. Since similar microstructures were observed in the present work in the central region of bulk samples, it is difficult to support the hypothesis of independent nucleation of Cd and Zn due to surface effects. The gradual change from a totally particulate microstructure to one in which both particulate and eutectic morphologies co-exist (Fig. 4a), suggests that the first regions to nucleate lead to the particulate microstructure, but the recalescence resulting from this reduces the undercooling and favours the formation of equilibrium eutectic regions. However, the scale of microstructure is too coarse to have formed by precipitation at room temperature. It is likely that the decompositon occurs at a relatively higher temperature and is caused by the recalescence during solidification. This microstructure could also be considered as a degenerate eutectic. However, it is difficult at this stage to establish the actual mechanism unequivocally.

4. Conclusions

The present investigations have shown that the microstructure of solid Cd–Zn eutectic alloy is a function of the undercooling achieved in the melt. There is evidence to suggest that progressive supersaturation of the primary phase occurs with increasing undercooling of the melt. The supersaturated solid solutions thus obtained are metastable and either undergo lamellar decomposition or give rise to particulate morphologies.

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