

# Crystallographic orientation relationships in the tin–lead–cadmium ternary eutectic

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The orientation relationships developed between the phases during unidirectional growth of the tin–lead–cadmium ternary eutectic have been determined by electron diffraction to be:

$$\begin{aligned} \text{Lamellar interfaces} & \parallel (0\bar{1}10)_{\text{Sn}} \parallel (1\bar{1}1)_{\text{Pb}} \parallel (0001)_{\text{Cd}} \\ \text{Growth direction} & \parallel [0001]_{\text{Sn}} \parallel [011]_{\text{Pb}} \parallel [2\bar{1}\bar{1}0]_{\text{Cd}}. \end{aligned}$$

It is concluded that the simple, parallel morphology exhibited by this alloy is a consequence of the development of mutually compatible lead–cadmium and lead–tin interfaces of low energy with close-packed directions in all three phases parallel to the growth direction. Orientation relationships for the lead–cadmium and tin–cadmium binary eutectics are also reported.

## 1. Introduction

The rod or lamellar morphologies observed in binary non-faceted/non-faceted metallic eutectics are apparently favoured because of the short diffusion distances involved and hence the relative ease with which solute can be redistributed ahead of the solid–liquid interface during growth. These morphologies, however, generate large interfacial areas per unit volume of crystal and theories of eutectic growth suggest that, in order to minimize the total energy of the structure, the lamellae will develop with interphase boundaries of low energy. In fact, reported habit planes in lamellar eutectics are generally close-packed high-symmetry planes in both phases and rational orientation relationships are frequently observed.

The growth morphologies of ternary eutectics are generally more complex than those of binary systems. Even for regular eutectics where the component binary morphologies are simple rod or lamellar, the ternary structure may consist of rod–lamellar combinations, non-parallel lamellae or more random configurations [1–3]. In addition to the fact that solute redistribution during growth will be more severe in these cases compared to binary growth, reducing the total energy of the structure by selection of suitable planes and

directions in the interphase boundaries will be more problematical because of the complication of attempting simultaneously to satisfy orientation relationships between more than two phases.

The tin–lead–cadmium eutectic is unusual in that its morphology is relatively simple, growing with mutually parallel lamellae of the three phases. The lamellar sequence however, is of the form ABCB rather than the superficially more obvious ABCA (Fig. 1). Orientation relationships in this system have not previously been reported and are of interest since they may provide further evidence of the importance of low energy configurations in determining the growth morphologies of aligned structures.

## 2. Experimental work

Rods of the ternary eutectic, 5 mm diameter, were prepared from high-purity materials using the vertical Bridgman technique. The crystals were grown in Pyrex tubes at a rate of 0.09 mm sec<sup>-1</sup> and with a temperature gradient in the melt ahead of the interface of approximately 4 K mm<sup>-1</sup>. After removal from the tubes, the rods were machined to 3 mm diameter in a miniature lathe and discs were then spark-machined from them. These discs were carefully ground to a

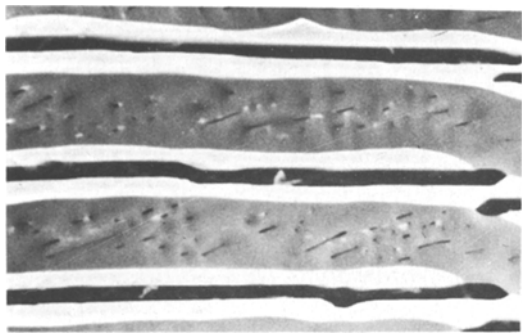


Figure 1 Microstructure of the tin-lead-cadmium eutectic. Tin-rich phase grey, lead-rich phase white and cadmium-rich phase black. The plate-like precipitate in the tin-rich phase is believed to be the result of a eutectoid reaction. SEM  $\times 12\,000$ . Transverse section.

thickness of 0.2 mm and foils prepared for the transmission microscope using a Tenupol jet polisher and electrolytes based on perchloric acid, glycerol, ethanol and water. Uniform thinning of the discs proved to be very difficult because of the different reactivities of the three phases in the structure to any of the polishing solutions used. It was therefore not possible to produce foils with electron-transparent regions containing all three phases side-by-side and hence some degree of uncertainty must exist in the reported results. However, foils usually contained regions from which electron diffraction patterns could be obtained for at least one of the phases and, by varying the concentrations of reagents in the electrolyte, each of the three phases was

successfully thinned and characterized in terms of a dominant crystal orientation.

The foils were sections transverse to the growth direction of the crystal and were examined in the untilted condition. The lamellar interfaces were assumed, in the analysis of electron diffraction patterns, to be normal to the foil surface.

Since no crystallographic information appears to be available in the literature for the lead-cadmium binary eutectic, orientation relationships were also determined for this system using a crystal grown at  $0.07\text{ mm sec}^{-1}$  and prepared in a manner similar to that for the ternary eutectic.

### 3. Results

Fig. 1 shows the microstructure of the ternary eutectic. Energy-dispersive X-ray analysis in the scanning electron microscope was used to confirm the identity of the three phases in the structure and typical electron diffraction patterns from the phases are shown in Figs. 2 to 4. Although these diffraction patterns were the dominant ones, less frequently patterns with  $[011]$ ,  $[112]$  and  $[0001]$  zone axes were observed for the tin-, lead- and cadmium-rich phases, respectively. Indexing of the cadmium- and lead-rich phases was straightforward but that for the tin-rich phase requires some explanation.

The pattern of the tin-rich phase could be indexed only by assuming the structure to be body-centred tetragonal, the normal low-temperature form of the tin lattice. However,

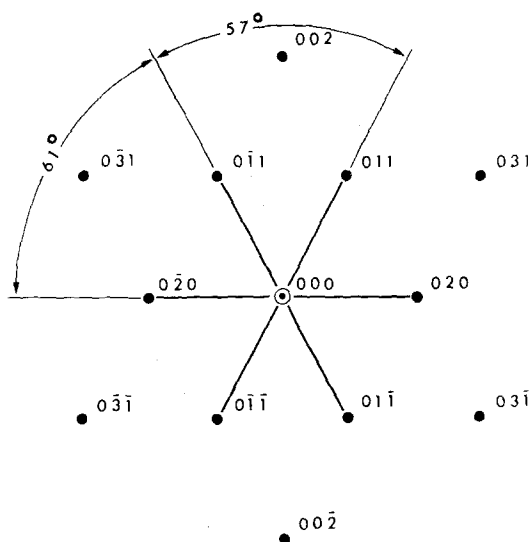


Figure 2 Electron diffraction pattern from the tin-rich phase in the ternary alloy. Zone axis  $[100]_{\text{Bct}}$

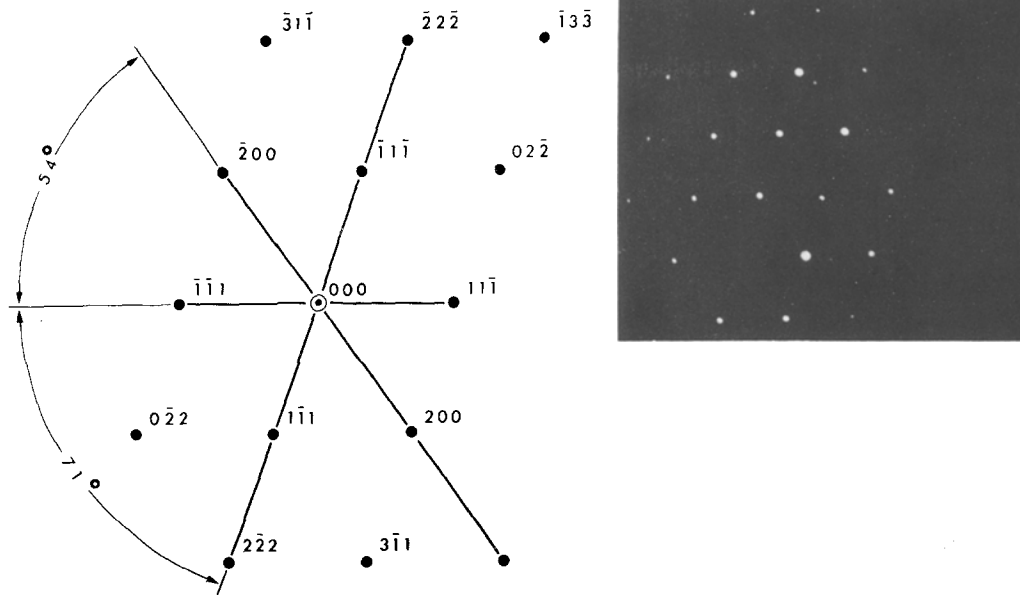


Figure 3 Electron diffraction pattern from the lead-rich phase in the ternary alloy. Zone axis  $[011]_{fcc}$ .

as may be seen in Fig. 1, there is evidence of parallel, plate-shaped precipitate in the tin-rich phase. The appearance of these precipitates closely resembles that described by Racek *et al.* [4] in the tin-cadmium binary eutectic and identified as cadmium-rich plates produced by a eutectoid reaction at 406 K. Samples of the ternary eutectic were examined in a Mettler TA 3000 differential scanning calorimeter and,

on heating, an endothermic reaction was observed at 405 K which strongly suggests that a eutectoid reaction also occurs in the ternary alloy. In the binary case, the eutectoid reaction transforms the structure of the tin-rich phase from the high-temperature hexagonal form to body-centred tetragonal and it may be assumed that a similar transformation occurs in the ternary system. Since it is experimentally difficult to analyse

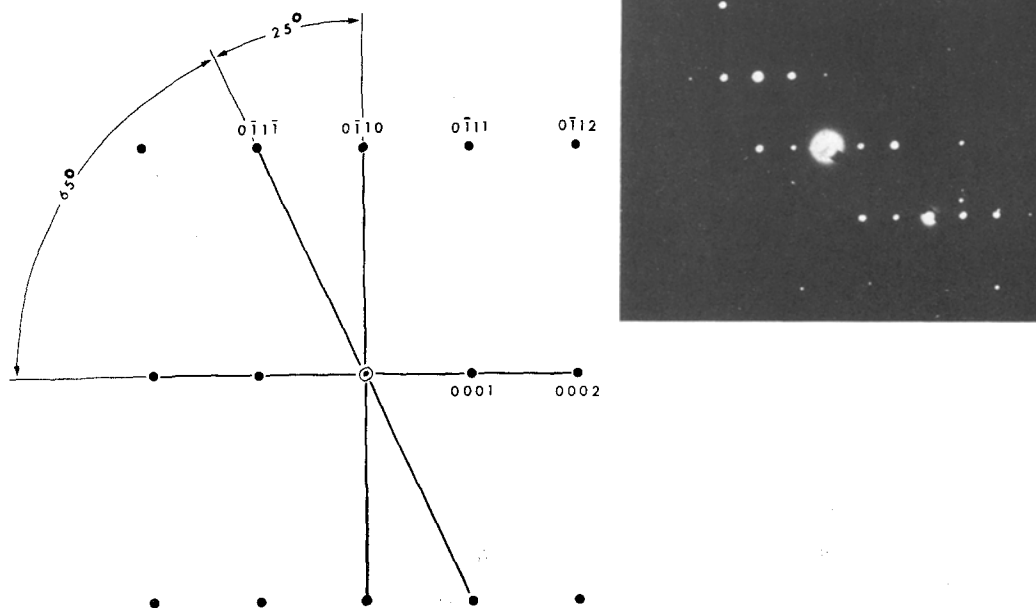
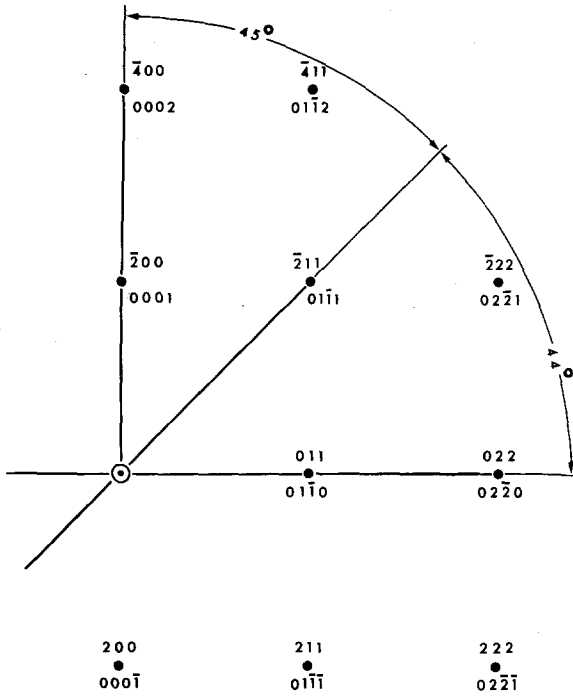


Figure 4 Electron diffraction pattern from the cadmium-rich phase in the ternary alloy. Zone axis  $[2\bar{1}\bar{1}0]_{hex}$ .

Figure 5 Electron diffraction pattern from the tin-rich phase in the tin-cadmium binary alloy. Zone axis  $[0\bar{1}1]_{bct}$  or  $[2\bar{1}\bar{1}0]_{hex}$ .



the hexagonal tin-rich phase at elevated temperature or to retain it at low temperatures, information on its orientation during growth can only be inferred from the orientation of the room-temperature body-centred tetragonal form.

In a previous investigation [5], samples of a tin-cadmium binary eutectic had been examined to determine the orientation relationship in this system. It was found that the tin-rich phase was characterized by an electron diffraction pattern (Fig. 5) which could be indexed equally well as either body-centred tetragonal or hexagonal, implying the existence of the following simple orientation relationship between the two tin-rich polymorphs:

$$\begin{aligned} (0001)_{hex} &\parallel (100)_{bct} \\ (0\bar{1}10)_{hex} &\parallel (011)_{bct} \\ [2\bar{1}\bar{1}0]_{hex} &\parallel [0\bar{1}1]_{bct} \end{aligned}$$

In the case of the ternary alloy, the dominant body-centred tetragonal pattern indicated that:

$$\begin{aligned} \text{lamellar interface} &\parallel (011)_{bct} \\ \text{and} \\ \text{growth direction} &\parallel [100]_{bct} \end{aligned}$$

Assuming that the hexagonal to body-centred tetragonal transition occurs in the ternary by a eutectoid reaction, the following orientation of the hexagonal tin-rich phase can be derived from

the relationship given above:

$$\begin{aligned} \text{lamellar interface} &\parallel (0\bar{1}10)_{hex} \\ \text{growth direction} &\parallel [0001]_{hex} \end{aligned}$$

Combining this result with the observed orientations of the other two phases yields:

#### *Sn-Pb-Cd eutectic*

$$\begin{aligned} \text{lamellar} \\ \text{interfaces} &\parallel (0\bar{1}10)_{Sn} \parallel (1\bar{1}1)_{Pb} \parallel (0001)_{Cd} \\ \text{growth} \\ \text{direction} &\parallel [0001]_{Sn} \parallel [011]_{Pb} \parallel [2\bar{1}\bar{1}0]_{Cd} \end{aligned}$$

A typical diffraction pattern obtained for the lead-cadmium binary eutectic is shown in Fig. 6. The orientation relationship determined for this system was found to be:

#### *Pb-Cd eutectic*

$$\begin{aligned} \text{lamellar interface} &\parallel (1\bar{1}1)_{Pb} \parallel (0001)_{Cd} \\ \text{growth direction} &\parallel [011]_{Pb} \parallel [2\bar{1}\bar{1}0]_{Cd} \end{aligned}$$

The complete relationship for the tin-cadmium system was determined [5] as:

#### *Sn-Cd eutectic*

$$\begin{aligned} \text{lamellar interface} &\parallel (0\bar{1}10)_{Sn} \parallel (0001)_{Cd} \\ \text{growth direction} &\parallel [2\bar{1}\bar{1}0]_{Sn} \parallel [10\bar{1}0]_{Cd} \end{aligned}$$

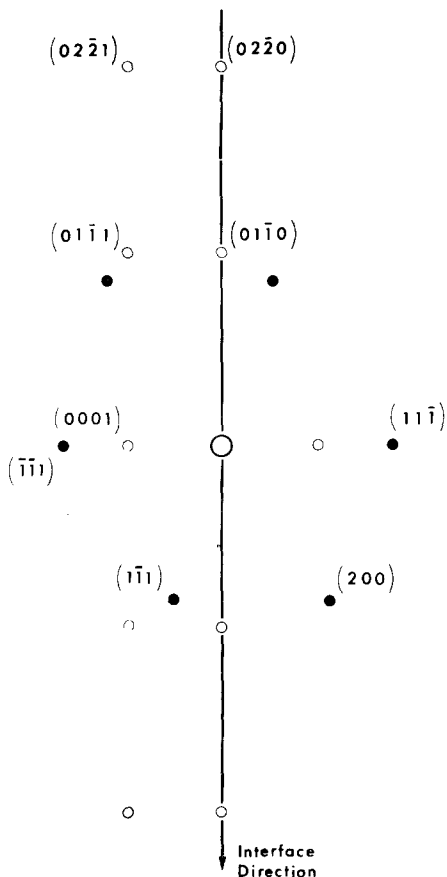


Figure 6 Electron diffraction pattern from the lead and cadmium phases in the lead-cadmium binary alloy. Zone axis  $[011]_{\text{Pb}}$  and  $[2\bar{1}\bar{1}0]_{\text{Cd}}$ .

#### 4. Discussion

The lamellar sequence adopted by this ternary eutectic is, at first sight, difficult to reconcile with the concept of minimizing the interfacial energy of the structure since, for the same interlamellar spacing, it generates one extra interface per unit volume of crystal compared with the ABCA sequence. Cooksey and Hellowell [1] have pointed out, however, that this sequence reduces from three to two the types of lamellar interface in the structure and therefore allows a greater possibility of simultaneously satisfying preferred orientation relationships between the phases in contact across the lamellar interfaces. Delamore and Hill [6] have also noted that the solute concentration profiles in the liquid ahead of the growing interface are symmetrical about the A- and C-phases in the ABCB sequence and that this would be expected to lead to easier solute redistribution during growth.

Of the three possible combinations of the

ABCB sequence, the system chooses Sn Pb Cd Pb, i.e., the Sn/Cd interface is eliminated from the structure leaving only Pb/Cd and Pb/Sn interfaces. Although notoriously difficult to estimate, the Pb/Cd binary interfacial energy is probably the lowest of the three binary systems. Clark and Elliott [7] quote a value of  $39.6 \times 10^{-3} \text{ J m}^{-2}$  for the Pb-Cd system compared with  $56 \times 10^{-3}$  and  $140 \times 10^{-3} \text{ J m}^{-2}$  for Sn-Cd and Pb-Sn, respectively. From the results of this investigation, it appears that the ternary system retains the preferred relationship of the Pb-Cd binary eutectic and that the tin-rich phase accommodates to the orientation of the common lead-rich phase. It is not possible directly to compare the orientation relationships between the eutectic lead and tin phases in binary and ternary alloys since the high-temperature hexagonal tin-rich phase does not occur in the binary system. However, the matching of the structure of the lead-rich phase and the transformed body-centred tetragonal tin-rich phase is identical with that reported by Hopkins and Kraft [8] for the lead-tin binary, although the growth directions are  $30^\circ$  apart in the two cases, i.e.  $[100]_{\text{bct}}$  for the ternary and  $[211]_{\text{bct}}$  for the binary.

The resulting orientation relationships in the ternary system are, in fact, such that close-packed planes in all three phases occur at the lamellar interfaces, noting that hexagonal tin has an unusually low  $c/a$  ratio which results in the  $\{10\bar{1}0\}$  planes being closer packed than the basal planes in this case. Additionally, the growth direction coincides with close-packed directions in all three phases, the interplanar spacings across the liquid-solid interface are almost identical and the liquid-solid interface plane has a high atomic density.

If, as suggested, the selection of the Pb/Cd interface dominates the growth pattern, then the only alternative sequence possible is Sn Cd Pb Cd and in this case, assuming that the tin-rich phase would adopt the same orientation with cadmium as in the binary eutectic, the growth direction would not coincide with a close-packed direction in the tin-rich phase. Recent work on the cadmium-zinc eutectic [9] has shown that if a cellular substructure develops during growth, the lamellar habit plane is lost where the lamellae curve at cell boundaries although the preferred growth direction is maintained. This result would suggest that a close-packed direction is at least as important as a preferred lamellar interface plane, per-

haps because it allows the maximum rate of accretion of atoms to the solid. It is also possible that splitting the cadmium-rich phase (which has the lowest volume fraction of the three phases), would reduce the volume fraction of the individual cadmium lamellae below that at which even highly favourable low-energy interfaces would prevent the lamellar to rod transition.

We conclude that the tin-lead-cadmium eutectic is able to grow with a simple, parallel morphology because it is possible to establish a set of rational orientation relationships for which the lamellar interfaces have low energies, and growth proceeds parallel to close-packed directions. This situation is likely to be uncommon and most ternary and higher order systems would not be expected to display such simple growth morphologies.

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