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THE MORPHOLOGY OF THE CELLULAR PRECIPITATION REACTION IN A Pb-3.0 WT% Sn ALLOY

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ABSTRACT

The complete development of the cellular precipitation structure at selected grain boundaries in a Pb-3.0 wt% Sn alloy during aging at 34°C and 23°C was investigated by light microscopy. The cellular structure in this alloy consists of lamellae of solute depleted lead solid solution and lamellae of β tin precipitate. The cellular precipitation reaction begins by local migration of a grain boundary with concomitant grain boundary precipitation of β tin. The grain boundary bows around the β tin grain boundary precipitates which then begin to lengthen in the direction of boundary migration thus forming the precipitate lamellae of the cell. The α' lamellae always preceed the β tin lamellae. At early stages of cell development, the lamellae may grow cooperatively and an orientation and habit plane relationship between the lamellae forms as the cell structure stabilizes. Since the coherence between the lamellae is weak, the direction of cell growth is not confined to the initial habit plane of the β tin lamellae.

ACKNOWLEDGMENTS

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I. INTRODUCTION

The general characteristics of the cellular or discontinuous precipitation reaction were first described by Smith.[1] He showed that the reaction starts by local migration of a grain boundary into the adjacent grain accompanied by the formation of a lamellar structure composed of depleted solid solution and a precipitate phase. Thus the solid solution phase of the cell has the same orientation as the matrix of the grain from which it grew. Turnbull and coworkers[2-3] in a study of the kinetics of the cellular reaction in Pb-Sn alloys determined that the rate controlling process was the rate of solute diffusion in the advancing grain boundary. Gruhl and Ammann[4] and others[5-6] showed that the cellular reaction only occurs at highly mobile high angle or disordered grain boundaries. Tu and Turnbull were the first to consider the mechanism for the formation of the precipitate phase lamellae of the cell. In a metallograph investigation of the cellular structure in lead rich lead-tin alloys, Tu and Turnbull[7] described the nucleation and multiplication of β tin lamellae during the formation of cells in lead rich lead-tin alloys. According to their mechanism for the genesis of cellular precipitation resulting from this study, β tin platelets nucleate at the original boundary between two supersaturated lead rich grains with the platelet having a

semicoherent, low energy interface with one grain, characterized by a rigid habit and orientation relationship, and an incoherent, high energy interface with the other grain. The grain boundary then migrates around the high energy, incoherent interface replacing it with a low energy, semicoherent interface and imbedding the platelet in one grain. The driving force for this migration is said to be the reduction of α/β surface energy resulting from the replacement of a high energy interface with a low energy one. The above nucleation process then repeats itself along the boundary until several, identically oriented, parallel β platelets are imbedded in one of the grains. These platelets are then said to migrate forward, carrying the α/α' boundary along with them. This theory implies that the crystallographic relationship between the initial grain boundary allotriomorphs and one of the grains establishes both the direction of cell growth and the morphology of the cellular lamellae.

Fournelle and Clark[8] studied the development of the cellular precipitate structure in a Cu-9.5 wt% In alloy in which the cell lamellae grow cooperatively and there is not a strong orientation relationship between the cell lamellae. Although, at early aging times, plate-shaped allotriomorphs, similar to these observed in Pb-Sn were seen, it was shown that cellular precipitate in Cu-In alloys did not form from such allotriomorphs but that the cells developed by the mechanism illustrated in Figure 1.

Initially allortiomorphs form along grain boundaries which are high angle and highly mobile.[9] The allotriomorphs may or may not have an orientation relationship with one of the adjacent grain e.g. grain α_1 but they have an incoherent or high energy boundary with grain α_2. Under grain growth migration forces, the α_1/α_2 boundary migrates into the grain α_2 bowing around the allotriomorphs as shown at time 3 in Figure 1. As the boundary advances, solute diffuses along the grain boundary to the allotriomorphs leaving behind a region of solute depleted solid solution designated α'. With the development of a solute difference across the α_2/α' boundary, the much larger chemical energy drives the bowing boundaries and the α_2/α' boundaries bow more noticeably as shown at time 4. As the α_2/α' boundary continues to advance, solute diffuses along the grain boundary to the allotriomorphs which then begin to grow along the bowing α_2/α' boundaries thus forming the precipitate lamellae of the cells as shown at time 4.

It is seen that two very different mechanisms have been proposed for the nucleation and development of the cellular structure: the Tu-Turnbull mechanism in which the rate of growth and habit plane of the β tin lamellae determine the direction and growth rate of the cell, and alternatatively the mechanism, illustrated in Figure 1, in which the α' lamellae advance and the precipitate lamellae trail as the cell grows. It is possible that the mechanism shown in Figure 1 is operative only in special cases, such

as in Cu-In alloys where the coherency forces between precipitate and matrix are weak, and that the Tu-Turnbull mechanism occurs in the more general cases where precipitate-matrix coherency forces are large. However, close examination of the published pictures of cellular structures in Pb-Sn alloy reveals a characteristic of the cells that does not agree with the Tu-Turnbull mechanism. Namely, that the α_2/α' boundaries of the cells were always slightly ahead of the β lamellae and convex in the growth direction as shown in Figure 2. Even in dissolution of the cells, as studied by Tu and Turnbull,[10-11] the α_2/α' boundary was convex in the direction of the movement of the cell boundary in this case a contracting cell. This configuration of the cell boundary would seem to contradict the premise by Tu and Turnbull[12] that the cell growth and direction is determined principally by the growth of the β tin lamellae. Accordingly, the present study of cellular precipitation of Pb-3.0 wt% Sn alloy was undertaken.

II. EXPERIMENTAL PROCEDURE

The Pb-3.0 wt% Sn specimens were prepared from tin and lead of 99.99% purity by melting in a graphite crucible and chill casting into cylindrical ingots 1.4 cms. in diameter. The cast alloy rods were annealed 85 hrs. at 270°C and then swaged to 0.8 cm in diameter in four steps with intermediate 16 hour anneals at 270°C. Disc shaped specimens were cut from the swaged and annealed rods and given a solution anneal for 24 hours at 270°C to produce a reasonably coarse grain size.

The polishing and etching procedure for light microscopy of these very soft alloys was as follows. The alloy and discs were mounted in Bakelite, wet ground through to the 600 grit paper. The specimens were then rough polished with 0.3μ Al_2O_3 on Microcloth. The final polish was performed with a Vibromet polisher at a medium vibration setting using a slurry of 0.05μ Al_2O_3 on Microcloth. The polished alloys were dip etched for about 10 seconds in an etchant consisting of 1 part glacial (85%) acetic acid, 1 part HNO_3 and 4 parts Glycerol.

In order that the metallographic observation of cell development be completely unambiguous, it was necessary to develop a polishing and aging procedure so that the entire cell development at a selected grain boundary could be observed. The Bakelite mounted and polished alloy disc specimen was first solution treated by annealing

for 24 hours at 170°C followed by a water quench. The solvus temperature of the Pb-3.0 wt% Sn alloy is about 90°C and the Bakelite mounting material did not degrade during the 170°C solution anneal. The mounted specimen was then aged at either 23°C or 34°C for a time sufficient to start precipitation at the grain boundaries. After polishing with only the final step of the above procedure, followed by etching, light microscopy was used to study the early stage cellular formation. The specimen was then reaged for a short period and repolished using only the final polishing step. The specimen was etched and the cell development at the same grain boundaries was again observed. The procedure was then repeated several times. In this manner, a sequences of photomicrographs showing the complete cell development at a given grain boundary were obtained. It should be noted that the amount of material removed by the polishing and etching after each aging step was so small that distinquishing details of the cellular development could be traced throughout the sequence of photomicrographs.

III. RESULTS AND DISCUSSION

At the start of the investigation a survey of many specimens which had been given a short aging treatment did show many plate-shaped allotriomorphs which appeared to be undergoing replacive motion as in the model by Tu and Turnbull[7] (see Figure 3). According to the model such plate-like allotriomorphs will become the β tin lamellae of a cell. However, observation of many such allotriomorphs after long periods of subsequent aging revealed that the replacive motion did not continue and the cells did not develop from these plate-like allotriomorphs.

The complete morphology of a cell from the initial migration of the boundary to the well developed cellular structure is shown in Figure 4. A similar but less complete sequence is shown in Figure 5. It is apparent that the cells form by the mechanism illustrated in Figure 1. Consider the morphology shown in Figure 4. After 3 hours of aging, β tin precipitates begin to form along the grain boundary which is migrating toward the upper grain. The small precipitates locally pin the boundary forming cusps in the advancing grain boundary. With continued aging, the bowing of the grain boundary increases and the grain boundary precipitates of β tin grow in the direction of boundary migration becoming the precipitate lamellae of the cell. These precipitates not

only lengthen but also thicken as the grain boundary advances until the precipitate lamellae reaches an equilibrium thickness. This is seen best in Figure 5 which shows the V-shape of the thickening precipitate lamellae after 130 hours of aging at room temperature. Note also that in Figure 4 the bowing of the α' lamellae increases to a maximum at 120 hours of aging and then decreases somewhat as the cell structure stabilizes and reaches a steady state.

In agreement with Tu-Turnbull[7] the precipitate lamellae do not branch. Equilibrium spacing of the precipitate lamellae was attained by nucleation of additional plates along the boundary.

In certain cases, a lamellae would appear to lose contact with boundary and then reappear at a later time. Consider for example, the second lamellae from the right in Figure 4 at 419 hours and 587 hours of aging. Such effects are due to the sectioning of the cell by the sequential polishing technique. Tu and Turnbull[13] have shown that the β tin lamellae are blade shaped with rifts and holes. Sectioning by the plane of polish through a hole in the precipitate lamellae may give an erroneous impression of a lack of contact of the lamellae with the cell boundary. As shown in the subsequent section of 587 hours of aging, this lamellae is in contact below the plane of polish for 419 hours of aging.

Tu and Turnbull[13] report the orientation relationship of β tin in the lead solid solution matrix to be $(010)_{Sn}||(111)_{Pb}$ and $[001]_{Sn}||[110]_{Pb}$. They report that disregistry of tin precipitate along the close packed direction of the (111) Pb plane to be 0.10. This is a fairly large disregistry, therefore coherency forces will be weak and, at best, only a semicoherent boundary can exist between the β tin lamellae and the α' lead lamellae. During the early stages of cell formation when the forces of the bowing α'/α_2 interface on the incipient β tin lamellae are large, growth of the β tin lamellae in non habit orientation can occur as illustrated in Figure 6. It is seen that the β tin lamellae are following the bowing α'/α_2 boundaries as illustrated in Figure 1 rather than rigidly following a common (111) habit plane orientation with the α' lamellae.

As the structure of the cell stabilizes at longer aging times, the α' and β lamellae grow with the above orientation relationship. For example in the well developed cell of Figure 7, the β tin lamellae lie in only four directions indicating that in a later stage of growth the β tin lamellae have the above orientation relationship with the α' lead lamellae. The change from cooperative growth at early stages of cell growth to oriented growth at later times is accomplished by the β tin lamellae growing parallel to that (111) plane of the adjacent α' lead lamellae, which is nearest to the direction of cell growth.

However, even at later stages of growth, the growing β tin lamellae is not confined to a single (111) habit plane. Forces exerted by the α'/α_2 interface on the trailing β tin lamellae may cause the β lamellae to change direction of growth. For example, in Figure 8, it appears that initially the cell grew principally to the right and the β lamellae are lined up in this direction. However, at a later aging time, the upper cell boundary began to migrate and the β lamellae, as evidenced by their curved shape, changed direction to grow in this new direction.

In summary, at early stages of aging, the interfacial forces of the bowing α'/α_2 lamellae boundaries on the small β Sn lamellae may override the weak coherency forces of a semi coherent boundary between the lamellae and the lamellae grow cooperatively. As the cell structure stabilizes, the lamellae tend to grow maintaining an orientation relationship between the lamellae but even at this stage, the interfacial forces of the bowing α'/α_2 interface may change the direction of the growing β tin lamellae. In Pb-Sn alloys the influence of coherency on the cell morphology appears to be intermediate between that in Cu-In alloys when there is poor lattice matching and consequently the cellular lamellae grow cooperatively and that in Al-Ag alloys where there is good lattice matching and coherency forces between the lamellae significantly influence the cell morphology.[14]

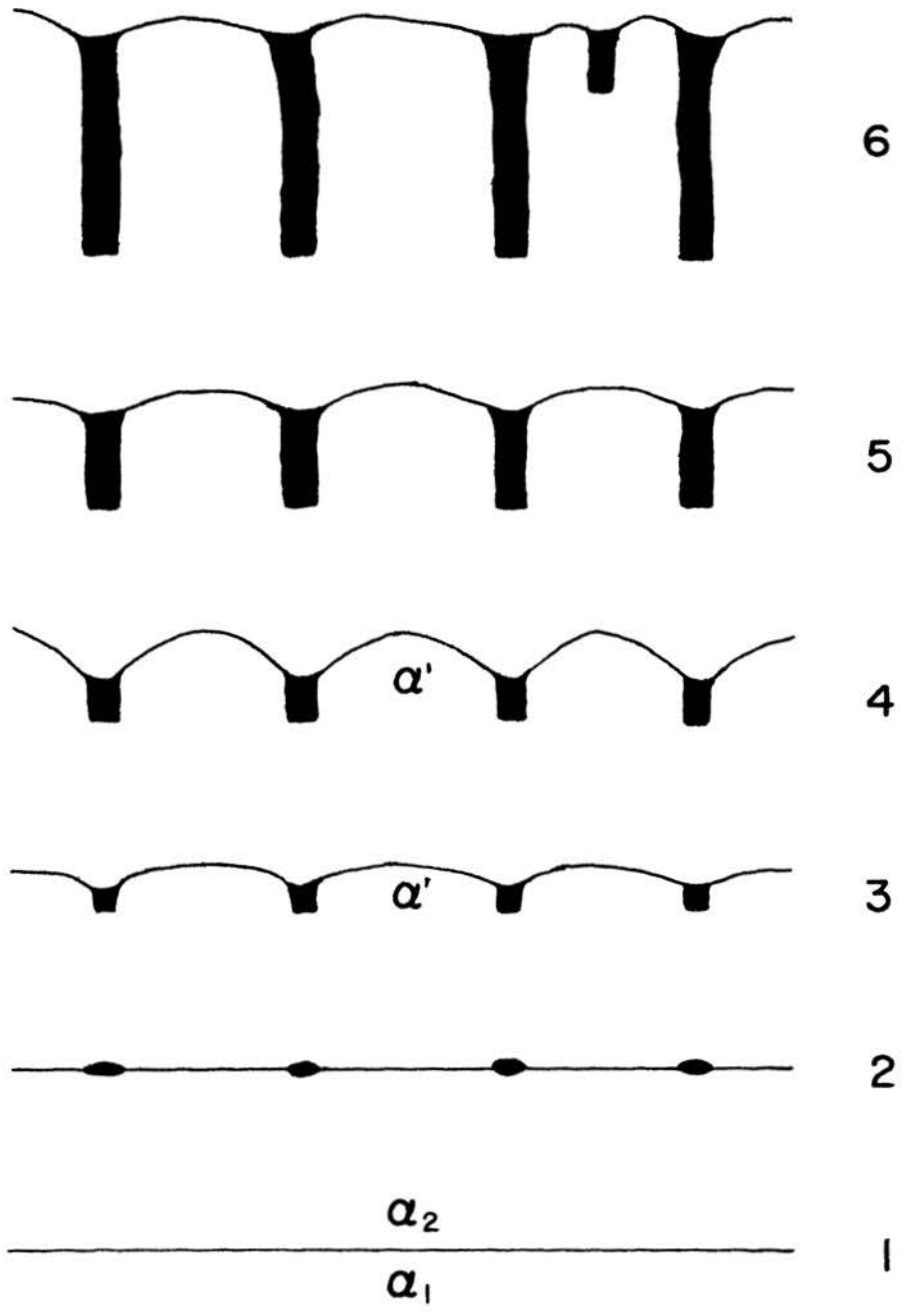

Figure 1. Diagram showing the morphological development of the cellular structure as observed in Cu-In alloys.[8]

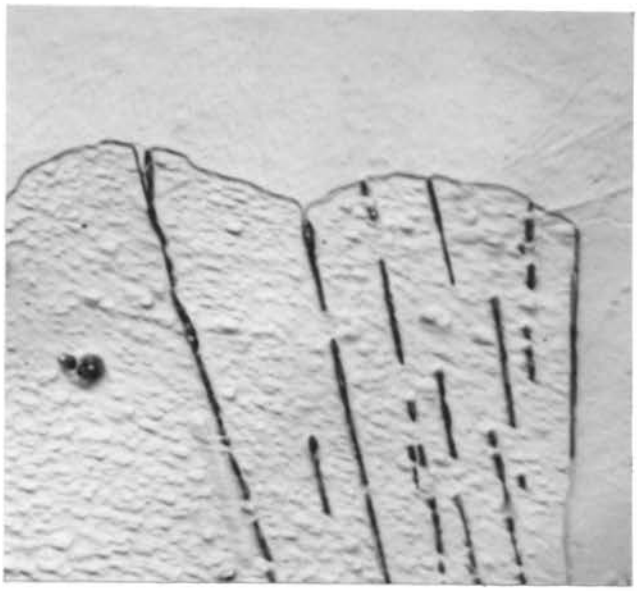

Figure 2. Cell boundary of Pb-3.0 wt% Sn alloy after aging for 360 hours at 23°C. Note that the α' lamellae (light gray) preceed the β tin lamellae (dark). X500

Figure 3. Plate-shaped allotriomorph in Pb-3.0 wt% Sn alloy after 53 hours of aging at 23°C. Apparent replacive motion by the grain boundary as reported by Tu and Turnbull.[7] X500

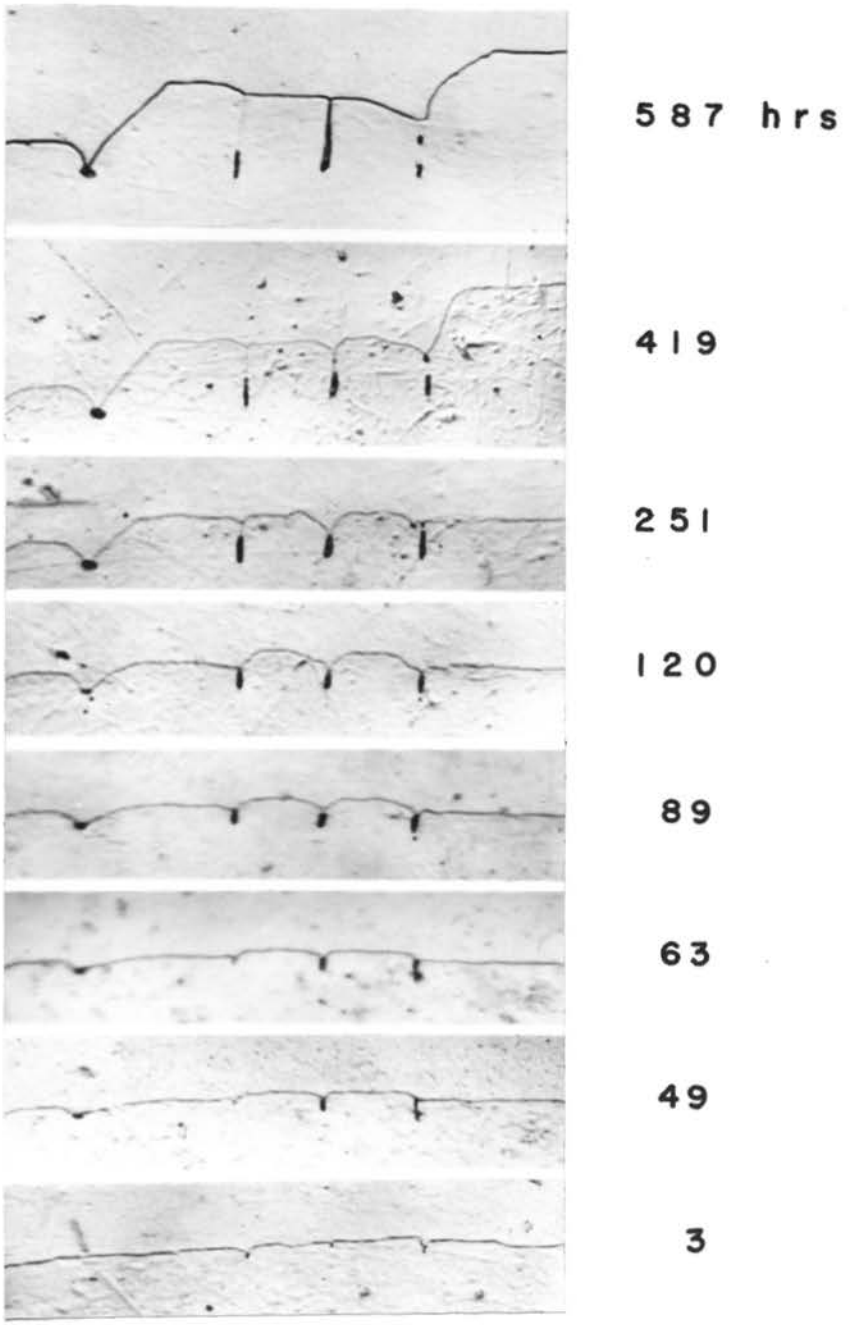

Figure 4. Development of a cell in a Pb-3.0 wt% Sn alloy during the aging for the hours indicated at 34°C. X500

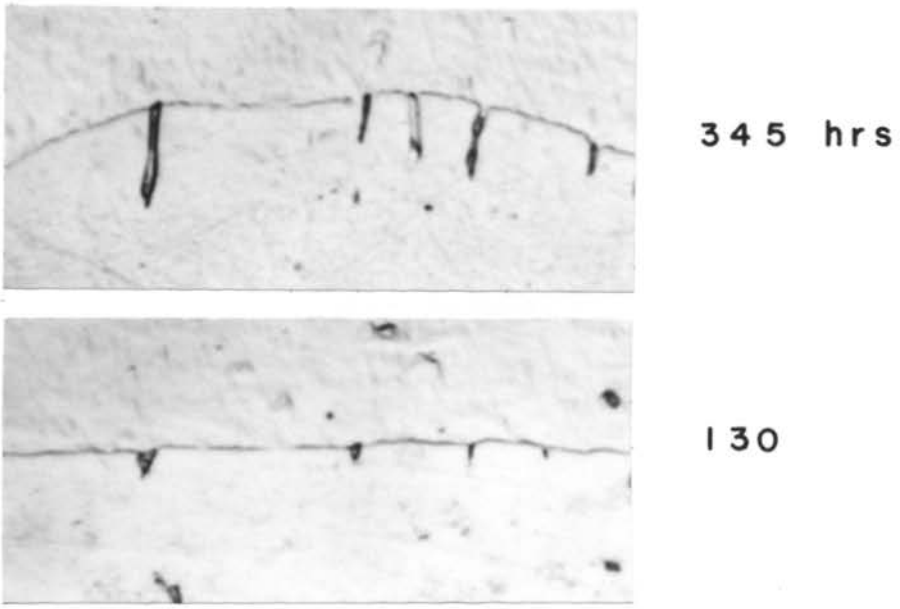

Figure 5. The development of a cell in a Pb-3.0 wt% Sn alloy during aging for the hours indicated at 23°C. X500

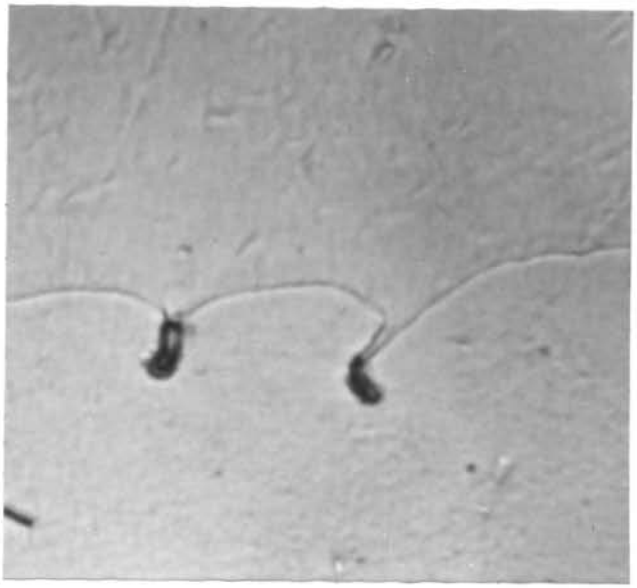

Figure 6. Formation of the β tin lamellae during the early stage of cell development of the Pb-3.0 wt% Sn after 76 hours aged at 23°C. Note the large bowing of the α'/α_2 boundary and the non habit orientation of the β tin lamellae. X2000

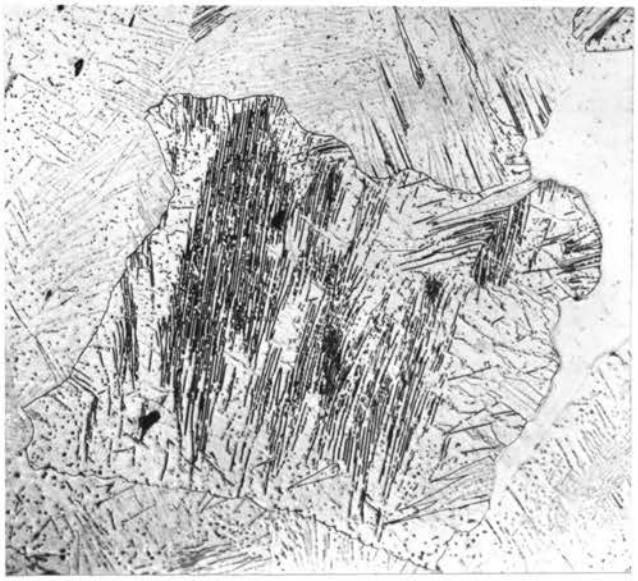

Figure 7. Well developed cell in a completely reacted Pb-3.0 wt% Sn alloy after 673 hours at 23°C. Note the four directions of β tin lamellae. X250

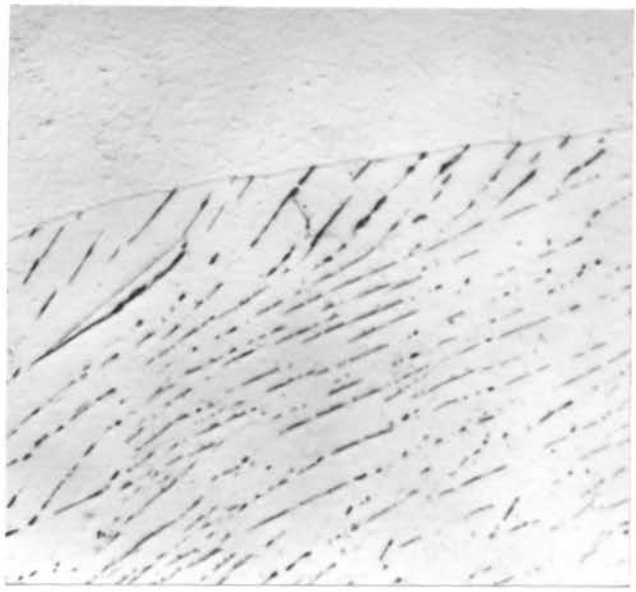

Figure 8. Pb-3.0 wt% Sn alloy aged 547 hours at 23°C. Note the change of direction of β lamellae in the upper part of the cell. X500

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VITA

Federico Sequeda Osorio was born on July 18, 1948 in San Andres, Santander del Sur, Colombia. He completed his primary and secondary education in Bucaramanga. He was graduated from the Universidad Industrial de Santander in December, 1970, receiving a Bachelor of Science Degree in Metallurgical Engineering.

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APPENDIX

ADDITIONAL ILLUSTRATIVE PHOTOMICROGRAPHS OF THE CELLULAR MORPHOLOGY

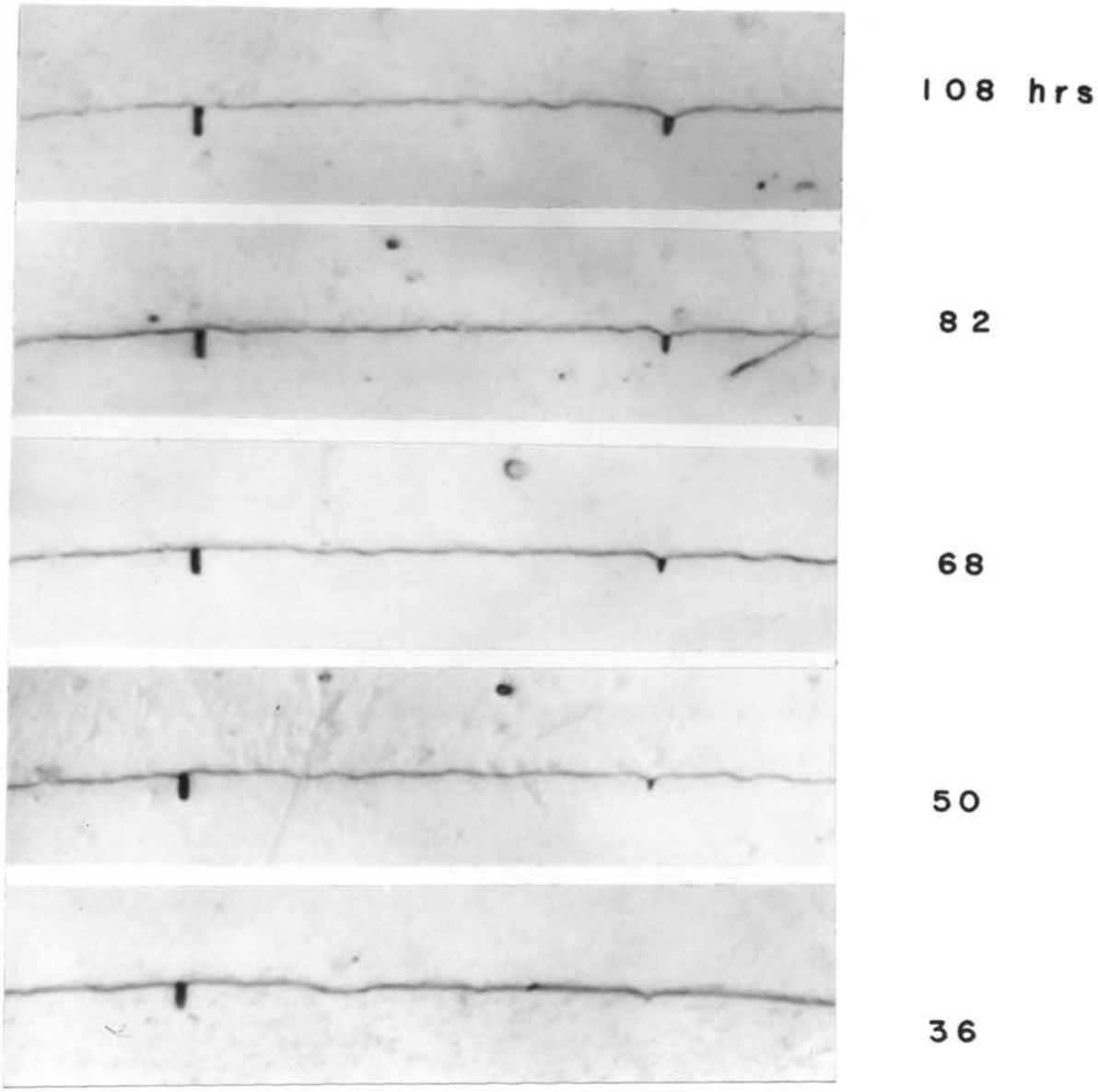

Figure A-1. Sequence of cellular development during aging of Pb-3.0 wt% Sn alloy at 23°C for hours indicated. Note the V shape of the β tin lamellae on the right at early aging times. X500

Figure A-2. β tin lamellae developing at edge of the cell. Note the different directions of the lamellae. Pb-3.0 wt% Sn alloy aged for 362 hours at 34°C. X500

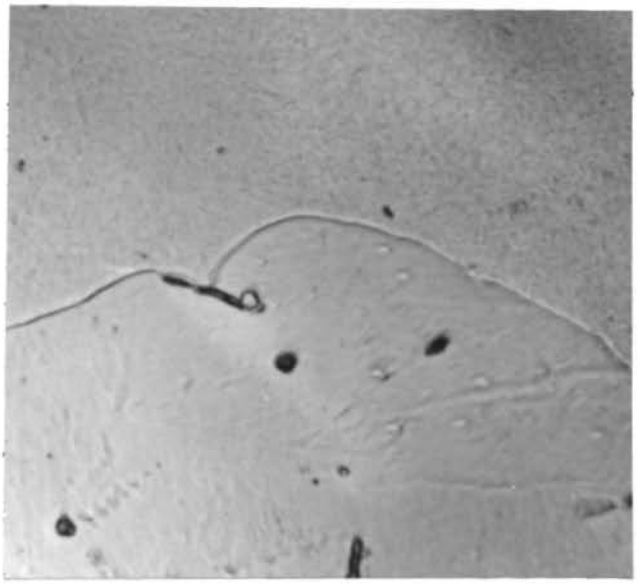

Figure A-3. Replacive motion of plate-shaped β tin allotriomorph. Pb-3.0 wt% Sn alloy aged for 76 hours at 23°C. X500