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THE MORPHOLOGY OF CELLULAR PRECIPITATION IN
ALUMINUM RICH ALUMINUM-SILVER ALLOYS

By

SANTIAGO IBARRA, JR., 1940-

A DISSERTATION

Presented to the Faculty of the Graduate School of the

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In Partial Fulfillment of the Requirements for the Degree

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ABSTRACT

The morphology of cellular precipitation in Al-29.8wt%Ag alloy has been investigated in bulk specimens by transmission electron microscopy and in solution treated specimens by means of hot stage microscopy. Both cellular and general precipitation were observed to occur simultaneously in quench-aged and isothermally aged alloys. By studying the early stages of precipitation in the hot stage, the mechanism for the growth of cells in Al-Ag alloys was developed. According to this mechanism, the grain boundary allotriomorphs begin to form, the boundary then interacts with the allotriomorphs by bowing, and then either trailing precipitation forms on the allotriomorphs or new lamellae form at the advancing interface.

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I. INTRODUCTION

The cellular or discontinuous precipitation reaction is one of the distinctive morphological characteristics of some age-hardenable alloys. Smith¹ showed that this reaction occurred by the local migration of a grain boundary into the adjacent grain leaving a lamellar aggregate of depleted solid solution and precipitate phase behind the advancing boundary. He proved that the depleted matrix phase characteristically had the same crystallographic orientation as the grain from which it grew and suggested that segregation of the excess solute occurred in the advancing interface since it is incoherent.

Subsequent investigations by Gruhl and Kramer² and Bohm³ have confirmed these observations. Kinetic studies by Turnbull^{4,5,6}, Cahn⁷, Hillert⁸, and others^{9,10} concentrated on descriptions of growth theories which predicted cellular growth. However, Tu and Turnbull^{11,12,13} were the first to describe the nucleation and multiplication of tin lamellae during the formation of cells in lead rich lead-tin alloys. They proposed that the precipitate cell lamellae develop from an interaction of the grain boundary with plate-shaped grain boundary precipitates. The initial platelet is proposed to have a semi-coherent, low energy interface with one grain and an incoherent, high energy interface with the other grain. The grain boundary migrates around the high energy incoherent interface, replacing it with a low energy semicoherent interface and imbeds the

platelet in one grain. The driving force for this motion is proposed to be the decrease in interfacial surface energy resulting from the replacement of the high energy interface with one of lower energy. Eventually, a number of platelets multiply identically and form a cell nodule. The theory then describes the α lamellae (Pb-Sn solid solution) of the $\alpha + \beta$ (Sn) cell as being carried along as the β (Sn) lamellae lengthens. The theory implies that the orientation relationship between the initial grain boundary allotriomorphs and one of the grains establishes both the direction of cell growth and the morphology of the cells.

Fournelle and Clark¹⁴ studied the development of the cellular precipitate structure in a Cu-9.5at%In alloy in which the cell lamellae grow cooperatively and there is not a strong orientation relationship between the cell lamellae. Initially, allotriomorphs form along grain boundaries which are high angle and highly mobile. The allotriomorphs may or may not have an orientation relationship with one of the adjacent grains. Under grain growth migration forces, a grain boundary advances into an adjacent grain, bowing around the allotriomorphs. As the boundary advances, solute diffuses along the grain boundary to the allotriomorphs, leaving behind a region of solute depleted solid solution. With the development of a solute difference, the boundaries bow more noticeably and continue to advance. Solute continues to diffuse along the grain boundary to the allotriomorphs which then begin to grow

and form the precipitate lamellae of the cell.

There are, therefore, two proposed mechanisms for the initiation of cellular precipitation. For the system in which precipitates are subject to strong coherency forces, the mechanism of Tu and Turnbull¹⁵ should be operative, and for alloy systems in which the coherency forces are weak, the mechanism of Fournelle and Clark¹⁴ should apply. The Al-Ag system was selected for study because of good lattice matching and strong coherency forces which exist between γ (Ag_2Al) precipitate and the α aluminum solid solution matrix¹⁶. Thus in this case, cellular precipitation would be expected to occur by the Tu and Turnbull mechanism. However, although the strong habit of the precipitate does effect the direction of cell growth, it was found that the growth is controlled by the α aluminum solid solution lamellae rather than the γ precipitate lamellae.

The structure of the Al-29.8wt%Ag alloy after a quench-age treatment at 220°C for 40 minutes is shown in Figure 1. First consider the interior of the grain reveals well developed Widmanstatten platelets of a transition lattice, γ' , of the equilibrium γ (Ag_2Al) precipitate. The crystal structures of the γ' and γ phases are close packed hexagonal, and these phases precipitate from the face centered cubic aluminum rich matrix with the following relationship¹⁷:

$$\begin{array}{l} (0001)_{\text{hcp}} // (111)_{\text{matrix}} \\ [11\bar{2}0]_{\text{hcp}} // [110]_{\text{matrix}} \end{array}$$

As one approaches the grain boundary there is a region free of γ' precipitate which contains spherical silver rich G.P.

zones. The γ' precipitate normally nucleates on vacancy debris, such as faulted loops, and also on extended dislocations. Clustering of Ag around the dislocation locally lowers the stacking fault energy, permitting the dislocation to separate into partial dislocations which are connected by narrow stacking faults. These stacking faults act as nucleating sites for γ' precipitate. During quenching from the solution temperature, these vacancies remain in the grain. However, during the quench the vacancies will migrate to nearby grain boundaries and produce an area lower in vacancy concentration adjacent to the grain boundaries¹⁸. Upon aging, the vacancy-free areas will not immediately form general precipitation. Consequently, the morphology will feature regions free of γ' precipitate adjacent to the grain boundaries. Finally along the grain boundary, cellular precipitation is seen to be occurring as a cell grows into the upper grain. Note that the γ lamellae of the cells are parallel to one of the habit planes of the general Widmanstätten γ' precipitate in the lower grain.

In the present study, transmission electron microscopy was used to determine the mechanism of morphological development of the cellular precipitate in the Al-29.8wt%Ag alloy. Bulk samples, which were aged for selected times and temperature and thinned for examination, and foil samples, which were thinned in the solution treated condition and aged under observation on a hot stage in the

electron microscope, were used to determine the details of the cellular genesis.

II. EXPERIMENTAL PROCEDURE

The aluminum-29.8 wt% silver specimens used in this investigation were prepared from aluminum ingots of 99.99% purity purchased from Consolidated Aluminum Corporation and silver shot of 99.99% purity purchased from Atomergic Chemetals Company. Three ingots of the Al-Ag alloy were prepared by melting appropriate quantities of the above components in a graphite crucible under a NaCl-KCl flux and chill casting the melt in graphite molds. The cylindrical ingots, 0.650 inches in diameter, were swaged to 0.600 inches and annealed for 168 hours at 515°C, after which one half ingot was swaged to 0.125 inches in diameter. Disc specimens for light microscopy were cut from these rods, solution treated for 20 minutes, and aged to the desired times for determination of T-T-T curves discussed below. Some of the rod stock was cold rolled with intervals of solution heat treatment. The resultant 0.007 inch foil was used for electron microscopy specimens. All heat treatments were carried out in salt baths and an electric furnace with temperature control of $\pm 1^\circ\text{C}$.

In order to aid in selecting heat treatment times and temperatures for the initiation of the cellular reaction, T-T-T curves for both quench-age heat treatment and isothermal heat treatment were determined by means of light microscopy. The criterion for the start of cellular precipitate was its initial appearance at 2000X.

For the quench-age T-T-T curves, specimens were solution treated for 20 minutes at 515°C, quenched, and held at room temperature no more than 10 minutes. The specimens were then immediately aged for a specific time. The isothermal T-T-T curve was obtained by using the above solution treatment and immediately transferring the specimens to the aging bath for specific times. All aging treatments were terminated in ice water.

A comparison of the two curves, Figure 2, shows that cellular precipitation will occur at lower temperatures and at later times in the isothermally aged samples. The nose of the quench-age curve is 60°C higher than that of the isothermal. Both types of heat treatment can be used for the study of the early stage cellular morphologies. General precipitation is present in both quench-age and isothermally aged specimens so competitive growth is present in both types of heat treatments.

Specimens for transmission electron microscopy were prepared by the "window" method¹⁹, using Lenoir's first solution at 80°C and applied voltage of 10 to 15 volts. Lenoir's first solution had the following composition:

722 cc phosphoric acid	85%
134 cc sulphuric acid	
156 gm chromic acid	
140 cc distilled water	

At the completion of thinning, the window specimen was rinsed thoroughly in a stream of distilled water and then placed in Lenoir's second solution for 10 seconds for the complete removal of corrosion products. The second

solution had the following composition:

20 gm	chromic acid
35 cc	phosphoric acid
940 cc	distilled water

The window specimen was again rinsed in water followed by a methyl alcohol rinse. The specimen was dried, sampled, and placed in the electron microscope.

The development of cellular structure on the hot stage of the electron microscope was accomplished by using a specimen of Al-Ag alloy foil which was solution heat treated at 515°C for 20 minutes and quenched in water (21°C). The foil was then cleaned and thinned by the window method, using the above procedure. A hot stage temperature of 219°C for aging was selected because at this temperature the growth of the general precipitate was sufficiently slow to permit continuous observation of the cell development. Cells were only observed to occur in the thicker sections of the foil which accounted for the lack of definition in the hot stage photographs. The quench-age observations are from previously developed cells, and thus the photographs taken from thinner areas of the foils are sharper.

All light microscopy specimens were rough polished through 0.5 micron diamond paste and polished electrolytically in Lenoir's first solution at 10-20 volts at 80°C. The specimens were rinsed in distilled water and alcohol and etched in 0.5% HF solution.

III. RESULTS AND DISCUSSION

A. Characteristics of Cellular Precipitation in Al-Ag Alloy

In order to understand the development of cellular precipitation in this system, it is necessary to observe the growth of cells occurring by the interaction of a grain boundary with the grain boundary allotriomorphs. Hot stage microscopy, in which the complete development of the cellular structure at a single grain boundary is observed, yields unambiguous observations as to the details of the morphology of the cells. This technique also obviates the misinterpretation of morphology due to sectioning or truncating of existing metallurgical structures during specimen preparation for light and electron microscopy. Therefore, the principal results in this work were obtained by the hot stage technique.

The morphologies in bulk specimens quench-aged and then thinned for transmission electron microscopy were identical to those obtained in thin foils on the hot stage in the microscope except that the hot stage structures did not have the γ' precipitate-free zones of quench-aged and thinned specimens, as shown in Figures 3 and 4. The absence of the PFZ in the hot stage specimens is attributed to the aging process in the thin foil. The hot stage specimen is thinned in the solution treated condition which required 30 minutes in the thinning solution at 80°C. During thinning, excess vacancies in the grain interiors,

which are needed to transport Ag to nucleation sites, escape to the surface. This situation is similar to the aged bulk specimens in which vacancies near the grain boundaries escape to the boundaries during the solution treatment quench. Thus, unlike bulk specimens, the hot stage foils do not have a vacancy gradient between the grain boundary regions and the grain interiors. Therefore in the hot stage foils, the γ' nucleation sites are distributed uniformly. The γ' precipitate appears evenly throughout the foil, and a precipitate free zone is not evident. The γ' are the same size throughout the foil, although they are somewhat larger than γ' produced for the same aging treatment in the bulk specimens because of the fewer nucleation sites.

Comparison of cell morphologies developed in the bulk material and in the foil on the hot stage showed no real difference due to the absence of the PFZ, as seen in the lamellae of Figures 3 and 5. In this system the growth rates of two hot stage sequences showed that the rates did not differ significantly from the bulk light microscopy measurements of Watanabe and Koda²⁰, as seen in Table I.

A plot of the maximum length of the γ lamellae in the cells as a function of aging time at temperature is shown for one sample in Figure 6. The plot reveals that the lamellar growth is essentially linear during the early stages. These results are similar to those obtained by Aaronson and Clark²¹. The comparisons further confirm

that the morphological results obtained by the hot stage technique are identical to those obtained in bulk specimens.

B. Cellular Precipitation Mechanism

The cell morphology was studied at selected grain boundaries in quench-aged specimens and at a single grain boundary by hot stage microscopy. In both cases, the precipitation sequence was as follows: the formation of allotriomorphs, followed by the development of general Widmanstätten γ' plates, and finally the cellular precipitation. Considerable aging time elapsed between the γ' precipitation and the initiation of the cellular reaction.

The marked bowing and local migration of the grain boundary, observed at early aging time in Cu-In¹⁴ and Mg-Al²² alloys, was not seen in the Al-Ag alloy. As shown in Figure 7, the boundary in the Al-Ag alloy shows only a slight tendency to bow around the pinning allotriomorphs. Marked advance of the boundary was only observed after the formation of γ lamellae. The electron micrograph in Figure 8 shows the beginning of a cellular structure, and Figure 9 shows the intermediate stage of cell development. The allotriomorphs that are present have a crystallographic relationship with the α matrix of the lower grain. As precipitation progresses, the grain boundary begins to bow out between the allotriomorphs. This is shown clearly in Figure 8 at X, in the direction shown by the arrow. With time, these boundaries continue to bow and the cell

structure forms as shown in Figure 9. Thus the initial allotriomorphs transform into the lamellae of the cell. It is seen that the lamellae form on one of the Widmanstatten orientations of the γ' precipitate of the lower grain. The direction of cell growth is determined by the lamellae, which rigidly retain the same orientation relationship as the cell boundary advances.

The details of the development of a cell are shown more clearly by means of hot stage microscopy, as seen in Figure 10. The partially developed cell shown to the right of the picture is growing upward and toward the left into the upper grain. This sequence specifically illustrates the grain boundary interaction with the allotriomorphs to form a lamella of the cell. In photo A, consider the area marked X. The allotriomorph at X has a flat side parallel to one set of γ' precipitates in the lower grain, indicating that the flat lower face is ordered and the upper curved face is disordered, i.e., it has a high angle interphase boundary. In photo B, the partially developed cell is moving toward the left to the allotriomorph marked X. The boundary adjacent to allotriomorph X bows forward and begins to envelop the allotriomorph. As the boundary continues to move, it deposits solute on the allotriomorph, causing it to thicken and form an ordered boundary as seen in photos C through G. This is illustrated schematically in Figure 11 at X. This boundary-allotriomorph interaction somewhat resembles "replacive" motion¹¹, but

actually a definite solute deposition occurs changing the disordered interface of the allotriomorph to an ordered interface as the α/α' boundary advances from time A to D. The sequence does not appear to depend on a "torque"²³ to start the motion of the grain boundary.

Consider now the allotriomorph marked Y in photo A, Figure 10. At the beginning of this sequence, this allotriomorph has been completely enveloped by the cell by the above mechanism and is already growing as a cell lamella in the rigid orientation of the lower grain. As the cell continues to grow, the α/α' interface to the left of Y bows forward, allowing only a thin lamella to grow (see photo A & B). The thinner lamella lengthens in photos B through D. However in photo E, the boundary bows upward so as to prevent continued growth. As seen in photo G, it is possible for lamellae to grow cooperatively as they attempt to find a new habit plane. Cooperative growth can also occur in the earlier stages of cell formation. Note that after the initial cell development most of the other lamellae nucleate at the advancing interface. The sequence at Y is again shown in Figure 11, illustrating how a completely enveloped allotriomorph becomes a lamella of the advancing cell.

The above hot stage sequence clearly shows the interaction of the grain boundary with the grain boundary allotriomorphs and their transformation into cell lamellae. If as in some cases, the initial allotriomorphs lie in

one of the Widmanstätten orientations parallel to the direction of cell growth, then the grain boundary envelopment occurs with very little solute deposition, giving an appearance closer to the "replacive" motion described by Tu and Turnbull¹¹. Since the lamella shape is changed by the movement of the grain boundary, the cell growth is controlled by α/α' boundary movement rather than by the growth of the precipitate lamellae, as reported by Tu and Turnbull for Pb-Sn alloy¹⁵.

The second sequence is shown in Figure 12. In this case the allotriomorphs lie at a larger angle to the original grain boundary and the allotriomorph configuration more closely resembles the initial stages of the Tu and Turnbull^{11,22} mechanism. In photo A well-developed cells are seen at each side of the photomicrograph. In these cells the lamellae lie parallel to one set of Widmanstätten γ' plates in the lower grain. Let us consider the development of a cell which is just beginning to form in the center of photo A. Consider precipitate X in photo A. Here the grain boundary has been twisted forward to position Z by the growth of allotriomorph X. Now consider the α/α' boundary to the left of the allotriomorph X. The α/α' boundary sweeps past the allotriomorph and solute is deposited forming an ordered face which is parallel to the orientation of the lamellae Y. When the α/α' boundary reaches Z in photo C, it continues to grow leaving a thinner lamella as seen in photo D. The

thinning of lamellae may be indicative of an increase in the speed of the α/α' boundary. Conversely, a slower boundary movement is noted at Y in photo A where the lamellae at Y has thickened.

The case of cellular precipitation at grain boundaries, in which the ordered interfaces of the initial allotriomorphs lie parallel to the grain boundary, is shown in Figure 13. An S-shaped development of cells is seen, in which one cell is advancing into the upper grain, and in an adjacent region another cell is growing into the lower grain. The allotriomorphs appear to have an ordered interface with the lower grain. Note the flat sides of the allotriomorphs are parallel to one of the Widmanstätten plates in the lower grain. Initially the upper curved interfaces of the allotriomorphs appear to have a disordered interface. Consider allotriomorph X in photo B. As the cell develops, the upper interface of this allotriomorph becomes ordered and is incorporated into the cell by the solute deposition mechanism as the α/α' cell boundary advances. Note, however, in this case most of the lamellae nucleate at the advancing interface.

It appears that, in an alloy system in which the cell lamellae lie on a single habit plane, if the initial allotriomorphs lie at too large an angle to the direction of cell growth, the cell lamellae cannot develop directly from the initial allotriomorphs. The "U" and "L" lamellae seen in the Cu-In cells¹⁴, where coherency forces are weak

and cooperative growth occurs readily, are seldom seen in Al-Ag cells, where coherency forces are high.

It is seen that the cell lamellae may develop directly from the grain boundary allotriomorphs when the ordered faces of the initial allotriomorph lie at an appreciable angle to the initial grain boundary, as shown in Figures 8 and 9. If, however, the ordered interfaces of the allotriomorphs lie at slight angles to the initial grain boundary, the allotriomorphs transform into lamellae by the solute deposition mechanism as shown in Figures 10 and 11.

In this case, however, most of the lamellae nucleate at the advancing cell boundary. Finally, if the ordered face of the initial allotriomorphs lies parallel to the boundary, the cell lamellae do not develop from the allotriomorphs (Figure 13) and all lamellae nucleate at the advancing cell interface. In all cases the α lamellae, not the γ lamellae, appear to control the development of the cell.

C. Comparison of the Driving Forces for Cellular Precipitation Reaction

The morphological characteristics of the cellular initiation are clear, but it is useful to compare the various driving forces which are postulated to control the cell growth. Consider the cell in the early stages of formation, shown schematically in Figure 14. Tu and Turn-

bull^{11,15,22} indicate that the driving force for moving the cell boundary during the initial stage is the difference in interfacial energy, $\sigma_{\alpha'/\gamma} - \sigma_{\alpha/\gamma}$, between the opposite sides of the grain boundary allotriomorph. The terms $\sigma_{\alpha/\gamma}$ and $\sigma_{\alpha'/\gamma}$ are the interfacial energies of the α/γ habit and the incoherent α'/γ interface, respectively. Let us compare the driving force obtained by a change in this interfacial energy by "replacive" motion along a α'/γ interface with the chemical free energy that is obtained by relief of supersaturation as the α/α' boundary advances.

The net free energy change for the conversion of one mole of supersaturated solid solution by the cellular precipitation reaction to depleted solid solution and precipitate phase has been given¹⁴ as

$$\Delta F = a\Delta F_{\circ} + b\sigma_{\alpha/\gamma}V + \frac{\sigma_{\alpha/\alpha'}V}{r} + Z(t) \quad (1)$$

where ΔF_{\circ} is the chemical free energy change for the formation of one mole of reaction products. The term $\sigma_{\alpha/\gamma}$ is the interfacial energy of the α/γ boundary, $\sigma_{\alpha/\alpha'}$ is the interfacial energy of the α/α' boundary, V is the molar volume, r is the radius of curvature of the α/α' boundary, and $Z(t)$ is the strain energy term.

The first term, $a\Delta F_{\circ}$, is the chemical free energy released during the reaction where a is the fraction of the total free energy, ΔF_{\circ} , available for the reaction. The second term, $b\sigma_{\alpha/\gamma}V$, is that portion of the chemical

free energy converted to α/γ interface during precipitation, where b is a dimensional term that is dependent on the size and shape of the precipitate phase. $\sigma_{\alpha/\alpha'}, V$, the third term, is that portion of ΔF associated with the curvature of the α/α' interface. For the case of the cellular growth into an undeformed matrix, $Z(t) = 0$, and the equation above becomes

$$\Delta F = a\Delta F_0 + b\sigma_{\alpha/\gamma}V + \frac{\sigma_{\alpha/\alpha'}V}{r} \quad (2)$$

The driving force for boundary migration at the start of aging in an undeformed matrix results solely from the curvature of α/α' boundary. Assuming that the interfacial energy of the original grain boundary is identical with that of the advancing α/α' boundary, the driving force is

$$\Delta F = \frac{\sigma_{\alpha/\alpha'}V}{r} \quad (3)$$

However, when precipitation has occurred and a depleted region is formed, equation 2 must change to

$$\Delta F = P\Delta F_0 + \frac{2\sigma_{\alpha/\gamma}V}{S} + \frac{\sigma_{\alpha/\alpha'}V}{r} \quad (4)$$

where $a = P$ and $b = 2/S$.

Now let us consider the relative energies in this equation by comparing the different contributions to the driving force ΔF in the aluminum silver system. The fraction of the overall driving force due to curvature of the grain boundary in the last term of equation 4 is deter-

mined first. Using $r = 1 \times 10^{-3}$ cm from Figure 13-A, $V = 10 \text{ cm}^3/\text{mole}$, and the α/α' boundary energy as 300 ergs/cm^2 , the driving force is $\Delta F = 0.075 \text{ cal/mole}$. This term is small and will not affect the results.

The fraction of the chemical free energy released during the reaction is determined by using the following formula

$$P\Delta F_{\text{O}} = RT \left[\chi_{\alpha} \ln \frac{\chi_{\alpha}}{\chi_{\alpha}'} + (1-\chi_{\alpha}') \ln \frac{(1-\chi_{\alpha})}{(1-\chi_{\alpha}')} \right] \quad (7,14) \quad (5)$$

where χ_{α} is the fraction of solute in the supersaturated solution and χ_{α}' is the fraction of solute in the depleted cell matrix. The use of χ_{α} instead of the equilibrium $\chi_{\alpha e}$ allows us to solve for the chemical free energy release without solving for P and ΔF_{O} separately. The fraction of solute in the supersaturated solution, χ_{α} , is 0.1. The fraction of solute in the depleted cell matrix, χ_{α}' , was estimated using the work of Aaronson and Clark²¹, who determined that the ratio of the experimental to equilibrium proportions of γ is 0.825. Using this figure yields χ_{α}' as 0.017 but a more conservative estimate would give χ_{α}' as 0.02 which is the figure used in these calculations. Substitution of these values in equation 5 gives $P\Delta F_{\text{O}} = -82 \text{ cal/mole}$.

The contribution of the α/γ interface which is produced during cell growth is

$$\Delta F = \frac{2\sigma_{\alpha/\gamma} V}{S} \quad (6)$$

where the molar volume is $10 \text{ cm}^3/\text{mole}$ and the spacing used is $1 \times 10^{-4} \text{ cm}$. The ordered interfacial energy $\sigma_{\alpha/\gamma}$ is 100 ergs/cm^2 . (2) Aaron and Aaronson²⁴ found the disordered interfacial energy in an aluminum-copper allotriomorph to be 300 ergs/cm^2 . This interfacial energy will be used as the estimate for the disordered interfacial energy for an aluminum-silver allotriomorph. Comparing the ordered and disordered interfaces by means of equation 6 yields

$$\Delta F_{\text{ordered}} = \frac{2\sigma_{\alpha/\gamma} V}{S} = 0.5 \frac{\text{cal}}{\text{mole}}$$

and

$$\Delta F_{\text{disordered}} = \frac{2\sigma_{\alpha/\gamma} V}{S} = 1.5 \frac{\text{cal}}{\text{mole}}$$

Thus the change in free energy obtained by transforming a disordered boundary to an ordered interface by "replacive" motion along a α'/γ interface in this system is about -1 cal/mole . This is very small compared to the -82 cal/mole obtained from the chemical free energy by relief of silver supersaturation as the α/α' advances. It is thus concluded that the driving force or energy netted by changing the allotriomorph interface from ordered to disordered structure does not contribute significantly to the driving force of the cellular reaction since the chemical free energy is larger by one order of magnitude.

IV. SUMMARY AND CONCLUSIONS

1. Cellular and general precipitation are observed to occur simultaneously at all aging temperatures up to 0.85 of the absolute solvus temperatures in quench-aged and 0.65 of the absolute solvus in isothermally aged Al-29.8wt%Ag alloy. Cellular precipitation in this alloy system occurs at lower temperatures and at longer times in the isothermally aged samples as seen in figure 2.

2. In all cases the precipitation sequence occurred as follows: general formation of G.P. zones, formation of allotriomorphs followed by the development of general Widmanstatten γ' plates, and finally the cellular precipitation. Considerable aging time elapsed after the γ' precipitation and the initiation of the cellular reaction. The marked bowing and local migration of the grain boundary observed at early aging time in Cu-In alloys¹⁴ was not seen in the Al-ag alloy. All the γ lamellae exhibit a definite habit plane relationship with the α matrix of the cells.

3. In general the γ allotriomorphs of the Al-Ag alloy form with one interface parallel to a habit plane of one of the adjacent grains, i.e., forming an ordered interface on one side of the allotriomorph. The interface with the other grain is disordered. The cellular reaction begins with the interaction of the locally migrating grain boun-

dary with the γ allotriomorphs. The angle of these initial allotriomorphs to the initial grain boundary determines the nature of the boundary-allotriomorph interaction and thus the mode of cell genesis as follows:

- a. If the ordered faces of the γ allotriomorphs lie at a considerable angle to the original grain boundary, these allotriomorphs are converted to the initial γ lamellae by the mechanism shown in Figure 12.
- b. If the ordered faces of the allotriomorphs lie at a moderate angle to the original grain boundary, the disordered interfaces are converted to the γ cell lamellae by the solute precipitation mechanism shown in Figures 10 and 11. However, after the initial stages of cell growth, new lamellae are nucleated at the advancing cell interface.
- c. If the ordered faces of the allotriomorphs lie parallel to the original grain boundary, the allotriomorphs are enveloped by the advancing cell, and the disordered interfaces of the allotriomorphs are converted to ordered interfaces by the solute deposition mechanism shown in Figure 13. However, in this case the γ allotriomorphs do not become γ lamellae of the cells, but all γ cell lamellae are nucleated at the advancing cell interface.

4. In cases 3a and 3b, in which the initial γ lamellae form by interaction of the locally migrating grain boundary with allotriomorphs, the initial cell structures form by the mechanism reported by Fournelle and Clark, modified by the strong coherency forces between the matrix and the precipitate, resulting in a rigid habit plane for the γ lamellae of cells. The mechanism reported by Tu and Turnbull for Pb-Sn alloys was not seen.

5. The principal driving force for the reaction is the chemical free energy derived from the relief of silver supersaturation in the aluminum solid solution rather than the free energy obtained by converting disordered interfaces of the γ lamellae to ordered interfaces.

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Figure 1

Characteristic morphology of a quenched and aged Al-29.8 wt%Ag alloy, showing cellular precipitation, general precipitation, and the precipitate free zone adjacent to the grain boundary. Solution treated 20 minutes at 515°C, water quenched and aged for 40 minutes at 220°C.

X15,000

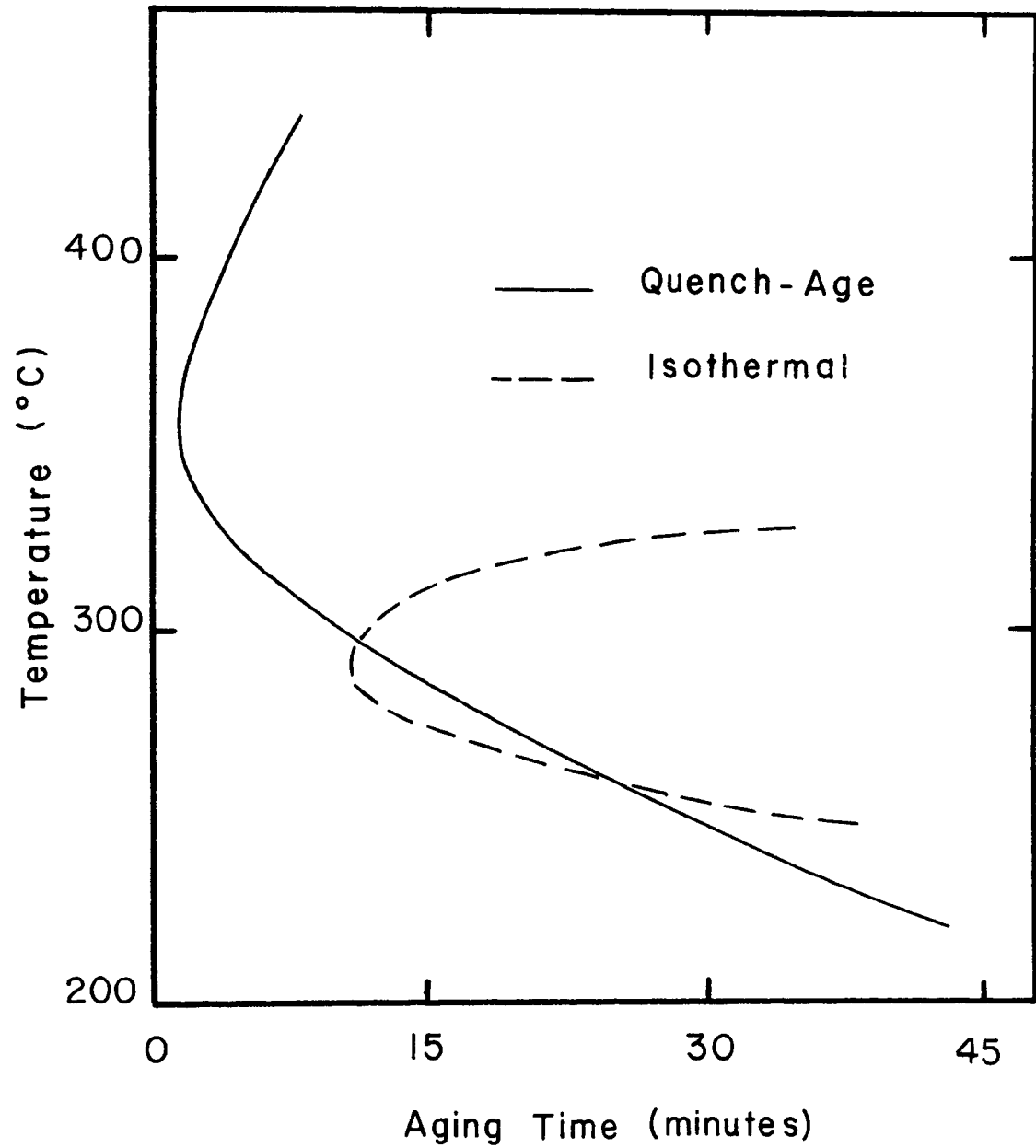


Figure 2
Time-Temperature-Transformation diagram for the start of cellular precipitation for the quench-age and isothermal heat treatments.

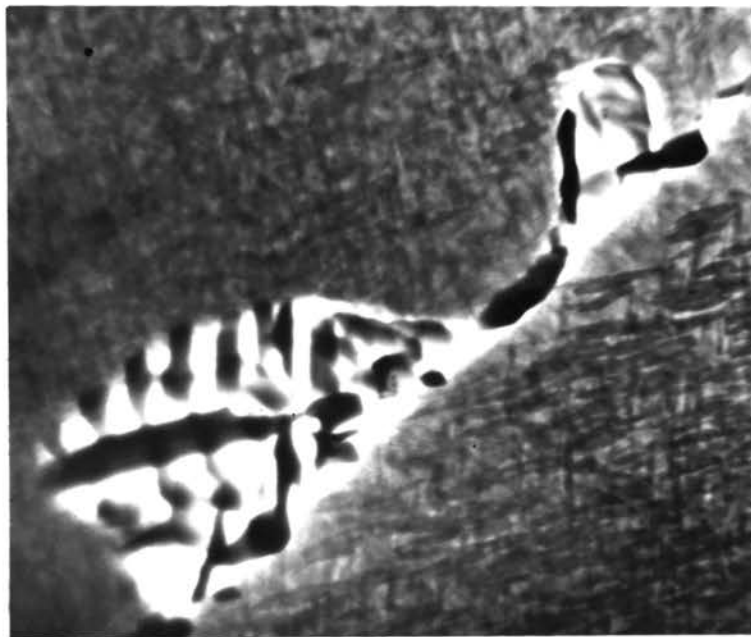


Figure 3
Al-29.8wt%Ag, solution treated 20 minutes at 515°C and
water quenched, aged in hot stage at 219°C.

X25,000

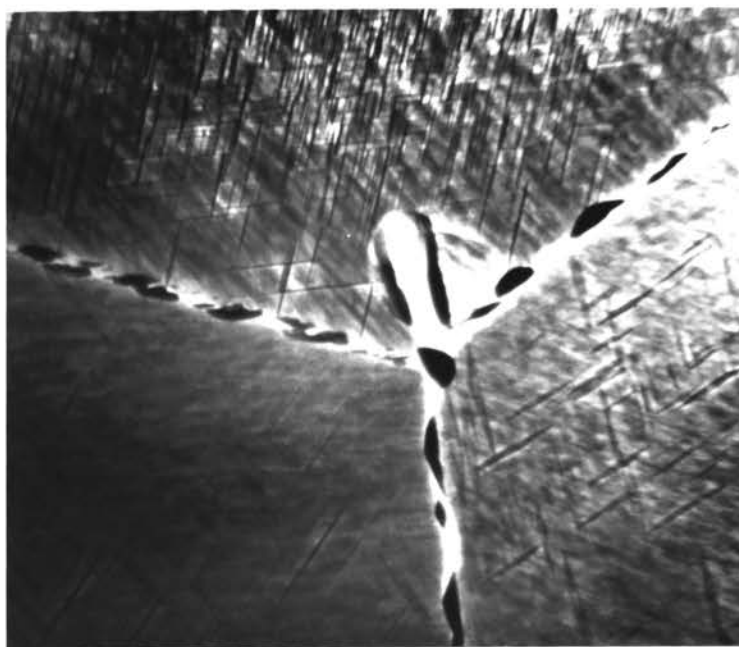


Figure 4
Al-29.8wt%Ag, solution treated 20 minutes at 515°C and
water quenched, aged in hot stage at 219°C.

X10,000

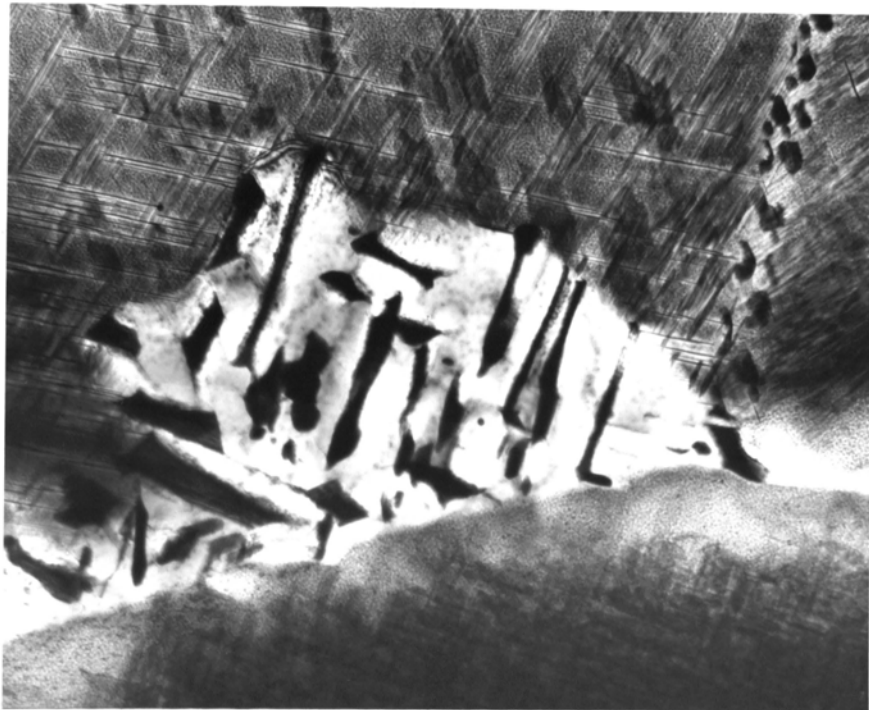


Figure 5

Characteristic morphology of a quenched and aged Al-29.8 wt%Ag alloy showing that initial lamellae are similar to hot stage work. Solution treated 20 minutes at 515°C, water quenched and aged for 90 minutes at 220°C.

X15,000

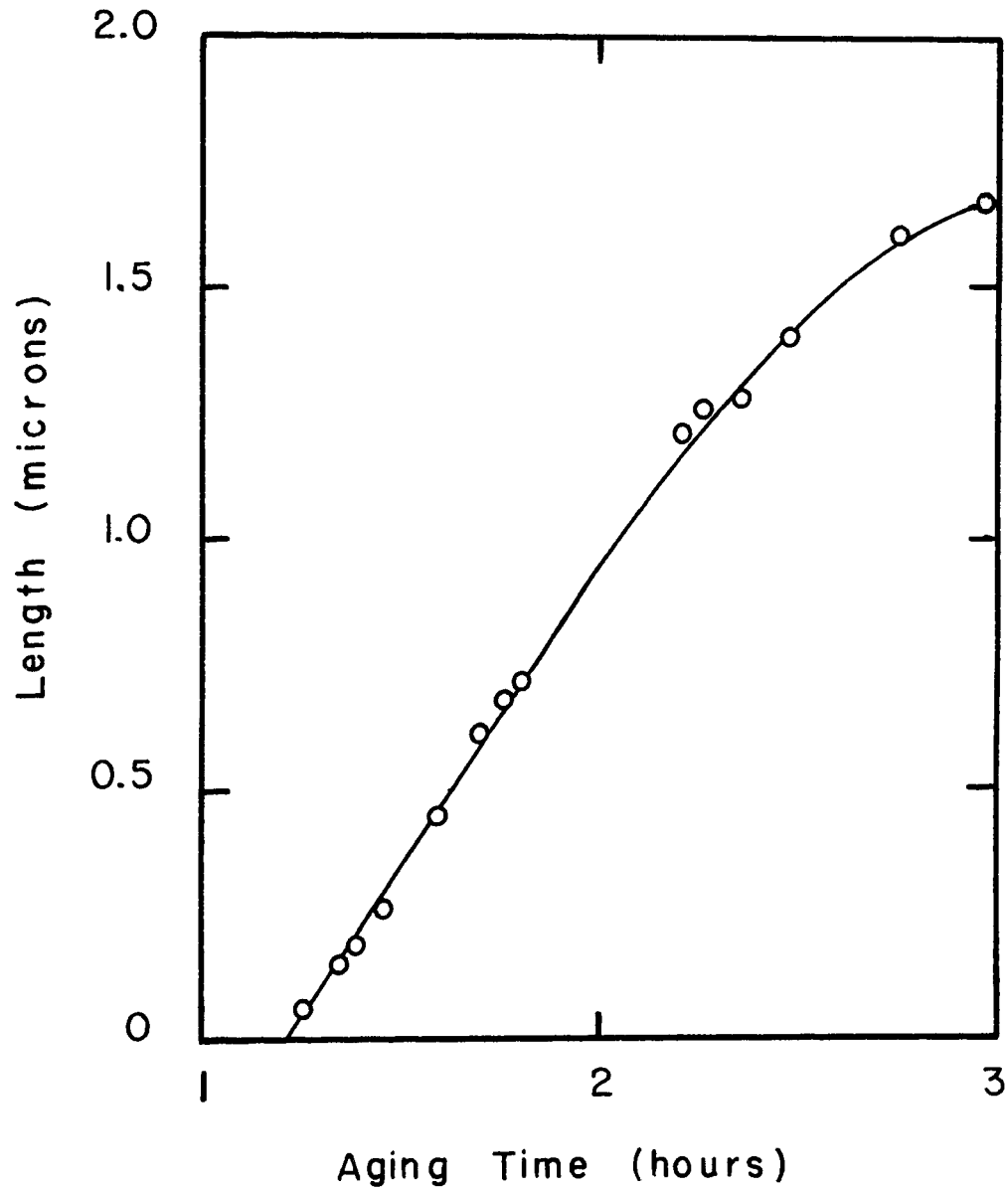


Figure 6
Length of the longest cell lamella in cell as a function of aging time for a hot stage specimen.

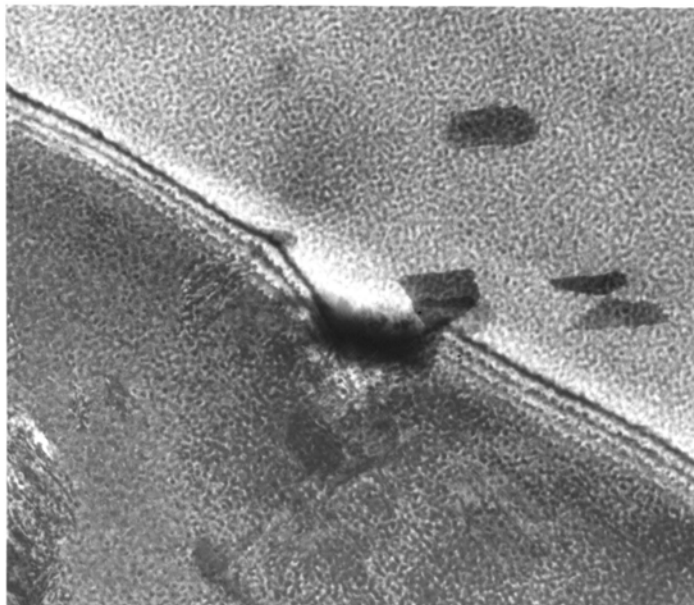


Figure 7

Initial stage of cellular precipitation: grain boundary allotriomorph forming at grain boundary with only a slight tendency for bowing. Solution treated at 515°C, water quenched and aged 20 minutes at 220°C.

X36,000

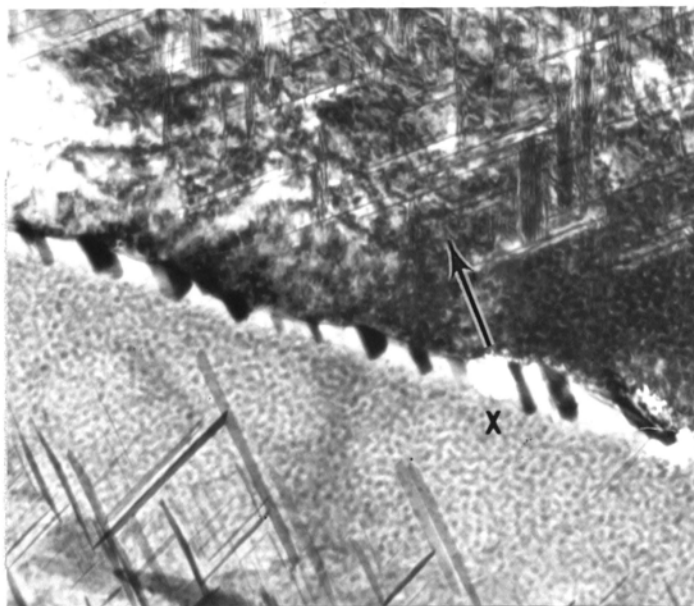


Figure 8

Initial stage of cellular precipitation: grain boundary allotriomorphs growing into cellular precipitation, with more noticeable bowing shown at X in the direction of the arrow. Solution treated at 515°C, water quenched and aged 20 minutes at 220°C.

X36,000



Figure 9

Intermediate stage of cellular precipitation: grain boundary allotriomorphs are clearly developing into cellular precipitation. Solution treated at 515°C, water quenched and aged 45 minutes at 220°C.

X13,500

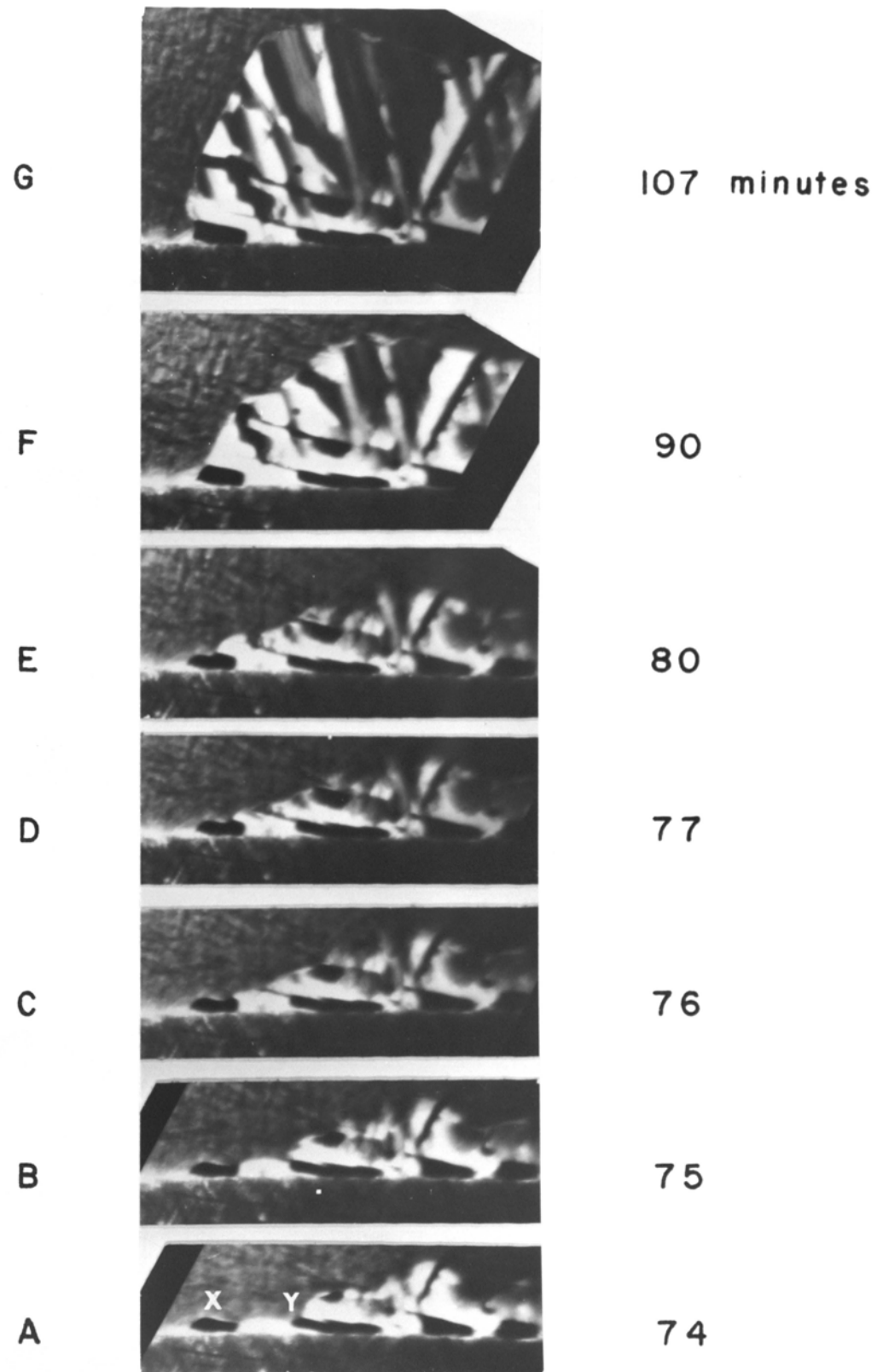


Figure 10
Development of a cell in Al-29.8wt%Ag alloy during aging
at 219°C in the hot stage of the electron microscope.
X14,500

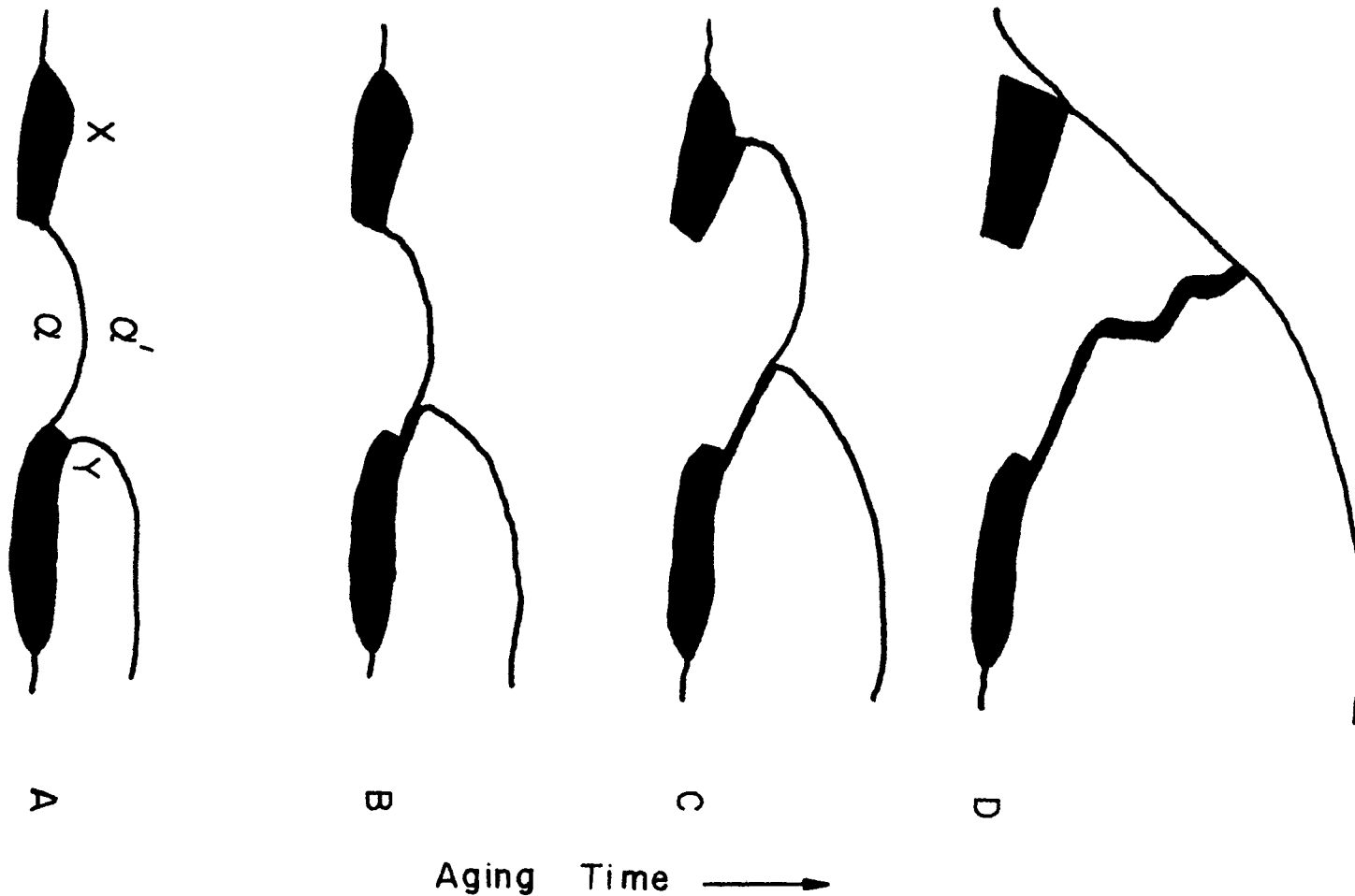


Figure 11

Schematic diagram showing the morphological development of the cellular structure as observed in the cell development of Figure 10.

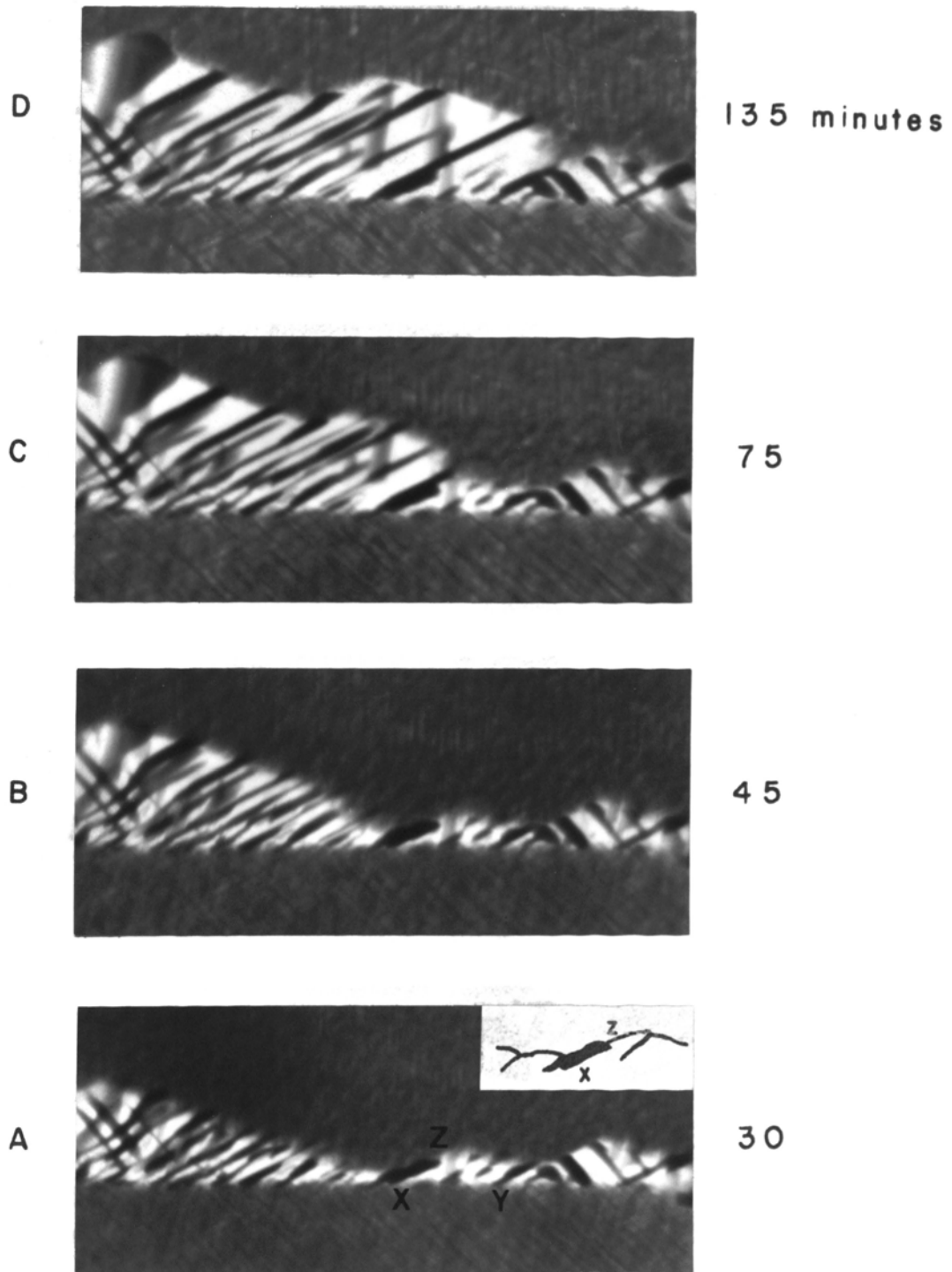


Figure 12
 Development of a cell with allotriomorphs that lie
 at a large angle to the original grain boundary.
 X15,500

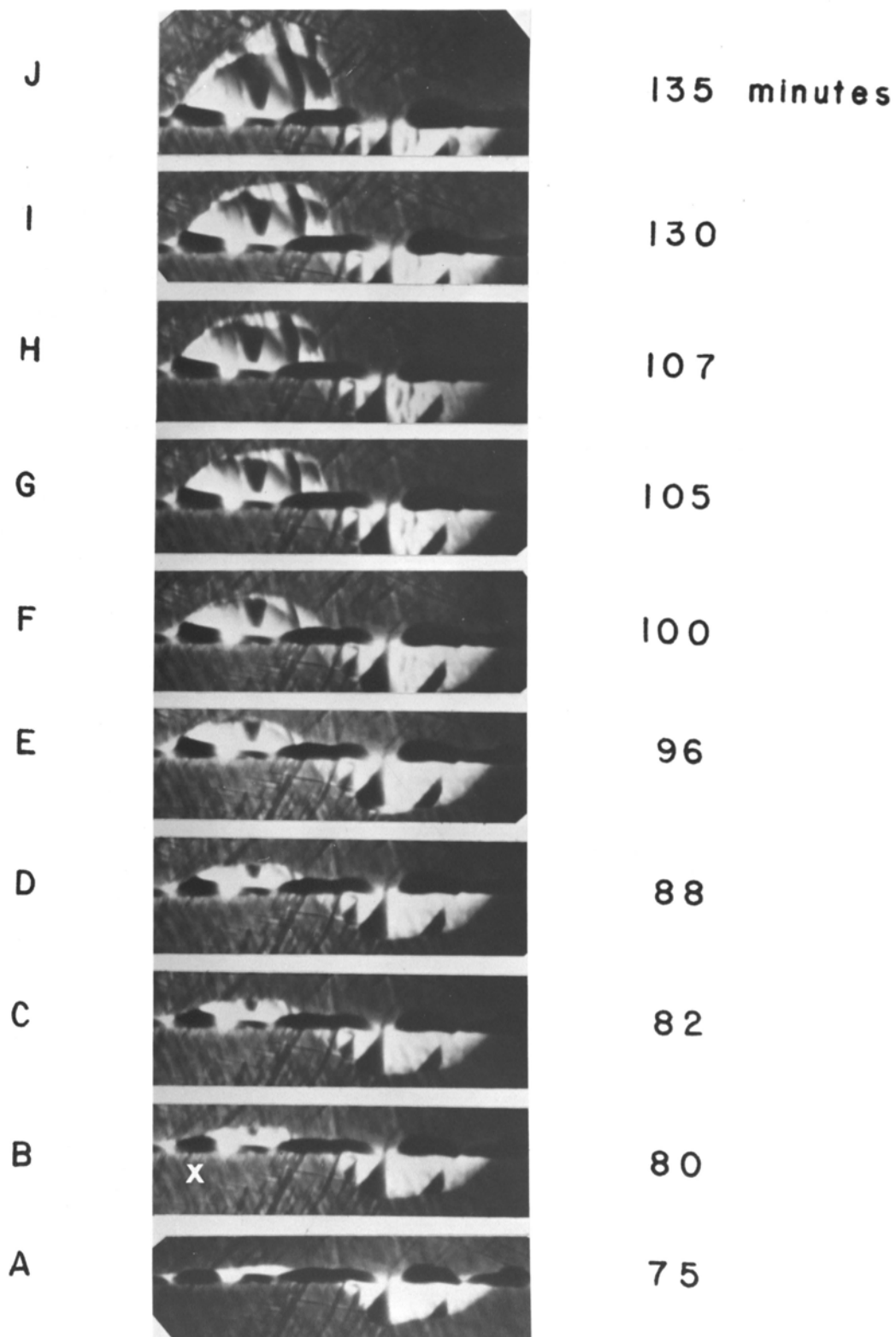


Figure 13
Cellular precipitation at grain boundaries in which the ordered interfaces of the initial allotriomorphs lie parallel to the grain boundary.

X11,000

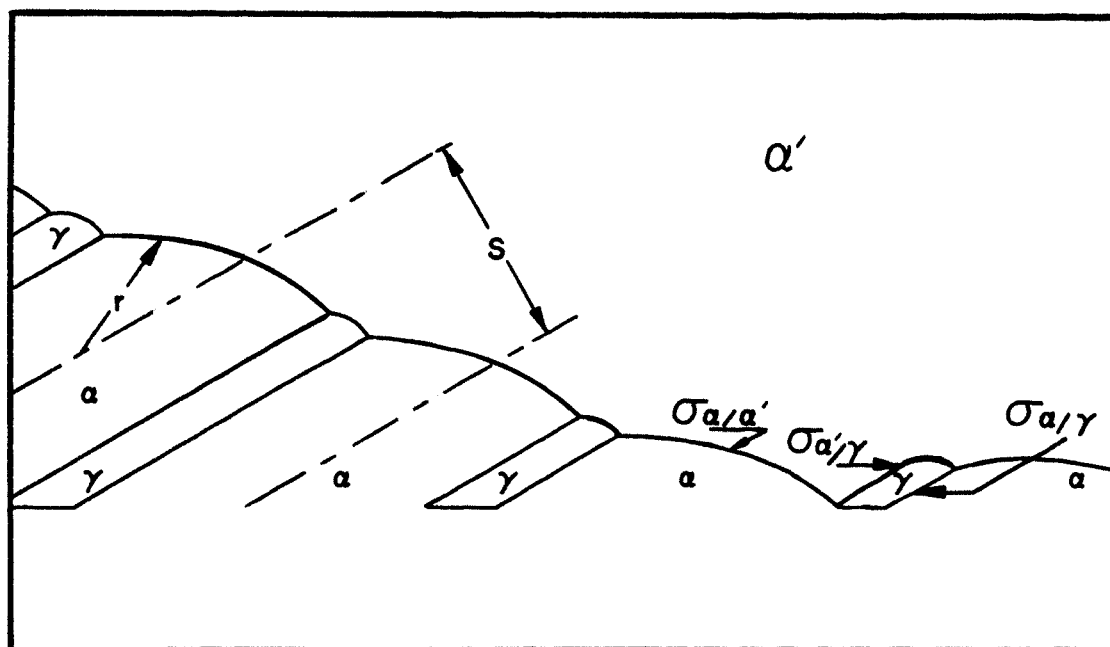


Figure 14
Schematic diagram showing the early stage of cell formation.

TABLE I

Table comparing the growth rates obtained in this study with those obtained by Watanabe and Koda.

Aging Temp. (°C)	Growth Rate (G)	
200°C	0.93×10^{-8} cm/sec	Watanabe & Koda
250°C	5.5×10^{-8} cm/sec	Watanabe & Koda
219°C	2.0×10^{-8} cm/sec	Present Study
219°C	6.2×10^{-8} cm/sec	Present Study

VITA

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