

Growth Mechanisms of Grain Boundary Allotriomorphs in Al-4Pct Cu at High Homologous Temperatures: Interfacial vs Direct Volume Diffusion

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The lengthening and thickening kinetics of θ allotriomorphs in Al-4 pct Cu were measured at 350°, 400°, and 450°C. Three different analyses all indicated that interfacial diffusion (*i.e.*, a right angle collector plate mechanism) was the predominant growth mechanism at 350° and 400°C, but that volume diffusion directly to the growing allotriomorphs made a significant contribution to growth at 450°C. Using the data of this and previous investigations one may conclude that volume diffusion of solute directly to the allotriomorph does not contribute noticeably to growth below $T/T(\text{solidus}) = 0.78$, plays a substantial but still a minority role at $T/T(\text{solidus}) = 0.84$ and 0.90 and becomes the major contributor at $T/T(\text{solidus}) \geq 0.91$ when the matrix is fcc.

THE presence of both grain boundaries and disordered allotriomorph:matrix interphase boundaries provides high diffusivity paths which can enhance the growth kinetics of grain boundary allotriomorphs. That this does occur in the case of θ allotriomorphs in Al-4 pct Cu at low homologous temperatures (200° to 325°C, or 0.54 to 0.69 of the absolute solidus temperature) has been recently demonstrated by Aaron and Aaronson.¹ They showed that both lengthening and thickening were much too rapid to be accounted for by the commonly accepted mechanism of volume diffusion of copper directly to the growing allotriomorphs. The "right angle collector plate" growth mechanism which they proposed to explain these results, and which was subsequently refined and extended by Brailsford and Aaron,² consists of a sequence of three processes: 1) volume diffusion of solute to the grain boundary; 2) solute transport along the grain boundary to the allotriomorph; and 3) interphase boundary diffusion and deposition of solute over the surface of the growing allotriomorph. Aaron and Aaronson restricted their treatment of this mechanism to the case in which the ratio of the grain boundary diffusivity, $D_{\alpha\alpha}$, to the volume diffusivity in the α matrix, D_v , is effectively infinite, *i.e.*, to low homologous temperatures and to substitutional diffusion. Brailsford and Aaron,² having developed improved descriptions of the diffusion field within the grain boundary, were able to incorporate into the model a finite diffusivity of solute within the grain boundary, thereby relaxing somewhat the low temperature restriction. But they retained the assumption that solute transport by volume diffusion directly to the allotriomorph can be neglected. At low homologous temperatures in Al-4 pct Cu, both versions of the model are in substantial agreement, both with each other and with the data. However, incorporation of a finite $D_{\alpha\alpha}/D_v$ (which reduces the rate of mass transport to the allotriomorph) gave a useful improvement in the accounting of the data, as well as of course, information on $D_{\alpha\alpha}$.

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At sufficiently high homologous temperatures, two effects may mitigate against the right angle collector plate mechanism being the predominant contributor to the growth kinetics of allotriomorphs. First, because D_v increases more rapidly with increasing temperature than $D_{\alpha\alpha}$ or $D_{\alpha\theta}$ (the interphase boundary diffusion coefficient), the assumption that $D_{\alpha\alpha} \gg D_v$ becomes progressively less accurate. Second, there may also be a significant contribution to growth by volume diffusion of solute directly to the allotriomorph. As will be discussed later in more detail, Hawbolt and Brown,³ studying the growth of grain boundary allotriomorphs only at very high homologous temperatures in a Ag-5.64 wt pct Al alloy, found that the direct volume diffusion mechanism is predominant at most of the temperatures they investigated.

The present investigation represents, experimentally, a direct extension of the original study of Aaron and Aaronson to higher temperatures, undertaken however for the purpose of ascertaining whether or not direct volume diffusion plays a significant role at these temperatures. This investigation did not become feasible until the availability of the Brailsford-Aaron analysis made it possible to dispense with the assumption that $D_{\alpha\alpha}/D_v = \infty$. Deviations from the growth behavior characteristic of lower temperatures can now be safely ascribed to the intervention of the direct volume diffusion mechanism.

1) EXPERIMENTAL PROCEDURES

The procedures are essentially the same as those previously employed.¹ Bulk samples of homogenized Al-3.93 wt pct Cu alloy, 0.023 cm thick, were solution annealed at 548°C for 2 hr and then isothermally re-acted for various times at 350°, 400°, and 450°C. The time dependencies of the half-thickness, S , and of the half-length or radius, R , of the allotriomorphs,* and

*The allotriomorphs were assumed to be oblate ellipsoids. R thus represents the radius of the circular cross-section in the grain boundary, and S the semi-minor axis of the elliptical cross-section perpendicular to the grain boundary.

also the mean interallotriomorph spacing, R_c , were determined using transmission electron microscopy. True values of these quantities were measured through the use of a tilting stage as previously described.¹

Since the growth of individual allotriomorphs could not be satisfactorily measured by the hot stage technique due to the interference of surface diffusion,⁴ the time dependencies of lengthening and thickening were determined by measurement of R and S of the thickest allotriomorph in each of the series of bulk samples reacted for successively increasing times at each temperature. Although some faceting of the allotriomorphs was observed, this was not pronounced (as was also found at lower temperatures¹); measurements were not made on markedly faceted allotriomorphs.

II) RESULTS

The lengthening and thickening data as a function of the total aging time for the three temperatures investigated are shown in Figs. 1 to 3. Table I contains the observed values of R_c and of the incubation times. These times, representing the shortest reaction times at which allotriomorphs were visible at high magnification in the electron microscope, were small enough to be neglected in the preparation of the figures and in the calculations based upon these figures. The kinetic data were plotted in logarithmic form in order not to obscure the short aging time observations. Each data point represents a different foil, with both R and S measured on the thickest of at least fifty allotriomorphs. (The curves in these figures will be discussed later.)

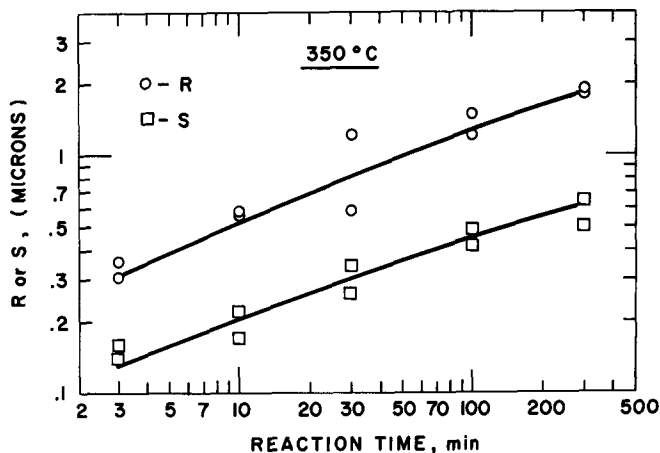


Fig. 1—Variation of half-length (R) and half-thickness (S) of the largest allotriomorph with time (350°C). Curves fitted in accordance with Brailsford-Aaron² analysis.

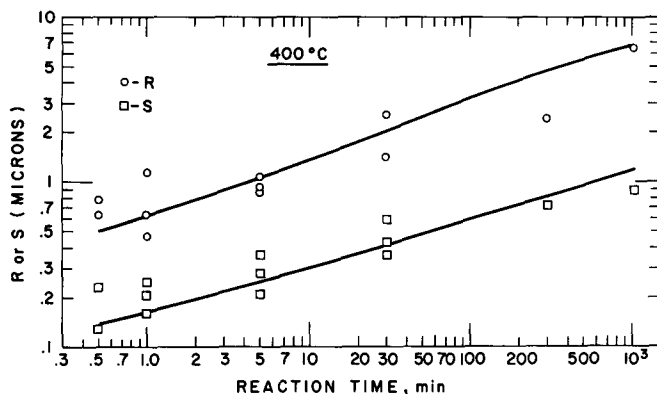


Fig. 2—Variation of half-length (R) and half-thickness (S) of the largest allotriomorph with time (400°C). Curves fitted in accordance with Brailsford-Aaron² analysis.

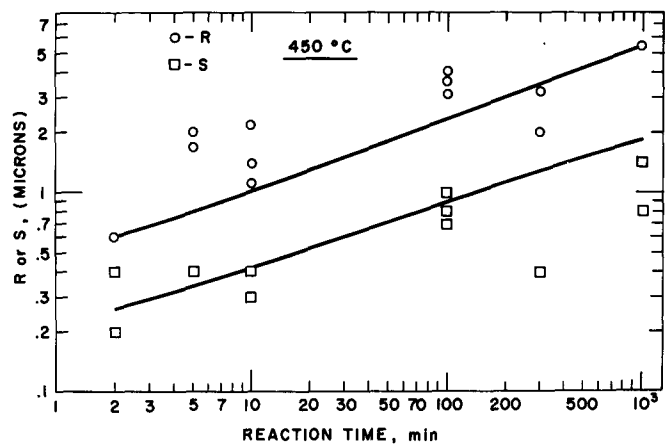


Fig. 3—Variation of half-length (R) and half-thickness (S) of the largest allotriomorph with time (450°C). Curves fitted in accordance with Brailsford-Aaron² analysis.

Table I. Summary of Allotriomorph Growth Measurements

$T, ^\circ\text{C}$	τ, sec	R_c, μ	$\beta, \text{cm/sec}^{1/2}$	$\varphi, \text{cm/sec}^{1/2}$	C
450	15 ± 15	20	1.5×10^{-5}	3.0×10^{-6}	5.0
400	7.5 ± 7.5	13	1.0×10^{-5}	2.2×10^{-6}	4.6
350	2.5 ± 2.5	6	2.5×10^{-6}	8.0×10^{-7}	3.1
200	90 ± 30	2.6	3.2×10^{-7}	1.0×10^{-7}	3.2

III) DISCUSSION

A) Comparison of Apparent and Conventionally Determined Volume Diffusivities

A useful preliminary assessment of the role which volume diffusion directly to grain boundary allotriomorphs plays in determining the growth kinetics of the allotriomorphs may be made by computing, from the measured kinetics of growth, the apparent volume interdiffusion coefficient, D_{app} , required to produce these kinetics, and comparing it with the literature value of the conventionally determined D_v at the same temperature. The measurements of D_v in α Al-Cu reported by Murphy⁵ provide a good basis for this comparison. In the previous study,¹ two values of D_{app} were computed at each temperature. One was obtained by matching the kinetics of lengthening to an analysis due to Hillert,⁶ and the other was determined from the thickening kinetics and a relationship derived by Zener.⁷ This procedure was especially valuable from the viewpoint of establishing individual steps of the collector plate mechanism. It has, however, two disadvantages which can become especially important at the higher reaction temperatures employed in the present investigation. The Zener equation assumes that the broad faces of the θ allotriomorphs are of effectively infinite extent. Since the thickness/length ratio of θ allotriomorphs (from 200° to 450°C) is in the range $\frac{1}{3}$ to $\frac{1}{5}$, this assumption can be shown to discount an appreciable flux of copper from the region of the α matrix lying outside of the projected volume of the allotriomorphs, and thus to yield too high values of D_{app} . The second difficulty is that this approach treats a single overall process as two separate ones,

and accordingly gives two (usually) different values of D_{app} at a given reaction temperature, neither of which is necessarily an accurate representation of the overall process. Both disadvantages may be remedied by approximating the shape of an allotriomorph as an oblate ellipsoid and employing the analysis of Horvay and Cahn⁸ for the direct D_v -controlled growth of this morphology.* The present application of the Horvay-

*Brailsford and Aaron² approximated the shape of a θ allotriomorph as two caps of an ellipse. Comparison with electron micrographs of representative θ allotriomorphs indicates that this is a better model for the shape of these crystals. The oblate ellipsoid, however, is the best approximation of the experimentally observed shape for which a solution to the problem of growth by direct volume diffusion is available.

Cahn analysis differs a little from that previously reported by Hawbolt and Brown,³ and may be somewhat more convenient. On this analysis, $R = \beta t^{1/2}$ and $S = \phi t^{1/2}$, where β and ϕ are the respective parabolic rate constants, Table I, and t = growth time. The aspect ratio of an allotriomorph is $C = \phi/\beta$. As developed in the appendix, when C is appreciably less than unity,⁸ which obtains in the present study,

$$\frac{x_\alpha - x_\alpha^{\alpha\theta}}{x_\theta - x_\alpha^{\alpha\theta}} = e^\Omega \cdot (\Omega + a) \cdot \sqrt{\Omega} \cdot \left[\frac{\pi}{\sqrt{a}} e^a \operatorname{erfc}(\sqrt{a}) - \frac{\sqrt{\pi}}{a} \left(1 - \frac{1}{2a} + \frac{3}{4a^2} \right) \operatorname{erf}(\sqrt{\Omega}) - \frac{1}{a^2} \left(1 - \frac{3}{2} + \frac{\Omega}{a} \right) \sqrt{\Omega} e^{-\Omega} \right] \quad [1]$$

$$\Omega = \frac{3C^2\beta^2}{4D}$$

$$a = \frac{3\beta^2(1-C^2)}{4D}$$

where x_α , $x_\alpha^{\alpha\theta}$, and x_θ = mole fraction of copper in α in the bulk alloy, in α at the $\alpha/(\alpha + \theta)$ phase boundary,

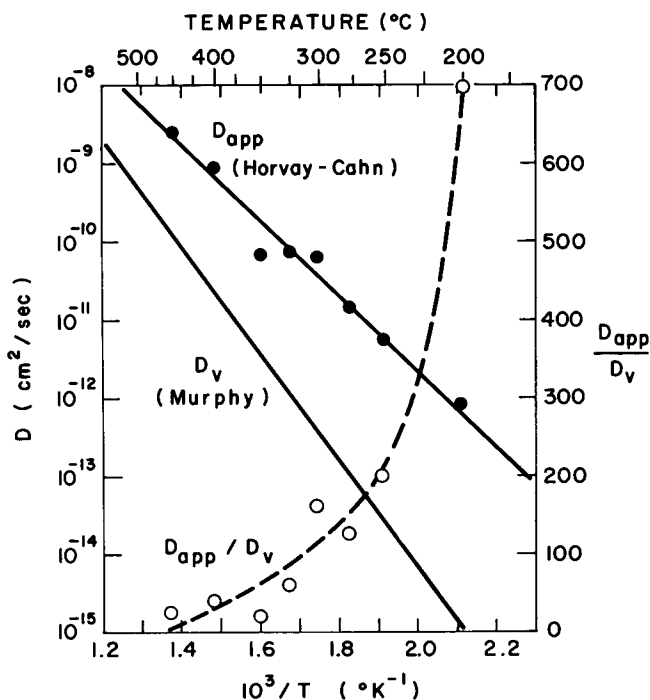


Fig. 4—Arrhenius plots of D_v (Murphy⁵) and $D_{apparent}$ (calculated via Horvay-Cahn analysis of allotriomorph growth), and the temperature dependence of the ratio of D_{app}/D_v .

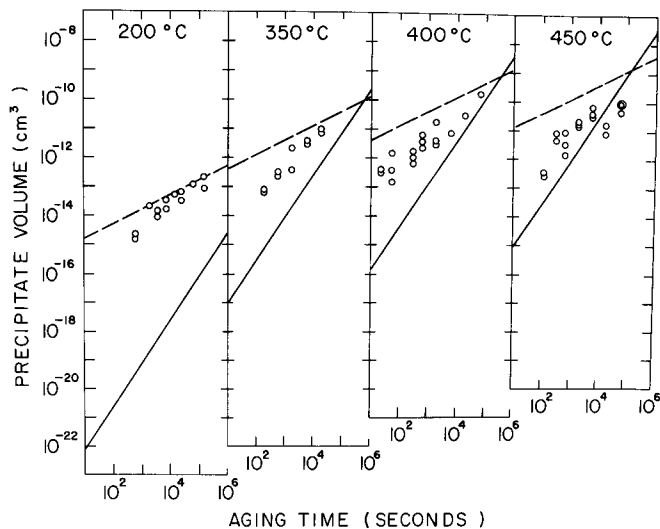


Fig. 5—Time dependence of precipitate volume at four representative temperatures showing experimental volumes (\odot), volumes which would result from volume diffusion of solute directly to the growing allotriomorph (—), and volumes computed from the "right angle collector plate" mechanism in the low temperature limit where $D_{\alpha\alpha}/D_v \rightarrow \infty$ (----).

and in θ , respectively. Fig. 4 is an Arrhenius plot of D_{app} and D_v ; the data previously reported¹ on the thickening and lengthening kinetics of θ allotriomorphs at 200° to 325°C have been reanalyzed in order to evaluate D_{app} from the Horvay-Cahn analysis over the widest practicable temperature range. Comparison of D_v and D_{app} supports the earlier finding that direct volume diffusion plays a negligible role in the growth of θ allotriomorphs at low temperatures. At the temperatures studied during the present investigation, however, the ratio of D_{app} to D_v is seen to be sufficiently small to suggest that, at least at the highest temperature D_v may now be making a detectable contribution to growth. It should be immediately noted that an analysis of allotriomorph growth which includes both direct volume diffusion and interfacial diffusion-aided volume diffusion has yet to be made—and would unquestionably be a most formidable task. However, the considerations of this discussion and the previously noted results of Hawbolt and Brown³ will be used to demonstrate that such an analysis must be attempted if a generally valid description of the growth of allotriomorphs is to be obtained.

B) Comparisons of Allotriomorph Volumes Produced Experimentally, by Direct Volume Diffusion and by the Collector Plate Mechanism

The volume, V , of an ellipsoid of revolution = $\frac{4}{3}\pi R^2 S$. Plots of the experimentally determined volume, V_{exp} , presented in Fig. 5 as a function of growth time at four representative temperatures, were constructed from the experimental values of R and S , Figs. 1 to 3 and Ref. 1. The volumes which would have resulted had growth taken place only by volume diffusion directly to an allotriomorph, V_{dv} , were computed from the Horvay-Cahn analysis on the basis of the D_v data of Murphy⁵ and the experimental values of C . The volumes produced when all growth takes place by the

collector plate mechanism, V_{cp} , were determined on the following basis. The volume of copper in α , $\nu(t)$, flowing to the grain boundary collector plate per unit time is simply:

$$\frac{d\nu(t)}{dt} = \frac{1}{\rho} \cdot \frac{dm}{dt} \quad [2]$$

where ρ = density of copper in α and dm/dt = rate of mass transport of copper to the boundary. Substituting the expression which Aaron and Aaronson¹ obtained* for dm/dt in Eq. [2] and integrating

$$\nu(t) = \frac{2A_v D_v^{1/2}}{\pi^{1/2}} (x_\alpha - x_\alpha^{\alpha\theta} e^{\gamma_{\alpha\theta} V_\theta / RT R_2 x_\theta}) t^{1/2} \quad [3]$$

where A_v = area of the collector plate per allotriomorph = πR_c^2 , $\gamma_{\alpha\theta}$ = energy of a disordered $\alpha:\theta$ boundary = 300 erg per sq cm, V_θ = molar volume of θ = 10 cu cm per mole, R = gas constant, T = absolute temperature, and R_2 = radius of curvature of the allotriomorph in the immediate vicinity of the allotriomorph-grain boundary conjunction = 10^{-5} cm. Since $\nu(t)$ is the volume of copper in α which has been transferred to the precipitate, the number of copper atoms in the CuAl_2 precipitate may be obtained by dividing $\nu(t)$ by Ω , the atomic volume of copper in the α matrix. (Ω = atomic weight of copper divided by the product of Avogadro's number and the density of copper). This gives the total number of copper atoms in the CuAl_2 precipitate. Since there are four copper atoms in a θ unit cell and the volume of this cell is 179 \AA^3 ,⁹ $\nu(t)/\Omega$ is readily converted to V_{cp} . This volume represents, however, the upper limit of V_{cp} , since the assumptions are made that all copper reaching the boundary is instantly transported to the allotriomorph and that the entire area of the collector plate is uniformly operative at $t = 0$. (Both assumptions thus hypothesize that $D_{\alpha\alpha}/D_v = \infty$.)

The plots of Fig. 5 show two definite trends. The first is that V_{dv} and V_{cp} intersect at times which decrease with increasing temperature. The second is that the V_{exp} data are displaced from near coincidence with V_{cp} at 200°C* to a position not far above

*Inasmuch as V_{cp} is not only an upper limit but is also based, at 200°C, upon an approximate value of A_v ,¹ only limited significance can be attached to the similar levels of V_{cp} and V_{exp} at this temperature.

(and even passing below) V_{dv} at 450°C. The intersection of V_{dv} and V_{cp} results from the circumstances that V_{dv} , though initially smaller, is proportional to $t^{3/2}$, whereas V_{cp} is proportional to $t^{1/2}$. The intersection point moves to shorter times with increasing temperature principally because V_{dv} is proportional to $D_v^{3/2}$, while V_{cp} is proportional to $D_v^{1/2}$.

Since V_{exp} falls an average of four orders of magnitude above V_{dv} at 200°C and still averages about $1\frac{1}{2}$ orders of magnitude larger at 400°C, direct volume diffusion must make a negligible contribution to growth under these conditions. At 450°C, however, V_{exp} and V_{dv} become similar. On the other hand, V_{exp} also lies close to V_{cp} at longer growth times. Since values of V_{cp} in Fig. 5 represent an upper limit, it is not possible to decide, on the basis of the volume analysis and the present experimental data, whether direct volume diffusion or the collector plate mechanism is

predominant at 450°C. Fig. 4 indicates, however, that the collector plate mechanism is still the most important contributor, but also implies that direct volume diffusion is now a significant factor in the growth of θ allotriomorphs.

C) Calculation of Interfacial Diffusivities from the Brailsford-Aaron² (B-A) Analysis

This analysis allows determination of both $D_{\alpha\alpha}$ and $D_{\alpha\theta}$ by trial and error determination of the curves of best fit through the experimental data on S vs t and R vs t . Additional kinetic data which must be furnished include the "average" value of R at the shortest growth time employed, R_c , D_v , and the dihedral angle at the allotriomorph:grain boundary conjunction.¹⁰ The curves thus obtained are plotted in Figs. 1 to 3. Quite satisfactory fits are seen to have been obtained at 350° and 400°C. At 450°C, however, even the "best" curves have shapes clearly inconsistent with the trends of the experimental data. This result is in agreement with and further supports that of Figs. 4 and 5: at 450°C, direct volume diffusion contributes to the growth of θ allotriomorphs to an extent sufficient so that the assumption of the Brailsford-Aaron analysis that it does not, visibly fails.

Fig. 6 plots the $D_{\alpha\alpha}$ and $D_{\alpha\theta}$ values obtained by application of the B-A analysis to the experimental data of the present investigation, and also the values which B-A reported on the basis of the data of Aaron

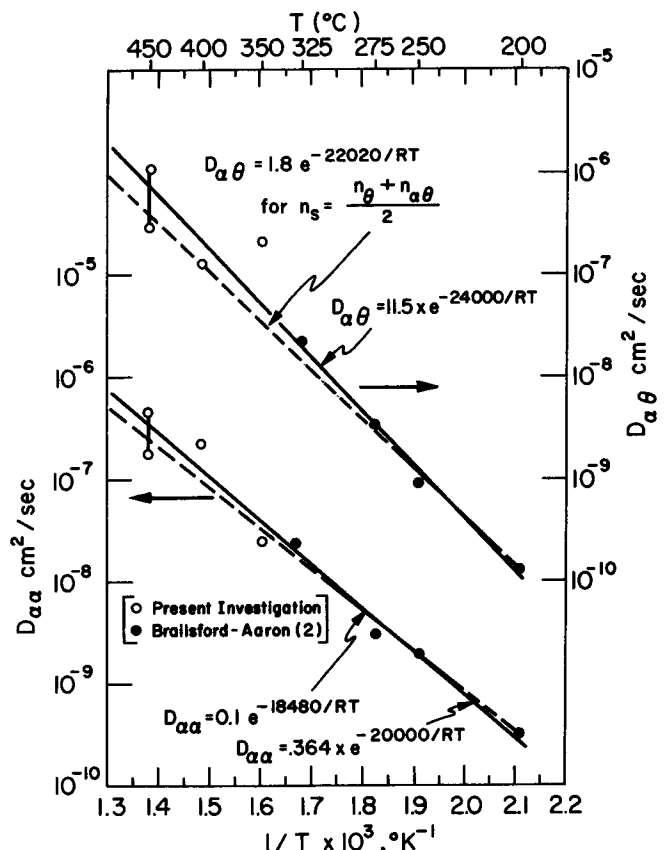


Fig. 6—Arrhenius plots of $D_{\alpha\theta}$ (for $n_s = (n_\theta + n_{\alpha\theta})/2$) and of $D_{\alpha\alpha}$, showing least square fit to low temperature data only (-----) $D_{\alpha\theta} = 1.8e^{-22,020/RT}$, $D_{\alpha\alpha} = 0.1e^{-18,480/RT}$ and least square fit to all data (——) $D_{\alpha\theta} = 11.5e^{-24,000/RT}$, $D_{\alpha\alpha} = 0.364e^{-20,000/RT}$.

and Aaronson. At 450°C, the scatterband represents the approximate range within which further choices as to accuracy of fit could no longer be objectively made. The new values of $D_{\alpha\alpha}$ and $D_{\alpha\theta}$ are seen to be generally consistent with those obtained at lower temperatures. New values of the constants of the Arrhenius equations for these diffusivities are indicated in Fig. 6; they are relatively little changed from those originally given by B-A, also shown in Fig. 6.

D) Comparison with the Results of Hawbolt and Brown³

In the present study, direct volume diffusion had no significant effects upon the growth kinetics of θ allotriomorphs at T/T_s (absolute reaction temperature/absolute solidus temperature) = 0.78 (400°C), but did enter the picture at $T/T_s = 0.84$. These results are qualitatively consistent with those of Hawbolt and Brown on the growth kinetics of β (bcc) allotriomorphs precipitated from α (fcc) in an Ag-5.64 wt pct Al alloy at higher homologous temperatures. These investigators assumed that growth was controlled by direct volume diffusion, and computed D_{app} from the Horvay-Cahn analysis for an oblate spheroid. They determined D_v in the matrix by means of independent diffusion couple experiments. Agreement between the two sets of diffusivities seemed close enough to allow the conclusion that growth was controlled by this mechanism. At the lowest temperature which they studied, $T/T_s = 0.90$ (674°C), however, $D_{app}/D_v \cong 5$, indicating from the viewpoint of the present study that the collector plate mechanism was the predominant mechanism of growth, but that direct volume diffusion had played an important role. Just below $T/T_s = 0.91$ (688°C), this ratio decreased to about two; the effects of interfacial diffusion upon growth kinetics at this temperature are therefore probably outside the limits of experimental error. At $T/T_s = 0.91$ (688°C) and 0.92 (700°C), the contribution of interfacial diffusion was no longer detectable by this method. Since volume and probably also interfacial diffusivities in fcc metals tend to be similar at a constant homologous temperature,¹¹ one may accordingly hazard the quite preliminary generalization that effective elimination of the effects of interfacial diffusion upon the growth kinetics of allotriomorphs in fcc matrices requires a T/T_s greater than ca 0.9. This generalization is supported by Fig. 7, in which the D_{app}/D_v vs T/T_s data for Al-Cu and Ag-Al are plotted on the same graph and are seen to exhibit a reasonable degree of continuity.

IV) SUMMARY

The half-length and the half-thickness of grain boundary θ allotriomorphs, and the average distance between them, were measured as a function of time in specimens of an Al-4 pct Cu alloy isothermally reacted at 350°, 400°, and 450°C. These data were then considered in conjunction with similar data reported at lower temperatures (200° to 325°C) in the same alloy¹ from the viewpoint of the temperature-dependence of the relative contributions of two different growth mechanisms: a) volume diffusion of solute directly to an allotriomorph, and b) volume diffusion of solute to the grain boundary "collector plate" surrounding an allotriomorph, followed by grain boundary diffusion

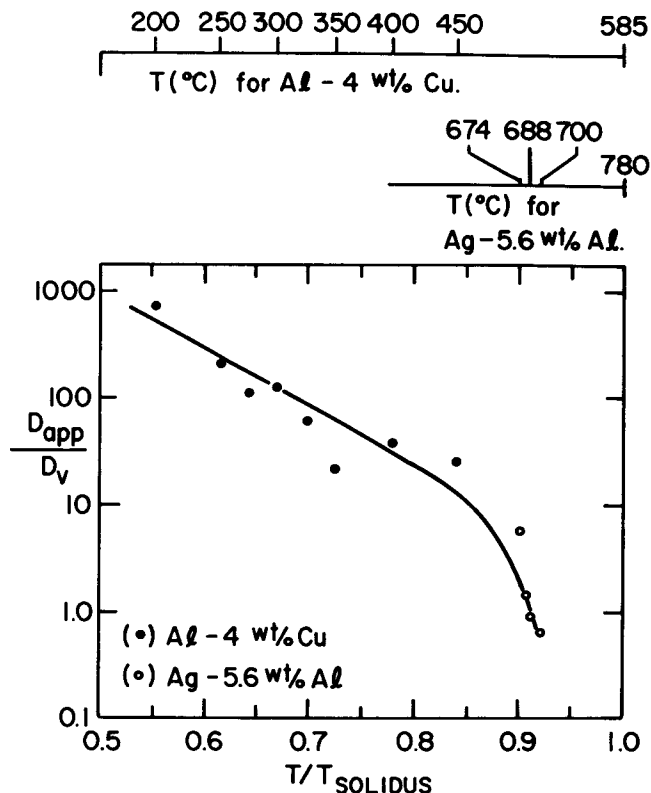


Fig. 7—The ratio of the apparent to the independently measured volume diffusivities for θ allotriomorphs in Al-4 pct Cu and for β allotriomorphs in Ag-5.6 pct Al³ as a function of reduced temperature.

to its edges and then interphase boundary diffusion over and deposition onto the allotriomorph. Assuming an allotriomorph to be an oblate spheroid, the apparent diffusivity (D_{app}) needed to produce the observed growth kinetics was determined from the Horvay-Cahn⁸ analysis. Fig. 4 shows that the ratio of D_{app} to D_v (the independently measured⁵ volume interdiffusion coefficient) decreases from ca 700 at 200°C to approximately 25 at 450°C, suggesting that direct volume diffusion may make a significant contribution to growth at the latter temperature. Comparison of the experimentally determined volume of the allotriomorph as a function of reaction time with that produced by direct volume diffusion alone and by the collector plate mechanism alone shows that the experimental volume is roughly that allowed by the collector plate mechanism at 200°C, but approaches the volume developed by direct volume diffusion at 450°C, indicating a similar variation of the relative contribution of the two mechanisms with temperature. Application of the Brailsford-Aaron² analysis to the experimental data yielded the grain boundary and interphase boundary diffusivities, $D_{\alpha\alpha}$ and $D_{\alpha\theta}$, respectively, and showed them to be consistent with the interfacial diffusivities previously reported.² This analysis also added a third piece of evidence for a significant role for direct volume diffusion at 450°C: uniquely at this temperature, the Brailsford-Aaron analysis was unable to fit satisfactorily the experimental data on half-length and half-thickness vs time.

The data of this and of the previous investigation cover the homologous temperature range T/T_s (T_s = absolute solidus temperature) = 0.54 to 0.84. Haw-

bolt and Brown³ have compared D_{app} with D_v for allotriomorphs precipitated in an fcc matrix in Ag-5.64 wt pct Al at $T/T_s = 0.90$ to 0.92 . Probably because diffusivities in fcc metals tend to be similar at a given homologous temperature, the two studies yielded consistent results. Direct volume diffusion was first observed to contribute noticeably to growth at $T/T_s = 0.78$, to play a substantial but still a minority role at $T/T_s = 0.84$ and 0.90 and to become the overwhelmingly predominant contributor at $T/T_s = 0.91$.

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APPENDIX

CONVERSION OF THE HORVAY-CAHN⁸ EQUATION FOR D_v -CONTROLLED GROWTH OF OBLATE SPHEROIDS FROM REDUCED TO CARTESIAN COORDINATES

The equation to be converted (using the Horvay-Cahn equation numbers⁸ unless otherwise noted) is:

$$U_f = e^{\Omega(\Omega + a)\sqrt{\Omega}} \cdot G\{\Omega; a\} \quad [67d]$$

where U_f = supersaturation = $(x_\alpha - x_\alpha^{\alpha\theta}) / (x_\theta - x_\alpha^{\alpha\theta})$ (these symbols are defined in conjunction with Eq. [1] in the present text), Ω = the square of the "reduced radius" = the value of ω at the position of the interphase boundary, a = an "oblateness" parameter, and G is a function of Ω and a . The relationship derived for ω in the case of an oblate spheroid is:

$$\omega^2 + (a - \chi)\omega - a\eta = 0 \quad [63a]$$

where, on Eq. [63c], $\chi = (X^2 + Y^2 + Z^2) / 4D_v t$ ($X = Y$ = radius and Z = half-thickness of an oblate spheroid [$X > Z$] in Cartesian coordinates and t = growth time) and $\eta = X^2 / 4Dt$. The aspect ratio, C , which must be obtained from experimental observations, is:

$$C = \sqrt{\frac{\omega}{a + \omega}} \quad [62]$$

Rearranging,

$$a = \omega \left(\frac{1}{C^2} - 1 \right) \equiv C' \omega$$

Substituting into Eq. [63a],

$$\omega = \frac{\chi + \eta C'}{1 + C'}$$

at the interphase boundary, using the relationship for χ , η , and C' ,

$$\omega = \Omega = \frac{X^2 + Y^2 + (Z^2/C^2)}{4D_v t / C^2}$$

$$a = \frac{(1 - C^2)(X^2 + Y^2 + (Z^2/C^2))}{4D_v t}$$

The time dependencies of X , Y , and Z are taken to be parabolic:

$$R \equiv X = Y = \beta t^{1/2} \quad \text{and} \quad Z = \phi t^{1/2} \equiv S$$

Hence,

$$\Omega = \frac{3C^2\beta^2}{4D_v} \quad [4]$$

$$a = \frac{3\beta^2(1 - C^2)}{4D_v} \quad [5]$$

In the unpublished report¹² from which Ref. 8 was extracted, Horvay and Cahn give limiting expressions for $G\{\Omega; a\}$ when a/Ω is small and when it is large. Noting that

$$\frac{a}{\Omega} = \frac{1 - C^2}{C^2}$$

and that $C < 1$ for oblate ellipsoid, when $C \leq \frac{1}{3}$, say, $a/\Omega \geq 8$, and the large a/Ω expression appears appropriate. This expression, a direct combination of Eqs. [81] and [82] in the Research Report, and Eqs. [4] and [5] are substituted into Eq. [67d] to obtain Eq. [1] in the text.

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