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Publication Date
1982-07-01
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July 1982
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LEDGE STRUCTURE AND THE MECHANISM OF $\theta'$ PRECIPITATE GROWTH IN Al-Cu

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ABSTRACT

The structure of growth ledges on the broad faces of $\theta'$ {001} plate precipitates in Al-4% Cu was studied by high resolution electron microscopy. In contrast to current models, it was found that single ledges were associated with a partial dislocation whose shear component was $a/2 \langle 100 \rangle$, analogous to the $a/6 \langle 112 \rangle$ Shockley partials in the nucleation of $\gamma'$ plates on {111} planes in Al-Ag. This experimental result is shown to be a necessary outcome of the existence of a lattice correspondence between the fcc matrix and the bct precipitate. A simple model of the structural transformation distinguishes between conservative and non-conservative growth ledges when $\theta'$ forms directly from solid solution. When $\theta'$ forms from $\theta''$ the vacancy supersaturation provided by dissolving dislocation loops initiates the transformation. It is concluded that the observed processes satisfy the demand for shape and volume accommodation. Double ledges with opposite shears minimize shape changes while observed superledges, 2.03nm high, correspond to the additional minimization of volume changes. Misfit in the broad faces is accommodated by epitaxial dislocations formed by combining growth partials. A comparison with other alloys such as Pt-C and Al-Ag suggests a more general applicability of the model.
INTRODUCTION

It is now generally accepted that plate shaped precipitates grow by a ledge mechanism (1). Model systems for the experimental verification of the theory of ledge growth have been γ' plates on {111} planes in Al-Ag and θ' plates on {001} planes in Al-Cu alloys. However, while the growth of γ' plates is known to proceed by the diffusion-controlled glide of Shockley partials on {111} planes, no such dislocation process has been found for θ' plates on {001} planes. Instead, ledges on the broad faces of θ' precipitates are considered to be disordered and precipitate plate growth has been modeled after the growth of crystals from the vapor phase. The fact that θ' grows from a solid rather than a vapor has been accounted for only in the diffusion equation.

For the past thirty years transmission electron microscopy has provided the opportunity for directly observing precipitate growth processes, and a number of detailed studies have been conducted (e.g., 2-6). However, while a good deal of information has been obtained on the kinetic aspects of the problem, the details of the growth mechanisms, even in simple systems, remain obscure. Recently new progress has been made by the application of a combination of high resolution imaging techniques. In an elegant study of the growth of θ' precipitate plates from Al-4%Cu solid solution, Stobbs and Purdy (7) showed that without exception the thickness of the growing plates assumed discrete values corresponding to specific multiples of half unit cells of θ'. Moreover, each discrete thickness was characterized by a consistent sign (interstitial or vacancy) of the elastic accommodation strain.

In a separate development Dahmen et al. (8) have demonstrated that the observed nucleation and growth of carbide plates on {001} planes in Pt-C alloys
can be accounted for by two basically simple mechanisms; namely, the nucleation and propagation of two types of partial dislocation. One of these dislocations corresponds to a conservative ledge and the other to a non-conservative ledge\(^*\), and their presence in the interface of a growing precipitate, either single or in various combinations, provides a variety of growth modes.

A significant aspect of this study was the discovery that not only was the carbide precipitate structure in the interstitial Pt-C system completely analogous to the \(\theta'\) structure (see Fig. 1) in the substitutional Al-Cu system, but that close parallels in their formation and growth mechanisms were also indicated.

In this paper the results of a high resolution TEM study on \(\theta'\) which supplement Stobbs and Purdy's observations are presented. An analysis of both sets of data in terms of the processes found to operate in Pt-C results in a surprisingly simple picture and a new understanding of the growth mechanisms.

**EXPERIMENTAL**

Homogenized pieces of Al-4wt%Cu, 150\(\mu\)m thick were solutionized in air at 550\(^\circ\)C for 1/2 h, water quenched and aged 4 h at \(-\)240\(^\circ\)C to form large, well separated precipitates of \(\theta'\). 2.3mm discs were punched from this material and electrochemically thinned by standard techniques. The foils were examined in a Siemens 102, a JEOL 200CX and a Kratos 1.5MeV microscope at 100, 200 and 400kV, respectively.

**MODEL**

The model used to explain our experimental observations is based on an extension of the principles of conservative and non-conservative growth ledges recently proposed for \(\{001\}\) plate precipitates in Pt-C (8). The simplest lattice cor-

\(^*\)As pointed out in (8) the terms conservative and non-conservative are more general than coherent and semicoherent.
respondence for the $\alpha$(fcc) to $\theta'$(bct) transition in Al-Cu is shown in Fig. 2a. The number of lattice sites (i.e. atoms) in the unit cell is conserved when the skewed cell (Fig. 2a) is sheared into the rectangular cell (Fig. 2d). The lattice correspondence does not relate primitive unit cells, hence the atoms inside the cell have to undergo rearrangements (shuffles) not accomplished by the homogeneous shear. The total transformation can be visualized in two simple steps: (1) the shear vector of the homogeneous transformation is $a/2<100>$ and may be envisaged as the passage of a partial dislocation with this Burgers vector (see Fig. 2b); (2) the shuffles indicated in Fig. 2c are necessary to obtain the final bct arrangement shown in Fig. 2d. The most important step in the shuffle is the jump by about one fcc unit cell of half a layer of Cu atoms into their appropriate sites in the lower half of the unit cell. Finally, it should be noted that these two steps describe the simplest way to achieve the structural part of the transformation. However, solute diffusion is still necessary to accomplish the compositional part of the transformation. Thus the unit cell outlined in Fig. 2d would also have to have the approximate stoichiometry of Al$_2$Cu.

The two-step process just described is the homogeneous transformation. Lattice sites are conserved in the process, and the transformed and untransformed unit cells are separated by the shear vector $a/2<100>$ of the transformation. Following the model outlined in ref. 8, there is also a heterogeneous or non-conservative growth mode. This is illustrated in Fig. 3. Here the number of lattice sites is not conserved and the skewed cell in Fig. 3a may be sheared by a vector $a/2<100>$ and expanded to transform to the $\theta'$ structure by adding Cu atoms at the sites indicated in Fig. 3b. This will "create" extra sites by leaving behind vacancies in the fcc lattice. The result is the formation of 1/2 unit cell of $\theta'$ (Fig. 3c) as opposed to one unit cell formed by the conservative process. The distinction between the conservative and the non-conservative process lies in the way Cu
atoms are brought into the sites in the half $\theta'$ unit cell. In the conservative process, this is achieved by shuffling atoms within the precipitate leaving behind vacant sites which become part of the structure (Fig. 2c,d). In contrast, the non-conservative process brings in extra atoms from the matrix by diffusion, thus creating matrix vacancies which diffuse away and do not take part in the structural transformation.

The conservative and non-conservative growth processes form the two basic building blocks of the structural transformation that describes the precipitation of $\theta'$ in Al-Cu, as shown in Figs. 4a and b. Multiple growth steps are made up of combinations of these two building blocks. Fig. 4c shows the combination of the conservative and the non-conservative process and Fig. 4d illustrates two conservative steps with opposite shears. Both types of single ledges (Figs. 4a and b) have a large shear of $a/2<100>$ associated with them but they differ in the sign and magnitude of the $c$ displacement (normal to the habit plane). The double ledges enable the shear components to be cancelled (Figs. 4c and d) and the total strain in the $c$ direction to be reduced (Fig. 4c). The expansions and contractions in nm are listed in Fig. 4. Since the non-conservative process results in only half a unit cell while the conservative building block produces a full unit cell, the differences between the two processes can be tested experimentally by observing the number of $(002)\theta$ planes added to the precipitate (also shown schematically in Fig. 4). The conservative building block results in two $(002)\theta'$ planes, or four when the shears are cancelled. The non-conservative unit results in one $(002)\theta'$ plane, or three when combined with a conservative unit. These predictions can be tested by combining high resolution lattice imaging with conventional weak beam contrast analyses of the dislocations and displacement fringes.
RESULTS

Fig. 5 shows a lattice fringe image of a $\theta'$ precipitate viewed exactly edgeon, i.e. the habit plane is parallel to the beam. The 0.290 nm spacing of the (002)$\theta'$ planes and the 0.202 nm spacing of the (002)\(\alpha\) planes are clearly resolved. A number of growth ledges are visible in the interface. Most of the ledges are characterized by four terminating fringes in the precipitate as shown in the enlarged view of the area encircled in Fig. 5b. This type of ledge corresponds to Fig. 4d. The ledge below A has eight terminating fringes. The entire precipitate was 0.41\(\mu\)m long and 15nm thick in the stepped central region shown in the lattice image. The outer regions of the precipitate (not shown in Fig. 5) were measured to be a uniform 8.1nm thick. Note that the ledges are located on both faces of the precipitate. Growth in this case has apparently started in the center and ledges are moving towards the periphery. Fig. 6a-d shows a series of weak beam images of the same precipitate after tilting the specimen through an angle of \(-55^\circ\) to expose the structure of the broad faces. It is clear that none of the ledges visible in Fig. 5 show strong dislocation contrast although fringe shifts, indicative of thickness changes, are apparent. This is further evidence that the ledges are formed by the double ledge mechanism whereby the shear strain is eliminated and only the small residual strain normal to the habit plane is imaged. The residual contrast of the ledges is, however, sufficient to see that they are approximately parallel to the [100] direction which is conveniently marked by the two precipitates (A, B) of the (010) variant at right angles to the (001) precipitate analyzed. This confirms that in Fig. 5 the ledges are seen approximately end-on. The wedge angle of the foil is apparent from the change in projected width of the precipitate, and the uniformity of the fringes on either side of the stepped area of the precipitate attests to its constant thickness. A small change in fringe contrast
(most apparent in Fig. 6a) at the lower end of the precipitate shows that only one ledge exists outside of the stepped center of the precipitate. Again no dislocation contrast is observed, hence this ledge must also have formed by a double shear mechanism as shown in Figs. 4c and d. Fig. 6e which was taken in exact [100] orientation shows that the two (010) precipitates A and B are aligned across the thick section of the growing precipitate. From this alignment and the matching thicknesses, it may be inferred that these two precipitates are shrinking away from their intersection with the center of the growing (001) precipitate and that this is a local event of Ostwald ripening.

Evidence for a single shear mechanism was found in the precipitate shown in Fig. 7. The dislocation marked 1, showing strong contrast in Fig. 7c and weak residual contrast in Fig. 7a, has a large component in the [010] direction and a small, or zero, component normal to the (001) habit plane. The contrast behavior exhibited in b) and d) is the \( g \cdot b = \pm 1/2 \) type behavior found for similar dislocations in Pt-C alloys (9). This dislocation is therefore of the type \( a/2[010] \) with possibly a small component in the [001] direction normal to the habit plane. The change in the intensity of displacement fringe contrast when crossing this dislocation (Fig. 7b and d) indicates that it is associated with a ledge. From a high resolution image of the same precipitate viewed edge-on, the ledge height was measured to be one half unit cell of the \( \theta' \) phase. The ledge is therefore of the non-conservative type shown in Fig. 4a. The adjacent ledge labelled 2 in Fig. 7 does not show dislocation contrast and comparison with the high resolution image shows that the ledge height is \( \frac{1}{2} \) \( \theta' \) unit cells with the ledge on the opposite face of the precipitate. Hence this is a double ledge, with one conservative and one non-conservative component whose opposite shears cancel as shown in Fig. 4c. The remaining strain field has no shear and only a small component normal to the habit plane. These two ledges are the only ones in this precipitate to allow a direct
comparison with the lattice fringe image since all other dislocations and ledges in the interface deviate significantly from the [100] direction and are thus not viewed end-on in the high resolution image. However, by direct comparison of the contrast behavior, other dislocations and ledges can be identified even without confirmation from the high resolution image. The dislocations marked 3 and 4 show contrast similar to the a/2[010] dislocation marked 1 (Fig. 7c). However, they are distinctly different because they are not associated with a ledge (cf. Figs. 7b and d). They are thus intruder perfect dislocations with Burgers vectors a/2[1\bar{1}0] (marked 3) and a/2[110] (marked 4) since they go out of contrast in g = \bar{1}11 and g = \bar{1}11, respectively. The growth ledge labelled 5 is in the process of sweeping across the interface laterally and is consistent with a displacement vector a/2[100].

Similar analyses could be given for all the observed dislocations and ledges but the good agreement between the experimental observations and the predictions of the model (Fig. 4) sufficiently proves the point that ledges are always associated with dislocations.

In accordance with a recent study of the precipitation of the Pt$_2$C carbide (8) (isomorphous with θ') both the conservative and non-conservative growth mechanisms were observed in Al-Cu. However, it should be noted that the non-conservative ledge growth in Al-Cu (Figs 4a and c) emits vacancies whereas the equivalent process in Pt-C absorbs vacancies. On the other hand, the absorption and collapse of vacancies is also possible in Al-Cu. A schematic of the transition from θ'' to θ' by this process is shown in Fig. 8. This structural transformation is essentially the same as the conservative mechanism outlined in Fig. 2 with the sole difference that the shear is replaced by a collapse. This leads to the elimination of lattice sites and hence the resultant nucleus is non-conservative. A comparison with the non-conservative process in Pt-C highlights an interesting difference; in
both cases the structural effect of the vacancy collapse provides the correct stacking sequence for the precipitate, but in Pt-C the volume effect aids formation of the oversized precipitate, whereas in Al-Cu it works against the strain field of the undersized precipitates. Nevertheless, this process is a possible mechanism for nucleating $\Theta$, especially since no long-range diffusion of Cu is necessary. This is clear from a consideration of Fig. 8. The stoichiometric composition of $\Theta^\prime$ is Al$_3$Cu while that of $\Theta$ is Al$_2$Cu. Removing a layer of Al by condensing a plate of vacancies thus provides the correct stoichiometry along with the necessary AA stacking. A shuffle of half the Cu atoms completes the transition, and a single unit cell of $\Theta^\prime$ is formed (see Fig. 8c). This process requires the presence of excess vacancies in a crystal containing $\Theta^\prime$ precipitates. Fig. 9a shows such a crystal obtained by quenching and aging 16h at 165°C. In addition to the high density of $\Theta^\prime$ precipitates, irregular quenched-in dislocation loops are visible. During in-situ heating at ~200°C a striking observation was made. As the loops dissolved by vacancy emission, the transformation of the coherent $\Theta^\prime$ to $\Theta^\prime$ occurred simultaneously and was marked by the appearance of dislocation loop contrast (see Fig. 9b). The model shown in Fig. 8 provides an explanation for these observations although quantitative confirmation is still lacking.

DISCUSSION

The most important conclusion to be drawn from the theory and experimental evidence presented above is that all ledges must and do have lattice dislocations associated with them. This is a direct consequence of the lattice correspondence shown in Fig. 2. The homogeneous transformation which brings the skewed unit cell outlined in the fcc lattice of Fig. 2a into the rectangular $\Theta^\prime$ unit cell shown in Fig. 2c is an invariant plane strain (IPS). Bilby has shown that any step (or ledge) in the habit plane of a region transformed by an IPS is associated with a
"transformation dislocation" whose Burgers vector is the strain vector characterizing the transformation (10). For a step of one $\Theta^\prime$ unit cell height, this is essentially an $a/2<100>$ dislocation. Figs. 4a,b show that the smallest units that can be added to the thickness of a $\Theta^\prime$ precipitate (one half or one $\Theta^\prime$ unit cell) are bounded by such partial dislocations. The picture that emerges for the structure of the edges and ledges of a $\Theta^\prime$ precipitate is sketched in Fig. 10a.* All single ledges will be associated with $a/2<100>$ shear dislocations, and circular ledges (pillboxes) are surrounded by shear loops. This model of a $\Theta^\prime$ precipitate is quite different from the conventional idea of disordered ledges shown in Fig. 10b where all ledges have only small c direction displacements. Experimentally the difference between the models is most evident for single ledges. For multiple ledges with self-accommodating (i.e. opposite) shear vectors such as a double ledge, the two models will be indistinguishable by TEM. The two opposite shears shown in Fig. 10a will cancel, leaving only the small c contraction shown in Fig. 10b. Because of the close spacing of the two shear dislocations, the contrast of an electron microscope image will be identical for the double ledges shown in Fig. 10a and b since there is no net shear component in the habit plane. The same conclusion holds for the periphery of the precipitates. An even number of opposite shear loops encircling a precipitate will cancel and show only a residual c strain component as observed by contrast analysis in TEM (11).

**Parallels Between Al-Cu and Al-Ag**

The fcc $\rightarrow \Theta^\prime$ (bct) transformation is entirely analogous to the fcc $\rightarrow \gamma^\prime$ (hcp) transformation encountered in Al-Ag alloys (e.g. (2)). It has long been known that $\gamma^\prime$ may be nucleated by dissociating a perfect dislocation into two Shockley

*Fig. 10a is almost identical to that used by Olson and Cohen (12)(their Fig. 2c) to explain their concept of coherency dislocations except that in our case two opposite shears are involved in the transformation.
partials (3) and that the edges of $\gamma'$ precipitates must be made up of Shockley partials on every other $\{111\}$ plane. Applying the present approach to this system, it becomes clear that single ledges on $\gamma'$ plates must be bounded by Shockley partials just as shown for $\theta'$ in Fig. 10a. The close analogy between the Al-Ag and Al-Cu precipitation systems shows that the dual role of Shockley partials as ledges and as dislocations is not unique to the Al-Ag system.

It is interesting to pursue further the analogy between the $\theta'$ in Al-Cu and $\gamma'$ in Al-Ag since it suggests the generality of a number of observations. The lattice correspondence for the fcc-hcp transformation in Al-Ag is shown in Fig. 11. The shear vector which describes the transformation of the skewed unit cell in the fcc lattice (a) to the rectangular unit cell in the hcp lattice (b) is a Shockley partial dislocation. Comparison with the lattice correspondence for $\theta'$ (Figs. 2a,c) shows the fcc/hcp case to be simpler. Nevertheless, a small shuffle (as opposed to the large shuffle in $\theta'$) is necessary in addition to the homogeneous shear in order to complete the structural change. The smallest unit (i.e. a single ledge) that can be formed this way has a height of one hcp unit cell or two $\{111\}$ fcc planes. In Al-Cu a single conservative ledge is one $\theta'$ unit cell high corresponding to three $\{002\}$ fcc planes (Fig. 4b). In both cases a single ledge is bounded by a (partial) shear dislocation, $a/6<112>$ in Al-Ag and $a/2<100>$ in Al-Cu. In order to accommodate the shear, a multiple ledge with mutually cancelling shear vectors is necessary. In Al-Cu where the $\{001\}$ habit plane has four-fold symmetry, this is achieved by double ledges with opposite shear vectors. However, in Al-Ag the $\{111\}$ habit plane has three-fold symmetry. Complete accommodation of the shear component of the transformation can thus be achieved only by a succession of three different Shockley partials in a triple ledge. This corresponds to six $\{111\}$ fcc plane spacings, again analogous to the shear-free double ledge in the Al-Cu system which corresponds to six $\{002\}$ fcc plane spacings.
The nucleation of $\gamma'$ has been reported to take place on dissociated perfect dislocations (3). The same mechanism may be envisaged for the nucleation of ledges on existing $\gamma'$ precipitates where an intruder dislocation with its Burgers vector lying in the habit plane dissociates into two Shockley partials: $a/2[110] \rightarrow a/6[211] + a/6[121]$. The identical mechanism could operate in the nucleation of ledges on $\theta'$ precipitates where the corresponding dissociation reaction would be: $a/2[110] = a/2[100] + a/2[010]$. In this case, the two partials span an \{001\} stacking fault which, with the appropriate shuffles and compositional changes, is identical to a new layer of $\theta'$. This heterogeneous initiation of a new growth step is an alternative to the homogeneous nucleation of a shear loop in the interface.

**Non-conservative Growth**

The mechanisms of ledge formation discussed above are based on the principle of conservation of lattice sites. All such ledge movement is therefore necessarily conservative. The shape change associated with the shear component of the transformation can be accommodated by the use of several variants of the lattice correspondence. However, any volume changes which may be part of the transformation cannot be accommodated in this way. The accommodation of excess volume can only be accomplished either elastically, or by the "non-conservative mechanism" (8). This mode of transformation brings about the same structural change as the conservative mechanism without, however, the constraint imposed by the conservation of lattice sites. The growth of non-conservative ledges therefore depends on the availability of excess lattice sites, i.e. point defects. It was shown that $\text{Pt}_2\text{C}$ carbide nucleates and grows mainly by the non-conservative process, both because of the availability of and the need for a high supersaturation of vacancies to accommodate the large volume increase during $\text{Pt}_2\text{C}$ precipitation (9). In Al-Ag the volume remains approximately constant during the fcc to $\gamma'$ transition. Thus excess vacancies cannot accommodate excess volume
and the observation (2) of the nucleation of $\gamma'$ on Frank loops is a good example of the pure structural role of the vacancies. By collapsing on a $\{111\}$ plane, a sheet of lattice sites is eliminated, and the structure changed locally from fcc to hcp stacking. In principle, the same process is possible for $\delta'$ precipitates. However, $\delta'$ is 4.3% undersized with respect to fcc Al, and volume accommodation would require interstitials rather than vacancies. Nevertheless, the vacancy process seems possible since it still serves to form the precipitate structure as well as to eliminate the excess vacancy concentration. It is believed that the in-situ observations shown in Fig. 9 represent this process since $\delta'$ forms from $\delta''$ only when the vacancy loops anneal. This transition is marked by a significant reduction in the $\delta''$ precipitate density which is consistent with the limited vacancy supply. The observations were made only in thick foils where the vacancies did not all escape to the surfaces. The importance of point defects in the $\delta'' \rightarrow \delta'$ transition has also been demonstrated by Sklad and Mitchell (13) who reported that increased rates of $\delta'$ nucleation and growth occurred during HVEM electron irradiation of Al-Cu. Seen in the context of vacancy involvement in the precipitation of $\alpha'_x$ Pt$_2$C in Pt and $\gamma'_x$ Al$_x$Ag in Al, the present observations complete the experimental verification of the postulated separation between the two roles of point defects (especially vacancies) in second phase precipitation—the volume effect and the structural effect. In Al-Cu, the structural effect aids the $\delta'$ precipitation whereas the volume effect opposes it since both the collapse of vacancies and conservative growth of $\delta'$ are associated with a volume contraction. This contraction makes further growth by the conservative mechanism increasingly difficult and a change to non-conservative growth should occur.

*Similar effects are found in Al-Si where the first $\{111\}$ platelets of Si form only as the quenched-in loops are shrinking (14).
A comparison of these two mechanisms shown in Figs. 3 and 8 reveals a symmetry in the role of point defects. Fig. 8 shows the non-conservative process whereby vacancies are absorbed and Fig. 3 shows the non-conservative process in which vacancies are emitted into the matrix as Cu atoms are incorporated into the θ' structure. Only this latter process can accommodate the volume contraction associated with the conservative mechanism. As illustrated in Fig. 3, it is only necessary that Cu atoms jump into their correct ("interstitial") sites to stabilize an \{001\} stacking fault and leave behind vacancies in the fcc lattice. Fig. 4a shows that an expansion of 0.088 nm results from such a non-conservative step and that it forms one-half of a θ' unit cell. In contrast, the elementary conservative step shown in Fig. 4b leads to a 0.026 nm contraction and a full θ' unit cell. Both are associated with the same a/2<100> type shear vector. The shape and volume accommodation of a growing θ' precipitate (in the absence of a vacancy supersaturation) can be accomplished by a combination of these two elements following two simple criteria: 1) a θ' precipitate should grow with paired ledges of opposite shears to accommodate the shape change. 2) conservative and non-conservative building blocks should be added in a sequence such that the volume change in the c direction is minimized.

The first unit allowed by these criteria is a fully coherent precipitate two unit cells thick shown in Fig. 3d, where the contraction of 0.05 nm, or 4%, is also indicated. Independent verification of this prediction has been given by Stobbs and Purdy (7). Their accurate measurements showed the thinnest θ' plates to be two unit cells thick, the same as the ledges shown in Fig. 5. In addition, they also determined that these plates had a vacancy-type strain field as predicted here for the coherent precipitate.
The next growth step must again be a pair of shears, but volume constraints require an interstitial type strain to counter the vacancy strain of the coherent nucleus. Fig. 4c shows the simplest such unit to be a conservative/non-conservative pair with a c-expansion of +0.062nm. This counters the -0.052 contraction of the first double layer precipitate leaving a total expansion of +0.01nm corresponding to an interstitial strain of 0.5%. The precipitate at this stage is $3\frac{1}{2}$ $\theta'$ unit cells high. Again Stobbs and Purdy's measurements accurately confirm both points.

Further growth should proceed by another conservative pair bringing the thickness to $5\frac{1}{2}$ cells and vacancy strain field, followed by another conservative/non-conservative pair to produce an interstitial seven-cell precipitate 4.06nm thick. Both these discrete steps were indeed observed by Stobbs and Purdy, providing excellent confirmation of our model. The only apparent discrepancy between the predicted and observed thickness and strain fields is the observation of a number of interstitial-type precipitates with about five unit cell thickness. This too can be explained, however, by the formation of a precipitate from one conservative double ledge (Fig. 4d) combined with two conservative/non-conservative double ledges (Fig. 4c), but it violates the second criterion of minimizing the volume strain since a smaller strain can be achieved with the $5\frac{1}{2}$ unit cell precipitate. A possible reason for this might be that the $\theta'$ contains Cu vacancies as part of its equilibrium structure (15). This would drive Cu atoms into "interstitial" sites and thus promote the non-conservative mechanism. It is interesting to note that the uniform thickness of the outer regions of the precipitate shown in Fig. 5 was 8.1nm, corresponding to 14 $\theta'$ unit cells or exactly four times the thickness of the $3\frac{1}{2}$ unit cell, low misfit unit measured by Stobbs and Purdy.
Epitaxial vs. Ledge Dislocations

Dislocations with Burgers vector of the type $a/2\langle 100 \rangle$ lying in the broad $\theta'$ matrix interface have often been reported (e.g. (2, 16). These were always interpreted as epitaxial dislocation whose function is to take up any misfit in the habit plane which develops as the precipitate grows and the strain begins to deviate from the invariant plane strain ideal. A model of such a precipitate enveloped by epitaxial dislocation loops (vacancy-type) is sketched in Fig. 10c. In contrast, the present analysis shows that at least some of these $a/2\langle 100 \rangle$ dislocations are transformation dislocations associated with a ledge. As discussed above, such transformation dislocations will nucleate as shear loops bounding a ledge (Fig. 10a) rather than edge loops accommodating misfit (Fig. 10c). Either mode is possible and it is clear that the epitaxial role becomes more important in the later stages of growth. In fact, ledge dislocations from opposite faces can combine to form a vacancy/interstitial pair of loops as shown in Fig. 12. Only one, the vacancy loop can serve as an epitaxial dislocation, its counterpart must glide out of the interface and be expelled into the matrix by the strain field of the precipitate. Of course, it is necessary for two such loops to combine to form a perfect dislocation before it can glide into the matrix. Nevertheless, this is a simple mechanism whereby the transformation dislocations serve the dual purpose of promoting precipitate growth and relieving elastic strain in the habit plane. Observations of dislocations paired across the thickness of the precipitate in Al-Cu (7) and Al-Ag (17) support the model. The advantage of this process, which is a simpler version of that suggested by Stobbs and Purdy (7), is that no extraneous dislocations are required to accommodate the developing elastic strain. This is not to suggest that matrix dislocations when available, would not be incorporated in the interface.
SUMMARY AND CONCLUSIONS

1. By establishing a lattice correspondence for the precipitation of $\theta'$ in Al-Cu, two simple nucleation and growth mechanisms have been identified.

2. Taken in various combinations, these basic building blocks predict growth processes which are in excellent accord with the experimental observations. Both the reported discrete steps in precipitate thickness and the nature of the matrix strain field are explained.

3. An interesting variation is found for the $\theta''$ to $\theta'$ transition. Both the structural and compositional requirements for the transformation are satisfied by incorporating a plate of excess vacancies.

4. The basic principles underlying the growth modes are minimization of shape and volume strains.

5. The success of the model in describing the experimental observations on Al-Cu, Al-Ag and, earlier, Pt-C suggests it may have a general validity.

ACKNOWLEDGEMENTS

We would like to thank J. Howe for several interesting discussions during the course of this study and M. Wall for expert sample preparation. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.
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Fig. 1. Unit cell of bct Q' structure.

Fig. 2. [001] projection of the conservative fcc to Q' transformation. Full circles represent atoms at z = 0.1 and broken circles are atoms at z = \frac{1}{2}. Circles with dot in center show one possible positioning of the Cu atoms. In a) a 6-atom unit cell is outlined in the fcc lattice. The same cell is shown in b) where the a/2 [100] shear component is resolved onto one plane. In c) the shuffles necessary after the shear are indicated, and d) shows the final structure of the 6-atom cell is identical to that in Fig. 1.

Fig. 3. [001] projection of the non-conservative fcc to Q' transformation with symbols as used in Fig. 2. The cell outlined in a) is sheared into the AA stacking by a/2 [100] shown in b), and diffusion of Cu into the sites marked with arrows completes half a Q' unit cell as shown in c).

Fig. 4. Simplified [001] projections of basic non-conservative (a) and conservative b) units for the fcc to Q' transformation and their combination (c) with opposite shear components. In (d) two conservative units have opposite shears. The expansion or contraction component in nm is shown for each unit. Also shown are the \{002\} planes at corresponding ledges in the interface between Q' (coarse lines) and the fcc matrix (fine lines). The dislocation symbols indicate the net magnitudes and directions of the Burgers vectors and show the absence of a shear component for double ledges (c,d).

Fig. 5. Edge-on view of (001) Q' precipitate in high resolution (b) Ledges are seen nearly end-on and from a magnified view (a) of the ledge encircled in (b), it is clear that these are double ledges, two Q' unit cells high (corresponding to Fig. 4d). The precipitate thickness in the center is 15 nm
and at the ends of 8.1nm. At A a precipitate of (010) variant is in direct contact.

Fig. 6. The same precipitate as in Fig. 5 after a ca. 55° tilt about [020]. Weak beam contrast analysis shows the absence of strong dislocation contrast in the broad faces as predicted for double ledges. In e) the same area is seen in the exact [100] orientation and shows that the intersecting precipitates A, B are not in contact with the growing precipitate except at one point.

Fig. 7. Weak beam contrast analysis as in Fig. 6 of a different precipitate giving evidence (at 1) for the existence of single ledges. The associated a/2[010] dislocation contrast is apparent. Note the change in fringe contrast across the ledge and the absence of dislocation contrast at the adjacent double ledge marked 2. Intruder dislocations are labelled 3 and 4, and a ledge sweeping across the interface is seen at 5.

Fig. 8. [001] projection of non-conservative transformation from Q' to Q using symbols as in Fig. 2. In a Q' precipitate of composition Al3Cu a layer of vacancies condensing on the line indicated in (a) changes the local stoichiometry to Al2Cu and produces a layer of AA stacking. A shuffle of Cu atoms (b) completes the full Q' cell (c).

Fig. 9. a) Microstructure of Al-4Cu aged 16h at 165°C showing {100} Q' precipitates and quenched-in loops. b) Same foil after in-situ heating at ~200°C showing thin faceted Q' precipitates. The magnifications, but not the areas of a) and b) are the same.

Fig. 10. Schematic cross-sectional diagrams showing a) precipitate growing by ledge mechanism propagating single and paired dislocation loops with cancellation of shear components; b) conventional model of the same
precipitate; c) epitaxial dislocations with similar Burgers vectors as transformation dislocations shown in a).

Fig. 11. [110] projection of fcc (a) to hcp (b) transformation by shear of a/6 <112>. As shown for Θ' in Fig. 2, the transformation may be separated into a homogeneous shear and a shuffle.

Fig. 12. Model for the loss of coherency by combining ledges (bounded by shear loops) in pairs across the precipitate plate (a) by annihilation of the screw components of the loops (b), leading to an interstitial* vacancy loop pair around the precipitate. The unfavorable interstitial loop is expelled into the matrix (c), while the vacancy loop remains in the interface as an epitaxial dislocation.
Fig. 1

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OAl  •Cu
Fig. 2

a

lattice correspondence

b

shear

c

shuffle

d

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Fig. 2
Fig. 3

a

shear

b

diffusion

c

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Fig. 4
Fig. 8
Fig. 11
Fig. 12
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