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PLATE PRECIPITATE GROWTH MECHANISMS

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The formation of plate precipitates in low index planes in a precipitation reaction can be described as an invariant plane strain (IPS) transformation. The habit plane of such precipitates is maintained parallel to the misfit-free invariant plane and thickening, i.e., plate growth normal to the habit plane, proceeds by a ledge mechanism. In recent studies the role of lattice defects and their relationship to ledges has been investigated in both interstitial (1-3) and substitutional (4,5,6) binary alloy systems and plausible growth mechanisms identified.

(i) Pt-C alloy (FCC $\rightarrow$ BCT interstitial)

In Pt-C, the interstitial system studied, semicoherent plates of carbon (α) initially form on 100 matrix planes by a vacancy/solute atom co-precipitation process. Subsequently these plates transform to a metastable Pt_2C phase (α') also with a 100 habit. The Pt_2C phase has a distorted fluorite structure and is 50% oversize in the matrix. Detailed contrast analysis indicated that lattice vacancies, present in supersaturation following quenching, play a dual role in the transformation. In addition to the well-known role of accommodating the excess volume of the precipitate (7,8) the systematic condensation of vacancy plates in

the $\{100\}$ planes constitutes a structural role in the transformation. By dislocation loop formation on alternate $\{100\}$ planes the Pt atom ABABA stacking sequence of the matrix is changed to the required AAA stacking of the precipitate structure. This non-conservative process is evidently limited to growth conditions where the vacancy concentration is high, e.g. following a rapid quench, at temperatures where quenched-in vacancy loops are dissolving, or where self-diffusion is rapid. However, it was also recognised that the same structural rearrangement could be achieved by a conservative shear process. Thus the propagation of a $\frac{1}{2}[10\ell]$ shear loop in the (001) precipitate habit plane (where ℓ is a small dilatational component) on alternate planes also produces the AAA Pt atom stacking of the precipitate framework. This alternative process is thought to dominate in situations where the transformation results in a small volume change.

These considerations lead to the general conclusion that the characteristic of a (homogeneous) invariant plane strain transformation, namely perfect structural matching in the habit plane, dictates changes in atom stacking that can be accomplished either by shear or by adding or removing layers of atoms.

We now use this concept to compare and contrast the predicted and observed behavior in other classes of alloy system.

(ii) Al-4Cu alloy (FCC $\rightarrow$ BCT substitutional)

(a) θ' formation from θ''

In Al-Cu the development of the metastable $\text{Al}_2\text{Cu}\theta'$ phase follows a path close to that of α' formation in Pt-C. The transformation in this substitutional alloy is also IPS in character but the volume change is much smaller. Consequently, initial precipitation can occur coherently via the classical sequence Supersaturated-Solid-Solution $\rightarrow$ GP zones $\rightarrow$ θ'' . Loss of coherency around the

precipitate plate periphery occurs during the transition of θ'' to θ' and recent observations (5) indicate that vacancies from dissolving quenched-in prismatic dislocation loops are incorporated into the θ'' structure and initiate the transition. A simple explanation for this process based on the Gerold model for the θ'' structure was suggested. Thus, the Al-Cu-Al-Al-Al atom stacking sequence of θ'' in (001) is changed to that required by the θ' fluorite structure by condensing vacancies in the layer marked . The final θ' structure is obtained by shuffling half of the Cu atom layer into nearby sites to give an $\text{Al}-\frac{1}{2}\text{Cu}-\text{Al}-\frac{1}{2}\text{Cu}-\text{Al}$ stacking sequence. In addition to providing the structural means for the transformation to occur, the vacancy condensation also induces the correct compositional change since stoichiometric θ'' (Al_3Cu) is converted to stoichiometric θ' (Al_2Cu). In spite of the disparity in alloy system type, the formation of the isomorphous phases Pt_2C and Al_2Cu thus occurs by a similar mechanism. The major difference lies in the stage at which vacancies are incorporated in the precipitate structure.

(b) θ' formation from solid solution

An alternate path for θ' formation also exists. By direct quenching to high aging temperatures the formation of GP zones and θ'' is bypassed and θ' nucleates directly from the supersaturated solid solution. Precise experimental observations have shown (4,9) that under these conditions precipitate plate thicknesses take on only certain discrete values, each with its own characteristic residual strain field. The observed sequence corresponds to θ' unit cell thicknesses of 2, $3\frac{1}{2}$, $5\frac{1}{2}$, 7 ... and is notable in that single unit cell plate thicknesses are never found. A logical explanation for this discrepancy is found in the model for θ' formation by the conservative shear process (5). According to this model precipitate growth is controlled by two considerations: accommodation of volume change, and avoidance of shape change. Basic conservative and non-conservative precipitate units related

to the matrix by a $\frac{1}{2}\langle 100 \rangle$ shear were identified and it was shown that the observed growth sequence could be completely accounted for by the two criteria. Almost without exception the smallest growth ledges arise in pairs of units which form by two shears of opposite sign to avoid a shape change. Direct support for this model was subsequently found when the elusive single unit cells of θ' were observed to nucleate on $\frac{1}{2}\langle 100 \rangle$ shear loops formed from dissociated climbing dislocations (4). By dissociating in a $\{100\}$ plane according to the reaction $\frac{1}{2}[110] \rightarrow \frac{1}{2}[100] + \frac{1}{2}[010]$ the dislocations provide favorable (100) plane stacking for a single θ' unit cell to form without shape change.

The Al-Cu system under these conditions can thus be considered a prototypical example of an IPS transformation occurring by the conservative shear mechanism. It is apparent that the small volume change during the transformation favors the shear process, and in the absence of dissociated dislocations, shape changes are avoided by nucleating the shear loops in opposite pairs.

(iii) Mo-HfN alloy (BCC $\rightarrow$ FCC mixed substitutional-interstitial)

Many other examples of precipitates formed under IPS conditions may be found in the literature, but to generalize the arguments the example of HfN precipitation in Mo is given. Mitchell (10) has performed a comprehensive study of the microstructures developed during nitriding of Mo-1%Hf alloys at high temperature. He showed that plates of HfN precipitated on $\{100\}$ matrix planes and exhibited contrast features consistent with growth by a coherent ledge mechanism. To compensate for the large volume increase (36%) he proposed that a vacancy dislocation loop was condensed in the precipitate structure at regular intervals. While this is a possible mechanism in principal, the results on Pt-C and the fact that the precipitation occurs at high temperatures (1300°C) suggests that the first unit cell of HfN should form by the co-precipitation mechanism, i.e. the

condensation of solute atom/vacancy pairs. However, HfN has the NaCl crystal structure and is related to the matrix Mo by the Bain correspondence. Consequently, no change in the stacking sequence is involved in the transformation and the precipitation of Hf and N solute atoms with a single plate of vacancies in $\{100\}$ would produce the wrong structure. If, on the other hand, two layers of Hf atoms and vacancies co-precipitate, the $\{100\}$ stacking sequence remains unchanged but the excess volume is accommodated. Subsequent thickening of the plate could then occur by coherent growth until the matrix strain developed to a point where further vacancy condensation was required. An early stage in the predicted growth sequence is depicted schematically in Fig. 1(a). According to this scheme the dislocations bounding the precipitates have Burgers vectors normal to the plates and this has been confirmed by contrast analysis. To test the model further, high resolution structure images of the HfN precipitate plates were obtained on the Berkeley ARM operated at 1 MeV. An example of an image recorded in the symmetrical $\langle 100 \rangle$ orientation with 13 beams excited is shown in Fig. 1(b). The thick plate of fcc HfN is viewed precisely edge-on and is readily distinguished from the bcc Mo matrix. Two features are clearly evident: (1) the precipitate-matrix interface is atomically smooth and (2) the precipitate contains no faults in the stacking sequence. The evidence is thus consistent with the proposed model and the resulting plate is predicted to have an 8% interstitial strain field.

(iv) Al-Ag alloy (FCC $\rightarrow$ HCP substitutional)

Studies of $\gamma'(Al_xAg)$ precipitation from Al-Ag solid solution almost equal in number those on Al-Cu, since it is also a model system of IPS involving only a small (1%) volume change. In early studies on this alloy (11,12) it was observed that γ' plates nucleated on quenched-in $\{111\}$ Frank loops, taking advantage of the

existing HCP structure of the stacking fault. It was also recognised that further growth by the ledge mechanism corresponded structurally to the propagation of $\frac{1}{6}\langle 112 \rangle$ Shockley partials on every other $\{111\}$ plane. It was commonly believed that this mechanism could operate only for the specific case of Al-Ag and only now can the generality of this conservative shear process together with its non-conservative counterpart be fully appreciated.

Discussion

The purpose of this contribution is to compare and contrast, for a variety of diverse alloy systems, the inferred growth mechanisms of plate-shaped precipitates. In each case the homogeneous transformation is an invariant plane strain characterized by a perfect structural match in the low-index habit plane. Consequently only the stacking order and the spacing of these planes may be altered during the transformation. The stacking sequence can be changed either by (conservative) shear or by (non-conservative) adding or removing layers of atoms. Only the latter process can accommodate excess volume, i.e. a change in plane spacing. The pattern that emerges is that precipitate growth normal to the habit plane (i.e. the invariant plane) is accomplished by nucleating and propagating lattice defects which transform the matrix crystal structure into, or close to, that of the precipitate. For transformations involving little change in volume the lattice defects are essentially shear loops and the process is conservative. If these shear loops occur in multiples they may accommodate each other's strain field. Similarly the strain field associated with a modified plane spacing (volume change) may be accommodated by the non-conservative formation of prismatic dislocation loops.

These two criteria of shape and volume accommodation result in an interesting symmetry in the growth processes in different alloy systems. The

precipitation of θ' in Al-Cu involves a change in stacking with nearly constant volume whereas HfN in Mo is characterized by constant stacking and a large volume expansion. To comply with the requirements of shape and volume accommodation pairs of dislocation loops are necessary in both systems. In Al-Cu two $\frac{1}{2}\langle 100 \rangle$ shear loops with opposite sign can produce the correct stacking while avoiding the large strain energy of a single loop, and in Mo-HfN two $\frac{1}{2}\langle 001 \rangle$ pure edge vacancy loops accommodate the volume expansion while avoiding the stacking violation of a single loop. In Pt-C single $\frac{1}{2}\{001\}$ vacancy loops can serve both functions since the precipitation of α' entails a change in both stacking sequence and volume. The precipitation of γ' in Al-Ag occurs at almost constant volume. The transformation is thus mainly a shift in stacking of the close packed planes parallel to the $\{111\}$ habit. Because of the three-fold axis of symmetry normal to the habit plane, complete shape accommodation would require triple shear loops with three different Shockley partial Burgers vectors, in contrast to the double loops necessary in Al-Cu where the habit plane has four-fold symmetry.

The differences in the alloy systems considered and the role of vacancies are highlighted in Table 1. Figure 2 illustrates the morphological similarities: 1) Due to good match in the habit plane all precipitates are plate shaped. 2) The habit planes have low crystallographic indices. 3) Thickening occurs by ledges. Only the height and detailed structure of the ledges is different in each case due to requirements of shape and volume accommodation and the availability of excess vacancies.

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Table 1

Alloy	Pt-0.08a/oC	Al-4w/oCu	Mo-1w/oHf-N	Al-15w/oAg
Type	Interstitial	Substitutional	Mixed Subst.-In	Substitutional
Matrix	fcc	fcc	bcc	fcc
Precipitate	$(\alpha')\text{Pt}_2\text{C}$	$(\theta')\text{Al}_2\text{Cu}$	HfN	$(\gamma')\text{Al}_x\text{Ag}$
Ppt. Structure	Fluorite	Fluorite	NaCl	HCP
Vol. Change	+50%	-4%	+36%	~0
Vacancy Role < Vol. Struct.	+ +	- +	+ -	0 +
Lattice Correspondence

Figure Captions

Fig. 1. (a) Schematic diagram of the end of a three-unit-cell thick HfN precipitate plate ($[110]$ projection) in a Mo matrix ($[100]$ projection). The two extra planes in the Mo correspond to the condensation of two $\frac{1}{2}(001)$ vacancy loops. (b) High resolution image of precipitate in the same orientation as the diagram (taken by R. Gronsky).

Fig. 2. Micrographs illustrating common features of $\sim 1\mu$ size precipitate plates in (a) Pt-C, (b) Al-Cu, (c) Mo-HfN, (d) Al-Ag.

XBL 8311-4637

Fig. 1a

XBB 839-7867

Fig. 1b

XBB 830-10400

Fig. 2

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