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Publication Date

1989-07-01

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

National Center for Electron Microscopy

To be presented at the International Congress on Intergranular and Interphase Boundaries in Metals, Paris, France, September 4-8, 1989, and to be published in *Journal de Physique — Colloque*

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July 1989

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

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ASPECTS OF FACETING IN THE STUDY OF PRECIPITATE INTERFACES

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Resumé - La formation de facettes à l'interface de précipités et matrices est étudié et illustrée pour plusieurs alliages observées par MET. La symétrie cristalline et les contraintes élastiques de la matrice sont démontrées être un facteur important dans le développement de la morphologie et de la structure de l'interface.

Abstract - The role of faceting in the formation of interface structures between a precipitate and its matrix is considered and illustrated with TEM observations on a number of different alloy systems. Crystal symmetry and elastic constraints from the solid matrix are shown to be important factors in the development of morphologies and interfacial structures.

1 - INTRODUCTION

The interface between a precipitate and the matrix in which it forms depends on the precipitate shape and orientation relationship with the matrix. These in turn are related to the strain energy, and to the structural and chemical components of the interface energy.

Because the strain energy density is lowest for thin plates it is not surprising to find that many precipitates adopt a plate shape /1/. The habit plane is usually a plane of small or no strain and often is a low-index plane in both the matrix and the precipitate lattice. The good atomic match and the resulting minimum in strain and interface energy then leads to an atomically flat interface which corresponds to a pronounced facet in the shape of the particle. It is well-known that under this condition, atomic attachment at these facets is controlled by the formation of ledges. Thus, as a result of faceting, growth must proceed by a ledge mechanism. The implications of this mechanism of growth have been, and still are, a subject of intense research activity, e.g. /2,3/. However, the focus is usually on the growth of precipitate plates dominated by a single interface facet or on the growth of crystals from the liquid or vapor phase. The present paper will address some aspects of faceting in the formation of precipitates that are due to the constraint from the solid matrix.

A number of examples from TEM studies of precipitation reactions will illustrate some effects of the constraining matrix and of the composite symmetry, common to matrix and precipitate, on the development of primary and secondary facets.

By a combination of conventional and high resolution TEM, the study of faceted particles can reveal important information about the atomic structure of interfaces and their crystallographic and mechanistic origins.

2 - θ' PLATES IN Al-Cu

It is well-known that θ' forms as flat plates on $\{100\}$ planes, e.g. /4/. This can be understood as a consequence of the good atomic match and the resulting low strain energy associated with this habit plane. The atomic arrangement of atoms in planes parallel to the habit plane is identical in both the matrix and the precipitate, the principal difference being in their stacking and chemical composition. For this reason the fourfold $[001]$ axes of the bct θ' precipitate (space group $I4/mmm$, $a = 0.407$ nm, $c = 0.580$ nm) and the fcc matrix (space group $Fm\bar{3}m$, $a = 0.404$ nm) are always accurately aligned. The symmetry of the Wulff plot is the set of symmetry elements common to matrix and precipitate /5/ and in the present case this is the $4/mmm$ tetragonal group. According to Curie's principle the equilibrium shape of θ' precipitates must have at least this symmetry /6/. In fact, under most conditions of growth, the particles grow in the shape of a flat circular disc with cylindrical symmetry, (∞/m), a supergroup of the tetragonal point group. Under these circumstances, only the thickening of a θ' plate is limited by the ledge mechanism. The Wulff plot of such θ' particles formed at high aging temperatures is dominated by a single deep cusp on the common (001) plane but its $[001]$ projection is circular.

However, at low aging temperatures the decreased effect of entropy allows secondary cusps to emerge. Figure 1 shows θ' precipitates developed by aging for 176 h at 144°C . At this temperature the circular cross sectional shape gives way to a clear tendency for faceting on (100) or (110) planes. Three θ' variants are seen in Figure 1a in an $\langle 001 \rangle$ zone axis. The secondary facets are most clearly seen on the $\{001\}$ variant that is face-on. The longest secondary facets follow $\{110\}$ planes with smaller facets on $\{100\}$ planes truncating the corners.

The vertical plate that is seen edge-on clearly shows its even thickness and plate shape due to the major (001) facet, but the secondary (100) facet at its top edge is parallel to the electron beam while the (110) facet at its bottom edge is inclined and consequently shows thickness fringe contrast. The interfacial misfit dislocations in this particle are also aligned along low index directions, and small ledges are faintly visible in the secondary facets (see arrows).

Although not all precipitates are this clearly faceted, a definite tendency for faceting is observable in the lower magnification view shown in Figure 2. A qualitative Wulff plot for the truncated square particle in Figure 2a is shown in Figure 2b. A quantitative determination of relative interface energy should be attainable by sampling a large number of precipitates and operating the Wulff theorem in reverse.

Because the facets that form during low-temperature aging lie on low-index planes the direct observation of the atomic structure by high resolution microscopy becomes possible. Figure 3 shows a secondary $\{100\}$ end facet on one such particle. Since this facet is parallel to the beam, no overlap along the projected direction can confuse the image. A number of interesting features are seen in this micrograph. The primary (001) facet is atomically flat on the top face while a ledge with the thickness of one θ' unit cell is added at some distance from

the end of the lower face. The secondary (100) facet that constitutes the end of this plate is remarkably flat, but the junctions between the (100) and (001) facets are not atomically sharp. Close inspection reveals a small periodic relaxation every three (001)_{Al} planes where they meet their counterpart in the θ' lattice. The particle thickness at the end is 4.85 nm, increases to 5.45 nm further to the right and remains at this thickness over its entire length (not visible here).

Elastic distortions are readily apparent by following the aluminum lattice along the right angle edges of the picture. An extra half plane ends at the top left edge of the particle (see arrow), leading to a twist of the lattice near the left edge of the picture.

A slight contraction of the Al lattice by about 0.2 nm (one (002) plane of the Al lattice) is visible near the right hand bottom edge of the image. This is consistent with the observation that in a conservative lattice correspondence 9 unit cells of θ' (9×0.58 nm) meet 13.5 unit cells of Al (27×0.202 nm). The difference of 0.23 nm must be accommodated elastically or by external dislocations.

Further evidence for distortions and dislocation activity near the end of θ' particles is shown in Figure 4. The slight crystal misalignment permits a clear view of the {200} Al planes parallel to the secondary facet. By viewing these planes at an oblique angle and following their alignment from right to left it can be seen that due to their coherency with the (200) θ' planes with slightly larger spacing ($\sim 0.6 - 1.2\%$) these lattice planes bulge out toward the end of the plate. Immediately adjacent to the end (secondary facet) a vacancy loop or dipole is visible as a missing plane (see arrows). Because this loop cancels the coherency strains there are no appreciable long range distortions. Whether this dislocation is actually of the $1/2 \langle 100 \rangle$ type suggested by this image and from earlier work /7/ or whether it is actually the projection of a $1/2 \langle 110 \rangle$ dislocation remains to be determined.

Another interesting feature is the strong distortion of the particle that gives it the appearance of a split end. This observation may be related to coherency strains since the conservative growth of θ' implies its contraction in the [001] direction; hence coherent particles will be under [001] tensile strain. However, the most significant observation made on the secondary facets at the end of θ' precipitates is the extra half plane or dislocation loop found at or near the end of most of these particles. This suggests that, like the thickening which is controlled by the nucleation of ledges and the volume strain accommodation, the broadening of θ' plates in this low-temperature regime may be governed by these two factors as well.

3 - HfN PLATES IN Mo

The crystallography of HfN precipitates in Mo is very similar to that of θ' precipitates in Al and leads to a similar distribution of HfN plates on {001} planes of the Mo matrix (see Figure 5a) /8/. However, due to the interstitial nature of nitrogen in the Mo lattice, the formation of HfN precipitates involves a large volume expansion (rather than a small volume contraction) and vacancies play an important part in the precipitation process /9/. Again, the atomic match in the (001) habit plane is excellent and, as seen at high resolution in Figure 5b, this interface is perfectly coherent. This image shows that the particle thickness is

such that the diagonal $\{110\}$ planes of the Mo matrix are in registry, i.e. there is no net shear displacement.

As seen in Figure 5a these plates have mostly a circular or irregularly curved shape with a very pronounced facet on the habit plane. As was the case for θ' , the composite symmetry of cubic HfN (space group $Fm\bar{3}m$, $a = 0.452$ nm) in cubic Mo (space group $Im\bar{3}m$, $a = 0.315$ nm) is tetragonal, but at this heat treatment temperature the average particle shape is that of a circular plate where only the major (001) facet is observed. However, it is likely, that under conditions of low-temperature aging, secondary facets would develop.

4 - CARBIDE PRECIPITATES IN Pt

In spite of its low solubility for carbon, carbide precipitates have been found to form readily in Pt during aging after a rapid quench /10/. As in the two previous examples the carbides form as thin circular plates on $\{001\}$ planes and thickening occurs by a ledge mechanism that can also be analyzed as a dislocation reaction. Again the interstitial nature of C in Pt necessitates vacancies for precipitation to occur, in fact C and vacancies are found to co-precipitate /10/. While faceted square plates have been observed under some aging conditions, the plates investigated here were the circular variety as shown in Figure 6a. From an analysis of stacking fault and dislocation contrast in conventional microscopy it was concluded that these particles were single layer carbides with a displacement vector of $\sim 1/3 \langle 001 \rangle$ and an interstitial strain field. The high resolution images shown in Figure 6b and c confirm this thickness and displacement directly. The image at Scherzer defocus is similar to that of a pure $\{001\}$ stacking fault while at -800 Å defocus small white dots appear at the positions of the carbon atoms. Whether or not carbon atoms are directly visible in such images remains to be determined by comparison with image simulations.

5 - Cr PRECIPITATES IN Cu

Body centered cubic Cr ($Im\bar{3}m$, $a = 0.288$ nm) precipitates in face centered cubic Cu ($Fm\bar{3}m$, $a = 0.362$ nm) in the form of laths along $\langle 761 \rangle$ Cu directions /11/. It has been shown that $\langle 761 \rangle$ is an invariant line direction in this alloy system and hence the precipitates tend to form as needles or laths aligned along this direction /12/. The orientation relationship adopted is near that of Kurdjumov-Sachs and has very low (triclinic) composite symmetry /5/. Nevertheless, at a low aging temperature (700°C), the particles tend to take on a faceted cross section as shown in Figure 7a in a conventional micrograph taken close to the axis of the three laths that are seen here to be connected to lattice dislocations. Their parallelogram type cross sectional shape appears to have twofold symmetry along the needle axis. Thus, as observed in the previous examples, the morphology has a symmetry higher than that of the orientation relationship. When viewed at high resolution, the low-symmetry crystallography prohibits observation of the interface on-edge with both crystals simultaneously in a zone axis orientation. Fig. 7b shows the shorter of the two facets (arrowed in Fig. 7a) seen along the common close packed direction which is within 7.5° of the needle axis. Periodic relaxations in this interface are readily apparent. This interface is within about 10° of the $\{110\}$ planes of the matrix. In order to see this boundary precisely edge-on, a 7.5° tilt along the common close-packed planes is required. However, this will destroy the lattice resolution obtained at this zone axis. It is thus necessary to

combine observations from different orientations and imaging conditions to determine the entire interface structure.

The origin of these facets on high index planes and their role in the growth mechanism of such particles is currently under investigation.

6 - PRECIPITATION OF Ge IN Al

Pronounced faceting is observed in the precipitation of Ge ($Fd\bar{3}m$, $a = 0.566$ nm) from Al-Ge solid solutions ($Fm\bar{3}m$, $a = 0.404$ nm). Similar to the case of Mo-HfN and Pt-C, vacancies are essential for the precipitation process to occur because of the large volume increase.

Interestingly, even though the crystallography is simple, a large variation in orientation relationships and morphologies is found. This is illustrated with two dark field images in Fig 8. The micrograph in Fig. 8a was taken near the $\langle 111 \rangle$ zone axis and shows precipitates that are triangular, lath-like and trapezoidal in this projection. It is apparent from the thickness contours that some of these are plates while others are actually tetrahedral in shape (see arrows) /13/. This observation is confirmed by the view along the $\langle 100 \rangle$ zone axis where the tetrahedra project as squares. It has been pointed out by Pond /14/ and by Hugo et al. /13/ that this tetrahedral morphology ($\bar{4}3m$) was due to the intersection of the space group symmetries rather than merely the point groups of the two crystals. Laths along $\langle 100 \rangle$ directions as well as laths or plates along $\langle 110 \rangle$ directions are also visible. These images illustrate the great variety of observed morphologies and at the same time show the usefulness of observations along high-symmetry zone axes in the analysis of morphologies.

High resolution observations allow accurate determination of interface structures and faceting. Many such observations were made on $\langle 100 \rangle$ needles such as that shown in Fig. 9. For this particular orientation relationship faceting was found on $\{111\}$ planes of the Ge precipitates. However, for orientation relationships of higher symmetry facets were found not on $\{111\}$ planes but on the more symmetrical $\{100\}$ or $\{110\}$ planes. Clearly, the orientation relationship is important in the formation of particular facets and hence the development of precipitate/matrix interfaces. Particles with multiple facets such as tetrahedra or multi-faceted plates are likely to exhibit growth mechanisms that reflect the preference for flat, faceted interfaces.

Note that in the example in Fig. 9 internal twins lead to ledges at the $\{111\}$ interface facets. It would be expected that these play a role in the growth of such faceted precipitates. Interestingly, the interfaces seen here show very little evidence of elastic relaxations of the type seen in the previous examples. No regular dislocations or long range distortions could be identified and it appears as though these interfaces, although faceted, could be incoherent or reconstructed. Further investigation of these latter points is presently underway.

ACKNOWLEDGEMENTS

We would like to thank J.-Y. Hignard and D. Ah-Tye for help with the sample preparation. This work was supported by the Director, Office of Energy Research,

Office of Basic Energy Sciences of the U.S. Department of Energy under contract #DE-AC03-76SF00098. One of us (MJW) thanks the University of the Witwatersrand for leave and FRD for financial support.

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FIGURE CAPTIONS

Fig. 1 Faceted θ' precipitates in Al-4% Cu after aging 176h at 144°C. The three different $\{100\}$ variants all exhibit well-developed facets on $\{100\}$ and $\{110\}$ planes (a); dislocations encircling the face-on precipitate and small steps in the facets are seen in (b).

Fig. 2 (a) Lower magnification micrograph shows that most but not all θ' plates are faceted under these heat treatment conditions; a schematic of a qualitative Wulff plot that can be constructed from such data is given in (b).

Fig. 3 High resolution image of the faceted end of a θ' precipitate shows the ledge structure, interfacial dislocations and matrix strain at the atomic level.

Fig. 4 Highly strained periphery of thin θ' plate with dislocation loop at the particle end accommodating the mismatch between (100) planes.

Fig. 5 Conventional (a) and high resolution (b) micrographs of $\{001\}$ plate precipitates of HfN in Mo.

Fig. 6 Conventional and high resolution images of $\{001\}$ carbide plate precipitates in Pt.

Fig. 7 A series of end-on Cr needle precipitates linked to lattice dislocations is shown in (a) and a high resolution image of the short facet in the Cr/Cu interface in (b).

Fig. 8 Triangular $\{111\}$ plates, $\langle 100 \rangle$ and $\langle 110 \rangle$ laths and needles, and tetrahedral-shaped Ge precipitates in an Al-1%Ge alloy are imaged in dark field in a $\langle 111 \rangle$ zone in (a) and a $\langle 100 \rangle$ zone in (b).

Fig. 9 A Ge needle with rhombus-shaped cross-section is shown with a single set of twins and $\{111\}$ interface facets. Note the disturbance in the facets where the twins emerge from the particle (micrograph by J. Douin).

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Figure 1

XBB 899-8133

Figure 2a

b

Figure 2b

XBB 899-8134

Figure 3

XBB 899-8135

Figure 4

Figure 5

Figure 6

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Figure 7

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Figure 8

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Figure 9

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