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IMPERFECTIONS AND MICROSTRUCTURE

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IMPERFECTIONS AND MICROSTRUCTURE*

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INTRODUCTION

The microstructures observed in crystalline materials, whether single or multiphase systems, are influenced to some extent by the presence of structural imperfections in the matrixes of the component phases. Such imperfections can themselves be the major microstructural feature of a material or they can be influential in determining character of the microstructures formed by diffusional or shear phase transformations.

In this paper we present basic descriptions of the nature and behavior of structural imperfections and illustrate the role of these imperfections in developing some of the microstructural features observed in crystalline materials.

Some characteristic surface microstructural features produced by structural imperfections are shown, but major emphasis is directed toward microstructures observed by transmission electron microscopy.

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STRUCTURAL IMPERFECTIONS

Structural imperfections can be considered local atomic scale mistakes in the repetitive three-dimensional equilibrium arrangements of atoms, molecules, or ions that make up the structure of a crystalline material. Because the imperfections are mistakes in the structure, their specific nature and behavior are unique for each material. However, structural imperfections can be classified into three general types based on geometry: point imperfections, line imperfections, and planar imperfections.

Point Imperfections

There are two types of point imperfections or defects: intrinsic and extrinsic (Fig. 1). Intrinsic point imperfections, or vacancies, exist where atoms are missing from their normal positions in the crystal structure. Extrinsic, or interstitial, point imperfections exist where atoms occupy positions other than their normal lattice sites; i.e., they are at interstitial sites.

A thermal equilibrium number of vacancies, N_o , is always present in crystals. This number is given by

$$N_o = N_s \exp (-\Delta F/RT), \quad (1)$$

where N_s is the number of lattice sites, ΔF is the free energy for formation of a mole of vacancies, R is the gas constant, and T is the absolute temperature. It is evident from Eq. (1) that the equilibrium number of vacancies increases with increasing temperature. Vacancies in excess of the equilibrium number can be created in crystalline materials as a result of quenching from high temperature, plastic deformation, and radiation damage.

Atoms are displaced from their normal lattice sites to interstitial sites by plastic deformation or irradiation processes. Irradiation produces equal numbers of vacancies and interstitial defects (Frenkel defects), as shown in Fig. 1c. Local dilations and contractions of the crystal lattice occur at the point imperfections, thus the defects are essentially small elastic strain centers.

Although they cannot be considered structural imperfections in terms of the definition presented above, dilute solid solutions of foreign atoms that occupy interstitial sites in a host crystal, such as carbon or nitrogen in iron, can be considered a type of extrinsic point defect.

Point imperfections move about in a crystal by a series of thermally activated jumps. The probability that a point defect will jump to an adjacent site is given by

$$P_j = \exp (-\Delta H_m/RT), \quad (2)$$

where ΔH_m is the activation energy for the jumps. Thus, the motion of point defects is more rapid at higher temperatures. Vacancies move from one lattice site to the next by exchanging with atoms on neighboring sites; interstitials move by a series of jumps to neighboring interstitial sites. In a given crystal, vacancy jumps generally require a higher thermal activation energy than interstitial jumps. Consequently, the interstitials usually move faster and at lower temperatures than vacancies.

LINE IMPERFECTIONS

Line imperfections or dislocations are linear regions of elastic distortion caused by atoms that are slightly displaced from their equilibrium lattice

positions. An edge or Taylor dislocation in a simple cubic crystal, which is composed of planes of atoms spaced distance a apart, is shown in Fig. 2. The edge dislocation, in this case, is produced by the extra half-plane of atoms (ABCD) that may have resulted when part of a complete plane was removed from the crystal below the EFGH plane. The remaining atoms shifted and occupied the space created by the partial removal of the plane. Actual edge dislocations in face-centered or body-centered cubic crystals are usually associated with two or three adjacent half-planes, however the effect is essentially as shown. The atoms near the lower edge of the half plane are elastically displaced and arranged as shown in Fig. 3. Similarly, atoms along the AB line are displaced from their equilibrium lattice separations. The line AB, along which the elastic distortion is concentrated is the linear imperfection. Everywhere else the crystal retains its structural perfection.

The dislocation is characterized by a Burgers vector, $\vec{b}$, which represents the direction and magnitude of the elastic shear distortion. The Burgers vector is determined by viewing the dislocation line from A to B (Fig. 3). A circuit of atoms is traversed around the line in a clockwise direction and makes an equal number of steps down, to the left, up, and to the right. When the structure is either perfect or contains only point imperfections, the Burgers circuit will close. When a dislocation is present, the Burgers circuit will not close by the lattice vector (e to a), which is the Burgers vector $\vec{b}$ for the dislocation. The Burgers vector is perpendicular to the dislocation line AB in Fig. 2, which is the defining geometric characteristic of an edge dislocation.

The Burgers vector in Fig. 3 is designated positive by convention, however, dislocations in crystals are commonly positive or negative. If the extra half

plane in Fig. 2 were in the lower portion of the crystal, below the EFGH plane, the edge dislocation would be inverted. The Burgers vector of that inverted dislocation would be of the same magnitude but in the opposite direction. Therefore, the vector of the inverted dislocation would be of opposite sign or negative.

The plane EFGH determined by the dislocation line and its perpendicular Burgers vector is the slip plane on which the edge dislocation is constrained to move or glide under an applied shear stress to produce plastic deformation. The glide motion of a dislocation is illustrated in Fig. 4 before and after a glide of one unit to the right. When the dislocation has moved to the right edge of the crystal, the portion above the slip plane will have been displaced to the right distance $\bar{b}$ relative to the lower portion. The same shear displacement would be produced by an edge dislocation of opposite sign moving to the left.

When the dislocation moves, slip occurs over an area of the slip plane traversed by the dislocation. In general, the dislocation is the line that separates the slipped from the unslipped portion of the slip plane. Consequently, the dislocation cannot end inside the crystal; either it must end on the surface, as shown at points A and B in Fig. 2, or it must form a closed loop inside the crystal. The places where individual dislocations end at the external surface are indicated by etched pits; closely spaced arrays of dislocation are indicated by etched boundaries (Fig. 5).

Generally the dislocation will not move as a rigid straight line; it may take any curved shape in the slip plane. Thus, it will not remain perpendicular to its Burgers vector at all points along its length and will not retain its completely edge character. Portions of the dislocation that become parallel to the Burgers vector are called screw or Burgers dislocations. The structural

mistake that results in the screw dislocation is a spiral ramp of displaced atoms that advances one Burgers vector per circuit of the dislocation.

Because the screw dislocation and the Burgers vector are parallel, they do not define a specific slip plane, as in the case of the edge dislocation. Consequently, screw dislocations are not constrained to move on a certain slip plane, but can move by cross-glide on any facile slip plane that has its vector normal perpendicular to the Burgers vector. Generally, the dislocation is oriented between perpendicular and parallel to the Burgers vector and has both edge and screw characteristics. Thus, the geometry of the elastic distortions of the atoms along the mixed dislocation line is a complex mixture of pure screw and edge dislocation geometries.

The elastic distortions around a dislocation produce a stress field that moves with the dislocation. The stresses around a screw dislocation oriented along the Z axis of a Cartesian coordinate system are given by

$$\sigma_{ZX} = \frac{Gby}{2\pi(x^2 + y^2)} \quad (3)$$

and

$$\sigma_{Zy} = \frac{GbX}{2\pi(x^2 + y^2)} \quad (4)$$

The stresses around an edge dislocation with the same Z axis orientation and the Burgers vector along the X axis are given by

$$\sigma_{XX} = \frac{Gb}{2\pi(1 - \mu)} \frac{y(3x^2 + y^2)}{(x^2 + y^2)^2} \quad (5)$$

$$\sigma_{yy} = \frac{Gb}{2\pi(1 - \mu)} \frac{y(x^2 - y^2)}{(x^2 + y^2)^2} \quad (6)$$

$$\sigma_{zz} = \mu(\sigma_{xx} + \sigma_{yy}), \quad (7)$$

and

$$\sigma_{xy} = \frac{Gb}{2\pi(1-\mu)} \frac{x(x^2 - y^2)}{(x^2 + y^2)^2}, \quad (8)$$

where G is the shear modulus and μ is Poisson's ratio.

These equations reveal that the stresses around both the edge and the screw dislocations decrease in proportion to the reciprocal of the distance from the dislocation. The stresses around a screw dislocation [Eqs. (3) and (4)] are pure shear and are parallel to the dislocation while those around an edge dislocation are dilatational [Eqs. (5), (6), and (7)] as well as shear [Eq. (8)]. As will be discussed later, these stress fields exert forces that directly influence the overall character of the dislocation arrangements. The elastic stresses and strains that are in the crystal because of a dislocation produce a lattice strain energy, which is known as the energy of the dislocation. A precise calculation of this energy is complicated by many factors, however, very sophisticated estimates indicate that the average dislocation energy Γ is proportional to the square of the Burgers vector and is given by

$$\Gamma = \frac{Gb^2}{2}. \quad (9)$$

In different crystal structures, dislocations can have quite different geometric configurations dictated by lattice geometry and minimum energy considerations. In fcc crystals, for example, dislocations are usually spread out in the slip plane into a lower energy dissociated configuration as illustrated in Fig. 6. The edge dislocation with total Burgers vector $\bar{b}$, (Fig. 6a) changes

its configuration by dissociating into two Shockley dislocations (Fig. 6b) with partial Burgers vectors $\bar{b}_1$ and $\bar{b}_2$ according to the reaction

$$\begin{aligned} \bar{b} &\rightarrow \bar{b}_1 + \bar{b}_2 \\ \frac{a}{2} [\bar{1}10] &\rightarrow \frac{a}{6} [\bar{2}\bar{1}1] + \frac{a}{6} [12\bar{1}] . \end{aligned} \quad (10)$$

The change in strain energy for this reaction is given by the difference in the dislocation energies involved. Thus, from Eq. (9) we obtain

$$\begin{aligned} \Delta u &= \frac{G}{2} \left\{ \bar{b}_1^2 + \bar{b}_2^2 - \bar{b}^2 \right\} \\ &= \frac{G}{2} \left\{ \frac{a^2}{6} + \frac{a^2}{6} - \frac{a^2}{2} \right\} = - \frac{Ga^2}{12} . \end{aligned} \quad (11)$$

Because this energy change is negative, the energy of the dislocation decreases and the dissociation will occur. The Shockley dislocations are separated by a planar imperfection called a stacking fault. Screw dislocations in bcc crystals can undergo a similar type of dissociation onto three different crystal planes thus producing an asymmetric configuration. Different configurations affect the behavior of the dislocations and can directly influence the character and physical properties of the microstructures in crystalline materials.

Planar Imperfections

Planar imperfections are any surface across which the atom positions in a perfect crystal are not preserved. Aside from the obvious external boundaries of crystals there are two planar imperfections, twin planes and stacking faults, that are common microstructural features in crystalline materials.

Twin planes separate the two parts of a twinned crystal, the parent and its twin, which are symmetrically related. The relationship between the two parts is described by the symmetry operation, which will bring one part into coincidence with the other. The two main types of twins are rotation and reflection. The type depends on whether the symmetry operation is a 180° rotation about the twin axis or a reflection across the twin plane. Twins in high-symmetry fcc crystals satisfy both the rotation and the reflection criteria; twins in bcc and hcp crystals satisfy the reflection criterion. The crystallographic symmetry relationships between the parent and its twin in an fcc crystal are shown in Fig. 7. The plane of the figure is the plane of the fcc lattice with Miller indices $(1\bar{1}0)$. The open circles represent atoms in the plane of the drawing and the filled circles those atoms just above or below the plane. The lattice on either side of the twin plane can be brought into coincidence by a mirror reflection across the (111) twin plane as indicated by the dashed lines or by a 180° rotation about the $[111]$ twin axis.

Twins are commonly found in fcc structures, such as α brass, nickel, and stainless steel, which have been cold-worked and annealed to cause recrystallization. These annealing twins are probably formed as the result of mistakes in the stacking sequence of (111) atom planes during normal growth of recrystallized grains. The (111) planes are hexagonal arrays of atoms, which can be represented as spheres that touch each other like racked billiard balls (Fig. 8a). If the atoms in the lowest hexagonal array occupy A positions, the atoms in the layer immediately above occupy the depression positions B. The atoms in the third layer occupy the alternate depressions, C, over the A layer, and the fourth layer of atoms is directly above the atoms in the lower A layer.

The stacking of hexagonal arrays of atoms in the (0001) basal plane of the hcp structure is similar to that of the fcc structure (Fig. 8b) with the second layer of atoms occupying the same B depressions over the lower A layer. The third layer of atoms in the hcp structure, however, occupy positions directly above the A layer. Thus, the normal stacking sequence of (111) planes in the fcc structure is ABCABC and the sequence for (0001) basal planes in the hcp structure is ABAB.

Suppose that a recrystallized grain in an fcc structure grows by adding layers of atoms parallel to the (111) plane in the sequence ABCABC. If a mistake occurs so that a layer of atoms occupies B positions instead of the normal A positions and subsequent layers occupy correct positions, the stacking sequence after the mistake will be BACBAC. The new growth sequence will produce an fcc structure that is the mirror image of the original in the twin plane (shown at the left of Fig. 7). Another result of the formation of the twin by the growth mistake is the stacking sequence BCB across the twin plane that corresponds to a single layer of atoms of hcp structure. The hcp structure differs from the fcc structure relative to the second nearest neighbors. Because the fcc structure is the stable phase, it has the lower free energy. Therefore, the free energy of the hcp structure of the twin plane is higher than other {111} crystal planes in the fcc structure.

Twins formed by different processes show different characteristics under the microscope (Fig. 9). Annealing twins usually appear as bands with straight edges. Twins formed by homogeneous shear deformation generally have a lenticular shape. Deformation twins in fcc crystals can be produced by shear displacement of (111) atom planes a distance $\eta(a/6)$ in the $[1\bar{1}2]$ twinning direction, as shown at the left of Fig. 7, where a is the fcc lattice constant and η is an

integer proportional to the distance of a given (111) plane from the twin plane. If it is assumed that the C layer at the twin plane and all layers below it remain unchanged, the first A layer immediately above shifts an amount $a/6 [1\bar{1}2]$ (shown by the arrows in Fig. 7) to position B, the second layer shifts $2a/6 [1\bar{1}2]$ from B to A, and the third layer shifts $3a/6 [1\bar{1}2]$ from C to C thus producing the same twin stacking sequence. Twins observed in bcc and hcp crystals are similar to those found in the fcc structure but are usually formed by shear deformation. In the bcc structure the principal twin plane is $\{112\}$ with a $\langle 11\bar{1} \rangle$ twinning shear. The hcp crystals normally twin on the $\{\bar{1}0\bar{1}2\}$ planes in the $\langle 10\bar{1}1 \rangle$ direction.

As described previously, the elastic strain energy of dislocations can be lowered by dissociation into Shockley dislocations, which are separated by a stacking fault. The stacking fault results from a mistake in the stacking of atom planes of the crystal similar to a twin plane formation. The fault is created in the slip plane by the shear displacement that is produced when one of the Shockley dislocations moves; it is removed when the other dislocation traverses the same area. A stacking fault and two Shockley partial dislocations in the (111) slip plane between stacking layers A and B in a fcc structure are shown in Fig. 10a. The Burgers vector of the total dislocation, shown by the arrow from B to B, has dissociated into Shockley partials b_1 and b_2 according to the reaction of Eq. (10). The stacking fault is produced by moving dislocation b_1 to the right a distance d relative to b_2 . The separation between the partial dislocations occurs because of the mutually repulsive force between the dislocations resulting from the interaction of their stress fields.

The stacking sequence of atoms on the (111) planes left of b_2 and right of b_1 is appropriate to the perfect fcc structure with the (111) layer of atoms just below the slip plane at A positions and atoms in the layer immediately above the slip plane in B positions. A different sequence exists between the two dislocations. Whereas atoms in the A layer and all layers below are unchanged, atoms in the B layer and all layers above are displaced by the vector b_1 . Thus, the atoms in the B layer move from B to C positions and those originally at C positions in the third layer move from C to A positions. These changes continue into the higher layers. Therefore, the splitting of the two Shockley partials results in the stacking sequence change shown in Fig. 10b. As can be seen there are two changes in stacking order associated with the stacking fault. Also, the fault consists of a planar region two atomic layers high with a stacking sequence corresponding to the hcp structure. Consequently, the stacking fault has an increased energy above that of a normal (111) lattice plane and about twice that of a (111) twin plane.

If only the reduction in elastic strain energy were involved in the energetics of the dissociation, the two Shockley partials would separate completely by gliding apart on the slip plane. But the stacking fault created increases the energy of the new configuration and an equilibrium separation is established when the increase in fault energy equals the decrease in elastic strain energy of the dislocations. The equilibrium separation of the Shockley partial dislocations in most fcc crystals is usually small ($<10 \text{ \AA}$) and the stacking faults are not easily resolved by transmission electron microscopy, except in alloys with very low fault energies. Wide stacking faults are often observed in deformed crystals where one of the partial dislocations is pinned by an internal barrier while the

other has moved under a local shear stress. In Fig. 11 the stacking fault in 304 stainless steel is characterized by dark-light fringes between the two partial dislocations A and B.

A similar analysis of stacking fault formation can be applied to bcc and hcp structures. In bcc crystals, the fault energies appear to be very high and the width of stacking faults in materials with this structure is too narrow to be resolved with an electron-microscope. Stacking faults observed on basal planes in hcp crystals consist of two layers with a stacking sequence corresponding to that of an fcc structure.

INTERACTIONS OF IMPERFECTIONS

Microstructure features involving imperfections are not generally the result of an individual defect but rather are products of the interactions of many defects. These interactions can provide the mechanisms by which the microstructures develop and can influence their characteristics. Several types of imperfection interactions contribute, in some degree, to all microstructures developed in crystalline materials.

Point defect interactions commonly occur in crystals with defect concentrations in excess of the equilibrium number and provide a means of reducing the concentration. The interaction process is simply the coalescing of individual point defects into clusters, similar to a precipitation reaction. The effects of clustering depend on specific conditions in the crystal. A super-saturated concentration of vacancies will coalesce into clusters of void platelets on specific crystallographic planes (Fig. 12a). When the

platelets reach a critical size they often collapse into intrinsic edge dislocation loops (Fig. 12b). Figure 13 shows a transmission-electron micrograph of intrinsic dislocation loops lying on (111) planes in aluminum. The loops were formed by the clustering of vacancies produced by quenching from just below the melting point.¹ The loops contain stacking faults, which exhibit fringes similar to those associated with the stacking faults in Fig. 11. In this case, the faults are produced by removing part of a (111) plane of atoms in B stacking positions by the coalescence of vacancies. The collapse of the resultant void then produces a faulted stacking sequence identical to that shown in Fig. 10b.

In cases such as gold, vacancy coalescence produces a more complex structure of (111) plane stacking faults in the form of tetrahedrons (Fig. 14).²

Interstitial point defects in excess of the equilibrium can undergo clustering similar to that of vacancies. The extrinsic platelet of interstitial defects (Fig. 15) is similar in appearance to intrinsic dislocation loops. The most distinguishing difference between the two is that the crystal matrix is in tension adjacent to the intrinsic loop and in compression adjacent to the extrinsic platelet.

In crystals with high concentrations of both vacancies and interstitials, as might be produced by radiation damage, a vacancy and an interstitial can interact to cause mutual annihilation, which is essentially a reverse of their formation. At elevated temperatures, where both vacancies and interstitials are mobile, this back reaction causes the radiation-produced defects to anneal out or to develop a steady state concentration. At low or moderate temperatures, when the thermal activation is sufficient for interstitial motion but insufficient

for vacancy migration, the interstitials can form into extrinsic clusters in the presence of the relatively immobile vacancies.

Under certain conditions, the vacancy clusters can be stabilized and grow into large internal pores. This often occurs in crystals where irradiation damage has produced an extrinsic gaseous species, such as helium or hydrogen. An electron micrograph of a replica of a freshly cleaved surface of a LiH crystal subjected to gamma irradiation at elevated temperatures³ is shown in Fig. 16. The principal damage in the crystal is the formation of an equal number of intrinsic and extrinsic point defects by the displacement of hydrogen ions from normal lattice sites to interstitial sites. The interstitial hydrogen ions interact to form H_2 molecules, which are trapped in the LiH lattice. The vacancies created by the irradiation coalesce into crystallographic clusters but, instead of forming intrinsic dislocation loops they interact with the H_2 molecules, which prevent their collapse. Then, by addition of vacancies and H_2 molecules the stabilized vacancy clusters grow into the rectangular gas-filled pores shown in Fig. 16.

The interaction of dislocations is caused by interactions of their stress fields. These interactions occur over relatively long distances compared with the interactions between point defects. The net effect of the interaction of many dislocations is quite complex and contributes to the development of a complicated structure of dislocation pile-ups and tangles observed in deformed crystals (Fig. 17).⁴ These dislocation structures are relatively high-energy structures in metastable equilibrium at the temperature of their formation. Over a period of time, and under the influence of the interaction forces aided by thermal energy fluctuations, the dislocations will attempt to arrange themselves into

configurations that reduce the elastic strain energy in the crystal (Fig. 16).⁴ This process is known as polygonization.

Although the stress field interactions between dislocations in structures like those shown in Figs. 17 and 18 are generally complex, some insight into their nature and effect can be obtained by considering the interaction of two edge dislocations A and B on parallel slip planes a distance y_0 apart (Fig. 19). The force per unit length that is exerted on a dislocation and causes it to move on its slip plane is given by the shear stress in the slip plane in the direction of the Burgers vector times the Burgers vector,

$$F_x = \tau b, \quad (12)$$

where F_x is the force that acts normal to the dislocation line and τ is the shear stress. Therefore, the force acting on dislocation B in the x direction at the x, y_0 position that is caused by the stress field of dislocation A at the origin of the coordinate system is given by Eq. (8).

$$F_x = \sigma_{xy} b_B = \frac{Gb_A b_B}{2\pi(1-\mu)} \frac{x(x^2 - y_0^2)}{(x^2 + y_0^2)^{3/2}} \quad (13)$$

(Although an equal and opposite force acts on dislocation A as a result of the stress field of B, for our purposes here dislocation A is held fixed and not allowed to move.) The variation of F_x with distance between the dislocations is shown by the solid curve in Fig. 19 for the case where $b_A = b_B$. When dislocation B is in the range $-\infty < x < -y_0$ or $y_0 < x < \infty$, the dislocations exert a force on one another that tends to move them farther apart on their slip planes. When dislocation B lies within the range $-y_0 < x < y_0$, the dislocations attract one

another and come to rest one above the other at $x = 0$. The interaction force when dislocation A and B are of opposite sign, $b_A = -b_B$, is shown by the dashed curve in Fig. 19. In this case the dislocations attract one another when B lies in the range $-\infty < x < -y_0$ or $y_0 < x < \infty$ and repel one another when B is in the range $-y_0 < x < y_0$. Dislocation B will come to rest at $x = \pm y_0$. Thus, as a result of the stress field interactions, an array of identical edge dislocations randomly distributed on parallel slip planes would arrange themselves by gliding on their slip planes into the configuration shown in Fig. 20a. The arrangement is a small angle tilt boundary (Fig. 20) similar to that at A in Fig. 18 if they are all of the same sign, or into the dipole configuration in Fig. 20b if they are of opposite signs. This highly idealized model of dislocation structures illustrates the factors involved in developing dislocation microstructures under conditions that allow dislocations to glide to positions determined by the interactions of their shear stress fields.

In real crystals the dislocations are not uniformly arranged on parallel slip planes a distance y_0 apart, but, consist of nonuniform tangles and piled up groups on several nonparallel slip planes. Under such conditions the stress field interactions are more complex than shown in Fig. 19 and the freedom of dislocations to glide on their slip planes is greatly restricted. Consequently, the dislocation structures shown in Figs. 18 and 20 are not usually attained in crystals at low or moderate temperatures. At elevated temperatures, where the concentration and mobility of vacancies is increased, the interaction of vacancies with the dislocation permits the dislocation an additional degree of freedom, climb, that greatly enhances its ability to develop equilibrium microstructures.

The process of climb is illustrated in Fig. 21, which shows an edge dislocation with a compressive stress σ_{xx} acting normal to the extra half plane. Under the action of this stress, a vacancy will jump into a position at the bottom of the extra half plane, thus producing an upward unit climb of a segment of the dislocation. The adsorption of many vacancies by the dislocation gives the dislocation a motion normal to its slip plane. In this way, edge dislocations that are restricted in their glide on a slip plane can climb to a parallel slip plane where glide is not restricted and where the dislocations can arrange themselves in the lower energy configuration (Fig. 20). For example, in addition to the shear stress interaction, the stress fields of like sign dislocations A and B in Fig. 19 produce a compressive stress $-\sigma_{xx}$ on B and a tensile stress σ_{xx} on A given by Eq. (5). Suppose that dislocation B lies within the range $-y_0 < x < y_0$ and is moving on its slip plane to the equilibrium position $x = 0$ as a result of the shear stress field action of dislocation A. If the glide of dislocation B on its slip plane is restricted by a barrier, the dislocation can climb up under the action of the compressive stress $-\sigma_{xx}$ to parallel slip plane, which has no barrier, and then glide to position $x = 0$. The tensile stress σ_{xx} on dislocation A causes it to climb down by the reverse process of emitting vacancies. Thus, the two like-sign dislocations tend to climb apart.

In a similar way, edge dislocations of unlike signs that develop the equilibrium dipole configurations shown in Fig. 20b exert compressive or tensile stresses on one another that cause them to climb toward one another by absorption or emission of vacancies. The combination of climb and glide produced by the stress field interactions eventually results in a mutual annihilation of the dislocations.

During the climb process, vacancies are either absorbed and annihilated or emitted at the dislocations. Thus, dislocations can act as either sinks or sources for vacancies and can locally change the vacancy concentration in a crystal.

Screw dislocations cannot climb, but their stress field interactions produce geometric equilibrium configurations and annihilations similar to those of edge dislocations.

The local crystal lattice strains around point imperfections can interact elastically with the stress field of a dislocation. The strength of the interaction depends on the nature of lattice distortions around the point defect and is, in general, more significant for interstitials than for vacancies or foreign substitutional atoms. These interactions result in the redistribution of interstitials around a dislocation into a cottrell atmosphere, which minimizes the interaction energy. In the presence of an excess of interstitials (above the thermal equilibrium concentration) there is a chemical potential gradient associated with the cottrell atmosphere that causes interstitials to accumulate at dislocations. The process is more pronounced when the interstitials are foreign atoms of a different size than the host atom. Such a case is carbon and nitrogen in bcc metals; the heterogeneous precipitation of carbide and nitrides is commonly observed on dislocations as shown in Fig. 22 where Mo_2C precipitates are shown on dislocations in carburized molybdenum.

The elastically distorted regions of the dislocation core can also be preferred sites for heterogeneous nucleation of precipitates that produce large elastic strains because of the difference in specific volume and structure of the precipitate and host matrix. The large elastic distortion near the dislocation

core can help to accommodate these strains by making heterogeneous nucleation at dislocations much easier than homogeneous nucleation in the perfect matrix. The effect of preferred nucleation and growth of Cr_{23}C_6 precipitates on grain boundary dislocations in 310 stainless steel is shown in Fig. 23.

Twins and stacking faults do not interact elastically with point defects or dislocation stress fields, because there is no lattice strain associated with them. Note that there is no precipitation on the twin plane at A in Fig. 23. Twins, however, can act as barriers to dislocation glide. As shown in Fig. 24, dislocation pile-ups at twin planes are often observed in the microstructures of deformed crystals containing twins.

Twin planes and stacking faults can interact chemically with solute atoms. This interaction is the result of changes in atomic bonding at the twin or stacking fault. As previously described, the twins and stacking faults in fcc crystals contain atom layers with hcp stacking; twins and stacking faults on basal planes of hcp crystals contain atom layers of fcc stacking. When a crystal containing either twins or stacking faults is heated into a temperature range where diffusion can occur, solute atoms will redistribute themselves between the fault and twin regions and a perfect crystal. This segregation of solute atoms to the planar imperfections can produce preferred nucleation and growth of a precipitate phase on the twins and stacking faults.

IMPERFECTION—MICROSTRUCTURE ANALYSIS

Analytical techniques such as chemical analysis, x-ray and electron diffraction, nuclear magnetic resonance, and differential thermal analysis used to determine

the chemical and structural identities of the microstructural features make a substantial complimentary contribution to the characterization of microstructures. While a complete discussion of the various methods and techniques is beyond the scope of this paper, some detailed examples of structural analysis and characterization of microstructures involving structural imperfections observed by transmission-electron microscopy are presented.

To interpret the information contained in a transmission electron micrograph it is essential to understand the factors that determine the image contrast produced by the diffraction of electrons in crystalline materials. The mechanisms of the image formation of the internal structure by transmission electron microscopy are illustrated in Fig. 25. An almost parallel beam of incident electrons accelerated at high voltage (commonly 100 kV) is scattered by the crystalline specimen into one or more diffracted beams that satisfy the Bragg conditions for coherent scattering of radiation. This condition is given by the equation

$$\lambda = 2d \sin\theta, \quad (14)$$

where 2θ is the angle between the incident and diffracted beams, d is the interplanar spacing of the diffracting crystal planes, and λ is the wavelength of the electron, $0.0370 \text{ \AA}$ at 100 kV accelerating voltage.

For common crystalline interplanar spacings of 2 to $3 \text{ \AA}$ the diffraction angle θ is very small, ~ 1 deg. Thus, only crystal planes nearly parallel to the incident beam produce Bragg diffraction. The electron beams that are diffracted and transmitted by the specimen are focused through a magnetic

objective lens onto an intermediate image plane. The intermediate image is then magnified and projected onto a fluorescent screen or photographic film plate by two additional magnetic lenses (intermediate and projector). The magnified image is a complex interference pattern formed by the recombination of various orders of diffracted beams with the undiffracted incident beam. When only one or two diffracted beams with the incident beam are allowed to reach the image plane by inserting a physical adjustable aperture at the back focal plane of the objective lens (Fig. 25a), a one-dimensional interference pattern is obtained. This pattern is a direct image of the crystal planes that produced the diffracted beams. Instrument resolution limits the direct imaging of the crystal planes to crystals with interplanar spacings greater than about $5 \text{ \AA}$. The interplanar spacings of most crystals are less than $4 \text{ \AA}$ and direct resolution of their crystal planes is not yet possible. Thus, electron transmission images of metallic and most other crystals are formed by a mechanism called diffraction contrast.

Diffraction contrast images are formed by inserting an objective aperture that allows either the transmitted incident beam or one of the diffracted beams to reach the image plane (Fig. 25b and c). If the aperture is adjusted so that all of the diffracted beams are blocked and only the transmitted incident beam reaches the image plane as in Fig. 25b, a "bright field" image is formed. If the aperture is adjusted to allow only one of the diffracted beams to reach the image plane as in Fig. 25c, a "dark field" image is formed. The diffraction contrast forming the image simply represents the intensity distribution of the electrons reaching the image plane. The bright field image is obtained by subtracting the intensity of the diffracted beams from the intensity of the

incident beam. The dark field image is obtained from the intensity of the diffracted beam allowed to pass through the aperture. Thus, a crystal oriented so that it produces strong diffraction of the incident beam will appear dark relative to a crystal that is not producing strong diffraction in a bright field image.

Bright field diffraction contrast images of polycrystalline niobium are shown in Fig. 26. A tilting device on the electron microscope permits changes in the specimen orientation relative to the incident electron beam. Thus the crystal can be tilted in or out of strong diffractions to produce changes in the image contrast. The changes in diffraction conditions and image contrast are shown before and after (Fig. 26a and b, respectively) tilting the specimen approximately 5 deg. The crystal grains at A and B are oriented to produce strong diffraction and are relatively dark in Fig. 26a. After tilting they are not diffracting strongly and are relatively light (Fig. 26b).

Because the contrast that forms the transmission images in crystals results from variations in diffracted electron intensity, any defect in the crystal that disturbs the local continuity or periodicity of the diffracting crystal planes (e.g., twin planes, dislocations, or precipitates) can cause a change in the intensity of diffraction. This local change in diffraction intensity produces a diffraction contrast image of the defect. The appearance of the defect image will depend on the nature of the crystal lattice disturbances it produces and on the electron diffraction conditions operating in the crystal. Thus, an unambiguous interpretation of the microstructure images in transmission electron micrographs requires knowledge of the diffraction conditions operating in the crystal. This information, and other quantitative crystallographic information is contained in the diffraction pattern.

The formation of the diffraction pattern is illustrated in Fig. 27. As in transmission image formation, the image formed on the intermediate image plane by the objective lens is focused by the intermediate and projector lens system and projected onto the viewing screen or a photographic plate. The intermediate and projector lenses can be adjusted to focus on the back focal plane. When this is done, the final image is a magnified pattern of spots, known as a diffraction pattern, which correspond to points where the incident and diffracted beams intersect the back focal plane.

The basic information contained in the diffraction pattern is shown schematically in Fig. 28. Imagine a cubic crystal, oriented as shown, at the center P of a sphere of reflection of radius $1/\lambda = 15,000$ miles. An area of the surface of this very large sphere is represented by the plane of reflection JKLM. An incident electron beam directed almost parallel to the -y direction is diffracted by the four cubic-crystal-planes parallel to the y axis with interplanar spacing d. These beams intercept the plane of reflection at points ABCD and O. The vectors $\vec{r}$ from the incident beam intercept to the intercepts of the diffracted beams are normal to the cube planes of the specimen producing the diffracted beams and are of length $|\vec{r}| = 2r \theta = 2 \sin \theta / \lambda$ for $\theta < 2$ deg. Substituting into Bragg's diffraction Eq. (14) gives $|\vec{r}| = 1/d$. Thus, the pattern of intercept spots is a two-dimensional reciprocal lattice.

The two-dimensional reciprocal lattice is only one plane of a three-dimensional reciprocal lattice of the crystal structure in the specimen. It has origin at O, points that define vectors from the origin normal to the respective crystal planes producing diffraction, and lengths equal to the reciprocal of the interplanar spacings. The diffraction pattern micrograph is

a reduced magnification of the two-dimension reciprocal lattice, which is formed on the film plate positioned in the microscope a distance below the specimen corresponding to distance p in Fig. 28. It can be seen from the figure that

$$S/\ell = p/r \text{ or } S = \ell p\lambda = K/d, \quad (15)$$

where K is the internal camera constant for the microscope.

The three-dimensional reciprocal lattice and its relationship to the crystalline specimen in electron diffraction microscopy is illustrated in Fig. 29. When the crystallographic orientation is changed by rotating or tilting the specimen in the microscope, the reciprocal lattice undergoes a corresponding change in orientation by rotating or tilting about its origin. When this occurs, the plane of reflection intercepts a new set of reciprocal lattice points, which correspond to new crystal planes that are oriented to satisfy Bragg's condition for diffraction. This new set of points forms a diffraction pattern that reveals the new crystallographic orientation of the specimen. The following examples are given to illustrate the procedure of indexing the diffraction pattern and its use in the interpretation of transmission micrographs.

The purpose of indexing the diffraction pattern is to identify the crystal planes producing various diffraction spots. Although, there are several techniques to expedite the task, for this example the trial and error method will be used. The internal structure of 304 stainless steel shown in Fig. 30a contains a random distribution of dislocations (C), grain boundaries (A), and annealing twin planes (B). The diffraction pattern produced by the circled portion of the specimen at the lower left of Fig. 30a is shown in Fig. 30b. The distances S from the incident beam spot to the diffraction spots are

related to their respective interplanar spacings by Eq. (15). By measuring values of S on the diffraction pattern and using a value for K of $19.8 \text{ \AA mm}$, the interplanar spacings for the various spots on Fig. 30b calculated from Eq. (15) are listed in the third column of Table 1. The interplanar spacings of any (hkl) planes of a cubic structure can be calculated from the equation,

$$d(hkl) = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}, \quad (16)$$

where a_0 is the dimension of the fcc unit cell equal to $3.56 \text{ \AA}$ for stainless steel. The interplanar spacings of several low-order planes in fcc stainless steel calculated from Eq. (16) are shown in column 5. Only those planes were selected for the calculation for which h , k and l are all even or all odd, since planes with mixed indices in the fcc crystals do not produce diffraction spots. A comparison of the interplanar spacing calculated from Eqs. (15) and (16), indicates that spot A results from diffraction from the $(1\bar{1}1)$ planes, spot B from (002) planes, C from $(\bar{1}11)$, D from $(\bar{2}20)$, E from $(\bar{1}13)$, and F from $(\bar{2}22)$. Because these spots represent the ends of reciprocal lattice vectors from the origin (the incident beam spot) and the vectors are normal to the crystal plane producing the diffraction spot, the angles between the vectors are equal to the angles between the corresponding crystal planes. The angle between any two (hkl) planes in an fcc crystal is given by

$$\cos \theta = \frac{h_1 \cdot h_2 + k_1 \cdot k_2 + l_1 \cdot l_2}{\sqrt{(h_1^2 + k_1^2 + l_1^2)(h_2^2 + k_2^2 + l_2^2)}}. \quad (17)$$

If the spots were indexed correctly, the angles measured between the vectors on the diffraction pattern should agree with the interplanar angles for the corresponding planes in the fcc crystal. It is left to the reader to verify these angles.

When the diffraction pattern is indexed, the identity of the reciprocal lattice plane it represents can be determined by inspection of the reciprocal lattice of the fcc crystal shown in Fig. 31. In this case, the indexing of the pattern corresponds to the (110) plane of the reciprocal lattice. The vector from the origin of the reciprocal lattice normal to the (110) plane is in the [110] direction and by definition is normal to the (110) plane of the specimen. Therefore, the crystallographic orientation of the lower left portion of the specimen in Fig. 30a is completely determined. It is viewed normal to the (110) plane and parallel to the planes indexed on the diffraction pattern.

The straight line image at B in Fig. 30a was identified as the trace of a twin plane and, therefore, should be oriented parallel to one of the {111} planes of the crystal. Reference to Fig. 30 shows that the $[1\bar{1}1]$ vector on the diffraction pattern is normal to this trace. Therefore, the twin plane is oriented parallel to the $(1\bar{1}1)$ plane of the crystal and normal to the plane of the micrograph.

In addition to quantitative information about the orientation and crystalline structure of the specimen portion under observation, the diffraction pattern reveals operating diffraction conditions that produce contrast in the transmission image. Because of such factors as curvature of the plane of reflection and bending of the crystal planes of the specimen, the diffraction conditions commonly occurring during operation of 100 kV microscopes are such that the image contrast is produced principally by one set of strongly diffracting low-order crystal planes.

Diffraction patterns corresponding to this condition are shown in Figs. 44 and 45. When the intensity of the diffracted beam is small compared with that of the incident beam, the diffracted beam intensity at the bottom surface of the specimen is the sum of the intensities of the electrons scattered by atoms at various depths in the crystal, taking into account differences in phases of the scattered electrons. Under these conditions, the intensities of the incident and diffracted beams oscillate with depth in a perfect crystal (Fig. 32). If an imperfection introduced into the crystal produces local atom displacements R from their normal positions, a change in phase of the waves scattered by the atoms given by $\alpha = 2\pi g \cdot R$ will occur, where g corresponds to $\bar{l}$ in Fig. 28 and is the normal to the planes producing the diffracted beam. This phase shift changes the intensity of the diffracted beam at the bottom surface of the crystal and produces a contrast image of the imperfection. If the displacement R is perpendicular to the operating g vector, then $g \cdot R = 0$ and no phase shift or image is produced. The phase shift and image contrast are maximum when R is parallel to g .

In the case of a planar imperfection such as a stacking fault running obliquely across a thin specimen, the phase shift produced by the fault at different depths in the specimen causes the intensity of the diffracted beam at the bottom of the specimen to vary periodically, thus producing a system of dark and light fringes parallel to the intersection of the planar fault and the surface of the specimen (Figs. 11 and 13).

This simplified discussion of transmission image contrast and electron diffraction in crystals involves several approximations and assumptions that do not have general validity. However, it does provide a qualitative guide to the interpretation of many features observed in transmission electron micrographs.

For a more thorough and quantitative treatment of the theory of transmission electron microscopy of crystals the reader is referred to Hirsch et al.⁵

One of the more important conclusions resulting from the discussion of electron diffraction contrast is that transmission electron micrographs such as Figs. 17 and 18 are not necessarily completely representative of the internal structure of the crystal. In these micrographs of dislocation substructure, the lattice displacements R producing the image contrast result from the stress fields of the dislocations and are principally shear displacements parallel to the dislocation Burgers vectors. Consequently, dislocations with Burgers vectors parallel to the operating g vector, for which $g \cdot b$ is maximum, will exhibit strong image contrast while those with Burgers vectors perpendicular to the g vector, having $g \cdot b = 0$ are invisible. Thus, a complete photographic characterization of the imperfection microstructure requires that the specimen be observed under a variety of diffraction conditions with different operating g vectors.

The bright-field images of annealing twins in transmission micrographs (Fig. 33) are similar to the images in optical micrographs on the surface of a polished specimen. Deformation twins, however, often occur on a very fine scale and are not readily distinguishable from several other structural features found in crystalline materials. Identification of twins in these cases requires analysis of diffraction patterns and dark field images of the microstructure. A bright-field micrograph of deformation twins produced by tensile straining hot-forged 304 stainless steel is shown in Fig. 34a. Irregular boundaries of the forged subgrain structure run horizontally across the micrograph and the straight edges of the fine deformation twins are at about 45 deg. The diffraction

pattern corresponding to this area is shown in Fig. 34b. This pattern of spots does not have the simple symmetry corresponding to a plane of the reciprocal lattice shown in Fig. 30b. There are extra, closely spaced spots in Fig. 31b. One possible explanation of the extra diffraction spots is either that more than one reciprocal lattice plane is represented on the pattern corresponding to two or more orientations of the same crystal structure or that two or more crystals of different structure are represented. If this interpretation is correct, the reciprocal lattice patterns and corresponding regions of the specimen can be sorted by analyzing dark-field micrographs of the crystal. Figure 34c shows a dark-field image of Fig. 34a using the diffraction beam corresponding to spot A, on the diffraction pattern for illumination. The bright regions in Fig. 34c contribute to the diffraction spot A while the dark regions do not. Thus, diffraction spot A belongs to a reciprocal lattice pattern produced by the light regions of the dark-field image. Furthermore, because the dark regions do not contribute to the diffracted beam they must be either of another crystal structure or of a different orientation than the light regions.

A similar analysis of other dark-field images using various diffracted beams revealed that there are two reciprocal lattices represented on the diffraction pattern as illustrated in the schematic drawing of the diffraction pattern in Fig. 34d. The dashed-line lattice contains spot A and corresponds to the dark regions in Fig. 34a and light regions in Fig. 34c. The solid-line lattice corresponds to the diffraction pattern from the light regions in Fig. 34a and the dark regions in Fig. 34c. Indexing of these patterns revealed that they both correspond to the (110) plane of the reciprocal lattice of the fcc structure of stainless steel.

This agrees with the information found as a result of indexing the diffraction pattern in Fig. 30. Thus, both the light and dark regions in Fig. 34a and c are the same crystal structure and are oriented with the (110) plane of the fcc structure parallel to the surface of the micrographs. Furthermore, the two lattices are symmetrically related by reflection across their common (111) plane or by 180-deg rotation about their common (111) direction, as indicated by the dotted lines. Thus, the fine-banded structure in Fig. 34 satisfies all of the crystallographic criteria for the twinned fcc crystal described in Fig. 7.

A bright-field micrograph of the microstructure of 304 stainless steel, which was given a high-temperature anneal and deformed in tension in a hydrogen atmosphere, is shown in Fig. 35a. The dark bands at A and D have a distinctive crystallographic morphology similar to the deformation twins in Fig. 34. The diffraction pattern in Fig. 35b exhibits a relatively complex pattern of spots, which suggests there are two or more crystalline orientations or structures producing overlapping reciprocal lattice patterns. These patterns are sorted out by systematically photographing the same specimen area in dark field and correlating the images with the illuminating diffraction spots. This process is illustrated in Figs. 35c and d. Figure 35 c shows the dark-field image obtained by using the diffraction spot a in Fig. 35b for illumination. The bright parallel bands marked A' in Fig. 35c correspond to the dark bands marked A in Fig. 35a. These bands contribute to a reciprocal lattice pattern that contains spot a. The dark-field image (Fig. 35d), taken with the illumination from spot b (Fig. 35b), shows that the bright regions B' produce another reciprocal lattice pattern containing spot b. These results, with additional

dark field experiments, revealed reciprocal lattice patterns A and B in Fig. 35e, which correspond to two orientations of an hcp ϵ martensite phase.

Correlation of the traces of the bands at A and D in Fig. 35a with the crystallographic orientation of the γ matrix (near $[111]$) revealed that the bands are thin sheets lying on $\{111\}$ planes of the γ phase. The orientation relationships of the fcc γ and hcp ϵ phases are shown in Fig. 35f. The (0001) basal planes of the ϵ phase are parallel to the (111) planes of the γ phase; the $[2\bar{1}10]$ direction in the hcp lattice is parallel to the $[\bar{1}10]$ direction of the fcc lattice. The unit cell dimensions of the hcp martensite phase have an ideal close-packed c/a ratio of 1.63 giving an (0002) interplanar spacing identical to the (111) interplanar spacing of the γ phase. Thus, the crystallographic relationships of the two phases are identical to the relationship described for the faulted fcc structure in Fig. 10. The ϵ martensite phase might have been formed by multiple shear faulting on every other (111) plane of the γ phase facilitated by the low stacking fault energy of 304 stainless steel containing dissolved hydrogen.

The preceding examples of imperfection microstructures in 304 stainless steel are characteristic of fcc crystals with low stacking-fault energies. It should be emphasized that crystals having the same kind of structure and imperfections can have quite different microstructures, depending on the specific nature and behavior of the imperfections. For example, fcc crystals, such as aluminum, which have relatively high stacking-fault energies generally do not exhibit twin faults or martensitic structures. The structure of these fcc crystals can be interpreted in terms of their high stacking-fault energies.

Thus far the microstructures discussed have been those in which individual imperfections or groups of imperfections form the major features of the structure or act as sites for heterogeneous nucleation and growth of precipitation phases. Imperfections are also involved in homogeneous diffusional phase transformations. One of their major roles is to provide a means of structurally accommodating the new phase in the host matrix. This accommodation involves adjustments for internal elastic strains in the crystals produced by differences in specific volume and lattice mismatches at the interface of the two crystalline phases.

The specific mechanisms by which structural imperfections interact in diffusional solid state phase transformations are varied and depend on the structural relationships of the phases in a particular system. The following example of homogeneous precipitation of hafnium nitride in molybdenum by internal nitriding a Mo - 1 at.% Hf alloy⁶ solid solution illustrates one of the ways imperfections are involved.

The internal nitriding process is analogous to internal oxidation and proceeds by the diffusion-controlled advance of a nitriding front, which remains essentially parallel to the external surface. At the advancing nitriding front, the inward interstitial diffusion of nitrogen and the outward vacancy diffusion of alloyed hafnium continuously provide concentrations in excess of those corresponding to the solubility product of hafnium nitride in the molybdenum matrix. Repeated nucleation and growth of hafnium nitride particles result.

Growth of the hafnium nitride precipitates occurs only at the advancing nitriding front. The rate of advance of the front decreases with increasing depth below the surface. Consequently, the precipitates nucleated at greater

depth have more time to grow during passage of the front, thus there is an increase in particle size with increasing depth below the surface. The structure of the precipitates can be examined at various stages of growth in this transmission specimens cut from different depths in nitrided specimens.

Figures 36 and 37 are transmission electron micrographs of the internal microstructure approximately 0.005 in. below the surface of a 0.050-in.-thick nitrided specimen. These micrographs show matrix strain and displacement fringe contrast from peripheral coherency at small plate-like hafnium nitride precipitates. The platelets are less than $20 \text{ \AA}$ thick and from 100 to $500 \text{ \AA}$ in diameter. The diffraction pattern in Fig. 36 exhibits streaking in the $\langle 100 \rangle$ directions of the molybdenum matrix and is characteristic of thin plate-like particles oriented on $\{001\}$ planes of the molybdenum matrix, shown schematically in Fig. 38a. The displacement fringe contrast of the small precipitates is similar to the fault fringes in Figs. 11 and 13 and originates from the same diffraction conditions described for stacking fault contrast. In the case of faults produced by the shear displacement of the Shockley dislocations and by collapse of vacancy voids into intrinsic edge dislocation loops, the phase shift, $\alpha = 2\pi \mathbf{g} \cdot \mathbf{R}$, in the diffracted wave produced by the fault is always $2\pi/3$ because of its crystallographic geometry. The phase shift producing the fringe contrast of the precipitates depends on the magnitude of the molybdenum matrix displacement $\mathbf{R}_n$ normal to the platelets and thus may take different values, which affect only the intensity of the fringes.

Transmission micrographs of the precipitates at 0.015 and 0.025 in. below the surface are shown in Figs. 39 through 41. The particles shown cover a wide variation in size. The larger particles are circular platelets

approximately 20 to 60 Å thick and several thousand angstroms in diameter. The rectangular appearance (Figs. 39 and 40) is caused by their intersection with the top and bottom (111) surfaces of the molybdenum foil. The large precipitates exhibit strong displacement fringe contrast in Figs. 39 and 40 and compressive matrix strain contrast in the dark-field micrograph of Fig. 41 (dark contrast on the side of positive g vector) indicating that they still retain substantial peripheral coherency with the molybdenum matrix. Only two of the three particle orientations in Figs. 39 and 40 show displacement fringe contrast. The particles in the third orientation on (010) molybdenum matrix planes produce a $[010]$ peripheral displacement R_n , which is normal to the operating $[10\bar{1}]$ matrix g vector. Therefore, $\bar{g} \cdot R_n = 0$ and these particles are consequently out of contrast.

Diffraction patterns in regions containing the larger particles exhibited secondary spot patterns which, as illustrated in the dark field micrograph in Fig. 42, were produced by the hafnium nitride precipitates. Analysis of the secondary spot patterns together with dark-field observations revealed the crystallographic precipitate-matrix orientation relationship (Fig. 43). It is evident from this figure that the lattice mismatch for a fully coherent hafnium-nitride precipitate platelet results in a large positive misfit normal to the plane of the platelet and a small positive misfit in the plane.

The displacement fringe contrast changes abruptly across dislocation loops that appear to grow in the plane of the particles (Figs. 39 and 40). Within some of the loops at A, the intensity of the displacement fringes increases, while within other loops at B, the fringes are very weak and in some cases absent. The change in displacement fringe intensity within these loops indicates that the

magnitude of the peripheral coherency strain is changed by the growth of the loops. Thus, the nucleation and growth of these loops appear to be important in the growth and degree of coherency of the hafnium nitride particles.

Transmission micrographs (Figs. 44, 45, and 47) show the precipitate morphology near the nitriding front in a specimen that was partially nitrified to a depth of approximately 0.020 in. Figure 44 shows a region containing particles approximately 600 Å in diameter. These particles contain a small loop.

Several of the particles at P in Fig. 44 have grown to approximately 5000 Å in diameter, and the loop has grown in the plane of the particles. The intensity of the displacement fringes is generally stronger within the loop. The increase in fringe intensity indicates that the compressive peripheral coherency displacement normal to the plane of the precipitate is increased by growth of the loop. Thus, these loops appear to be extrinsic in nature. The precipitates, as viewed along the [001] matrix direction are shown in Fig. 45. The particles lying in the plane of the photograph can be seen to contain one or more loops. Both the precipitate and the loop images display a line of no contrast normal to the operating [020] g vector. This contrast is characteristic of extrinsic or intrinsic edge dislocation loops lying in the plane of the micrograph with Burgers vectors normal to the plane of the loop.

According to the previously discussed criteria for image formation (i.e., $g \cdot R = 0$) these loops should be invisible because in this case $\bar{g} \cdot R_n [020] \cdot [001] = 0$. However, the stress field around an edge dislocation has a component σ_{yy} , given by Eq. (6), which produces a lattice displacement R_p normal to the dislocation line and parallel to the extra half plane or, in this case, parallel to the plane of the loop. The sides of the loop where R_p is parallel

to the operating $[020]$ reflection are in maximum contrast and the sides where R_p is perpendicular to the $[020]$ direction are out of contrast.

The loops seen in Figs. 44 and 45 appear to be coherent ledges that nucleate and grow on the surface of the particles and to constitute the mechanism of thickening, which is illustrated in Fig. 46. The growth of these extrinsic coherent ledges causes the compressive peripheral coherency strain in the matrix to increase and to produce an increase in displacement fringe intensity. The ledge in Fig. 46 has a height of one hafnium nitride unit cell. The magnitude of the associated normal displacement vector is $1.37 \text{ \AA}$. The magnitude of the displacement vector of the loops in Figs. 44 and 45 is unknown. These loops appear to be the first to form on the particles. They never grow completely to the periphery of the particles and were seen as the outermost loop on all of the large particles observed.

As shown at B in Figs. 44 and 47, several of the precipitates at this stage of growth contain a second loop inside the first loop. Within this second loop, the displacement fringes are extremely weak or totally absent. The disappearance of the displacement fringes within the second loop suggests that this is an intrinsic dislocation loop formed within the hafnium nitride particles by the coalescence of vacancies (Fig. 48). As shown in Fig. 48, growth of this loop relaxes the peripheral coherency strain so that within the loop the peripheral displacement R_p is small and the displacement fringe intensity is weak. Precipitates containing the second loop viewed along the $\langle 001 \rangle$ matrix direction are shown in Fig. 49. The irregular edge of a precipitate lying in the plane of the photograph can be seen at P, the extrinsic ledge loop at A, and the second loop at B. The edge view of these particles at J shows matrix strain contrast

only near the ends of the particles, as would be the expected result from growth of the intrinsic loop in Fig. 48. Thus, both the displacement fringe and matrix strain contrast are consistent with an intrinsic second loop.

Assuming that the peripheral lattice mismatch is compensated entirely by the compressive strain in the molybdenum matrix and that the matrix strain is completely relaxed within the intrinsic loop, the thickness of the hafnium nitride precipitate, Δt , can be estimated from the relation

$$\Delta t \frac{a_2 - a_1}{a_2} - a_2 = 0, \quad (18)$$

where a_1 and a_2 are the $\langle 001 \rangle$ unit cell dimensions of molybdenum and hafnium nitride, respectively. Using the values of a_1 and a_2 in Fig. 43 gives $\Delta t \approx 15 \text{ \AA}$, or three to four unit cells thick, which is in agreement with the $20 \text{ \AA}$ thickness estimated from the transmission micrographs.

A more advanced stage of particle growth is shown in Fig. 50, where it can be seen that several more loops at C, D, and E have formed concentrically within the first two loops. The consecutive growth of these new loops has restored the displacement fringes that were removed by the growth of the intrinsic loop B. Within these loops, the growth of another loop at F has removed the fringes. Loop F is then followed by loop G, which again restores the displacement fringe contrast.

The growth sequence of three fringe-restoring loops between two fringe-removing loops was observed on all of the large precipitates. Occasionally, a sequence of four fringe-restoring loops between two fringe-removing loops was observed. The fringe-restoring loops C, D, and E appear to be coherent ledges similar to loop A. The consecutive nucleation and growth of these ledges within

the intrinsic loop B thickens the precipitate and increases the periphery coherency strain in the matrix, which increases the displacement fringe intensity. Further thickening of the particle requires that this peripheral coherency strain be relaxed by the nucleation and growth of another intrinsic loop F. The thickening sequence of three extrinsic ledges followed by an intrinsic loop then repeats, as shown on the large particle at R in Fig. 40, where the loop growth sequence is repeated several times. The formation of three to four extrinsic ledges between two intrinsic loops indicates that the particle ledges are one hafnium nitride unit cell high. An increase of three to four hafnium nitride unit cells in particle thickness produces a peripheral coherency lattice displacement of from 4.11 to 5.48 Å, which, averages approximately the displacement relaxation produced by an intrinsic loop with Burger's vector of 4.57 Å.

These observations indicate that the hafnium nitride precipitates grow in the molybdenum matrix in a manner such that the precipitate-matrix interface is always fully coherent (Fig. 51). The particles are shown on edge at several stages of growth. Initially, the hafnium nitride particles probably develop at the nitride front by hafnium-nitrogen clustering in the molybdenum matrix. Small coherent hafnium nitride platelets one to two unit cells thick grow homogeneously from these clusters on {001} planes of the matrix. When they reach a thickness of approximately 15 to 20 Å and 200 to 300 Å in diameter, further thickening occurs by the nucleation and growth of a coherent ledge that appears as a dislocation loop on the surface of the particle. The ledge grows in diameter with the coherent diametral growth of the particle to 4000 to 5000 Å. At this stage, a second intrinsic loop forms within the particle and relaxes the peripheral

coherency strain. With continued diametral growth of the particle, thickening occurs by the repeated sequence of concentric growth of three to four extrinsic ledge loops and an intrinsic loop. The large particles developed by this growth process retain a significant amount of peripheral coherency strain. When the particles get very large, the ledges nucleate at more than one place on the particle surface and the loop geometry becomes very complex, as at S in Figs. 40 and 51. Near the outer edge of these large particles the ledges appear to coalesce into steps, as shown at T in Fig. 52.

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Table I

Spot	Smm	$d, \text{\AA}^a$	(hkl)	$d, \text{\AA}^b$
A	9.7	2.050	(111)	2.052
B	11.1	1.790	(200)	1.781
C	9.75	2.045	(220)	1.256
D	16.0	1.241	(113)	1.071
E	18.7	1.062	(222)	1.027
F	19.5	1.021		

Interplanar spacings calculated using Equations (15) and (16) for diffraction spots in Figure 30b.

^aEq. (15)

^bEq. (16)

FIGURE CAPTIONS

- Fig. 1. Point imperfections in crystalline materials: (a) vacancies, (b) interstitials, and (c) vacancy-interstitial pairs (Frankel defects).
- Fig. 2. Schematic illustration of an edge dislocation in a simple cubic crystal.
- Fig. 3. End view of an edge dislocation showing Burgers circuit.
- Fig. 4. Glide motion of edge dislocation showing atom positions (a) before and (b) after a unit glide of dislocation to the right.
- Fig. 5. Etched pits and boundaries in deformed BeO. Courtesy of S. DiGiallonardo and R. Vandervoort, LLL.
- Fig. 6. Schematic illustration of the dissociation of an $\frac{a}{2} [110]$ dislocation at (a) into two $\frac{a}{6} [112]$ partial dislocations at (b).
- Fig. 7. Schematic illustration of a twin in an fcc lattice.
- Fig. 8. Atomic stacking sequences (a) $\{111\}$ planes in fcc crystals and (b) (0001) planes in hcp crystals.
- Fig. 9. Surface appearance of annealing twins in (a) 304 stainless steel and (b) deformation twins in zinc.
- Fig. 10. Schematic illustration of the formation of a stacking fault in an fcc lattice by dissociation of an $\frac{a}{2} [\bar{1}10]$ dislocation. (a) Plan view of (111) showing atomic movements; (b) change in (111) plane stacking sequence as the result of a fault.
- Fig. 11. Transmission electron micrograph of a dissociated dislocation and stacking fault in 304 stainless steel.
- Fig. 12. Schematic illustration of vacancy clustering and intrinsic loop formation. (a) Formation of void by coalescence of vacancies; (b) collapse of void into intrinsic dislocation loop.

- Fig. 13.** Transmission micrograph of intrinsic Frenkel loops in quenched aluminum. Courtesy of Prof. Jack Washburn, UC, Berkeley.
- Fig. 14.** Transmission micrograph of stacking fault tetrahedra in quenched gold. Courtesy of Prof. Jack Washburn, UC, Berkeley.
- Fig. 15.** Schematic illustration of an extrinsic (interstitial) platelet.
- Fig. 16.** Replica micrograph of H_2 filled pores in irradiated Lill. Courtesy of Dr. Herman Leider, and Sam DiGiallonardo, LLL.
- Fig. 17.** Transmission micrograph of dislocation structure in deformed Fe-Ni. Courtesy of Sam DiGiallonardo, LLL.
- Fig. 18.** Transmission micrograph of equilibrium substructure configuration of dislocations in a tungsten-rhenium alloy. Courtesy of Dr. Richard Vandervoort, and Sam DiGiallonardo, LLL.
- Fig. 19.** Interaction force between two parallel edge dislocations.
- Fig. 20.** Equilibrium arrangements of parallel edge dislocations.
- Fig. 21.** Climb of an edge dislocation showing dislocation (a) before and (b) after unit climb by absorption and annihilation of a vacancy.
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- Fig. 23.** Transmission micrograph of grain boundary precipitation of $Cr_{23}C_6$ particles in 310 stainless steel.
- Fig. 24.** Transmission micrograph showing pileup of glide dislocations on a twin boundary in 21Cr-6Ni-9Mn stainless steel. Courtesy of Dr. R. Vandervoort and Sam DiGiallonardo, LLL.
- Fig. 25.** Schematic diagrams of transmission image formation. (a) Direct lattice resolution, (b) bright-field diffraction contrast, and (c) dark-field contrast.

- Fig. 26. Bright-field transmission micrographs of polycrystalline niobium showing effect of tilting the specimen in the microscope.
(a) Before tilting; (b) after 5-deg tilt.
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- Fig. 28. Geometry of the formation of an electron diffraction pattern.
- Fig. 29. Schematic diagram of the relationship of the reciprocal and crystal lattices.
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- Fig. 34. Transmission electron-microscopy analysis of twins in 304 stainless steel: (a) bright-field image, (b) dark-field image, (c and d) diffraction patterns.
- Fig. 35. Transmission-electron microscopy analysis of martensite in 304 stainless steel: (a) bright-field image, (b) diffraction pattern, (c) dark-field image using spot a, (d) dark-field image using spot b, (e) diagram showing reciprocal lattices of two orientations (A and B) of the ϵ phase, and (f) schematic illustration of crystallographic relationship of the ϵ and p phases.
- Fig. 36. Transmission micrograph showing matrix strain contrast near coherent hafnium nitride precipitates at a depth of 0.005 in.
- Fig. 37. Transmission micrograph showing displacement fringe contrast on hafnium nitride precipitates at a depth of 0.005 in.

- Fig. 38.** Schematic illustration of morphology of coherent hafnium nitride precipitates.
- Fig. 39.** Transmission micrograph of hafnium nitride precipitates at a depth of 0.015 in.
- Fig. 40.** Transmission micrograph of hafnium nitride precipitates at a depth of 0.025 in.
- Fig. 41.** Transmission micrographs of precipitate contrast of hafnium nitride particles at a depth of 0.025 in. (a) Dark-field image; (b) bright-field image.
- Fig. 42.** Dark- and bright-field transmission micrograph showing diffraction by hafnium nitride precipitates at a depth of 0.025 in.
- Fig. 43.** Schematic illustration of crystallographic precipitate-matrix orientation relationship.
- Fig. 44.** Transmission micrograph showing loops on hafnium nitride precipitates near the nitriding front at a depth of 0.020 in.
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- Fig. 50.** Transmission micrograph showing loop growth sequences on large hafnium nitride precipitates at a depth of 0.025 in.

Fig. 51. Schematic illustration of thickening and coherency strain relaxation mechanisms during growth of hafnium nitride particles.

Fig. 52. Transmission micrograph of hafnium nitride precipitates at a depth of 0.025 in. showing steps on particles.

Mitchell - Fig. 1

Mitchell - Fig. 2

Mitchell - Fig. 3

Mitchell - Fig. 4

Mitchell - Fig. 5

Mitchell - Fig. 6

Mitchell - Fig. 7

(a)

(b)

(a)

(b)

(b)

Mitchell - Fig. 11

Mitchell - Fig. 12

Mitchell - Fig. 13

Mitchell - Fig. 14

Mitchell - Fig. 15

Mitchell - Fig. 16

Mitchell - Fig. 17

Mitchell - Fig. 18

Mitchell - Fig. 19

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┐
┐
┐
(a)

┐
┐ T
┐ T
┐ T
T
(b)

(a)

(b)

Mitchell - Fig. 22

Mitchell - Fig. 23

Mitchell - Fig. 24

(a)

Mitchell - Fig. 25

(b)

(c)

Mitchell - Fig. 25

(a)

(b)

Mitchell - Fig. 27

Mitchell - Fig. 28

Mitchell - Fig. 29

(a)

(b)

Mitchell - Fig. 32

Mitchell - Fig. 33

(a)

(c)

(b)

(d)

(a)

(b)

(c)

(d)

(e)

(f)

Mitchell - Fig. 36

Mitchell - Fig. 37

Mitchell - Fig. 38

Mitchell - Fig. 39

Mitchell - Fig. 40

(a)

(b)

(a)

(b)

Mitchell - Fig. 43

Mitchell - Fig. 44

Mitchell - Fig. 45

$(010) \text{ Mo}$

- Mo
- Hf
- N

Mitchell - Fig. 47

- Mo
- Hf
- N

Mitchell - Fig. 49

Mitchell - Fig. 50

Mitchell - Fig. 51

Mitchell - Fig. 52