

# Structure and Properties of Electrodeposits

By R. Weil

The structure of electrodeposits determines their properties and performance. For example, adhesion, corrosion and wear resistance, hardness, internal stress, strength, brightness, electrical conductivity, magnetic properties, and leveling are all affected by structure. The intent of this report is to teach technical personnel who have no training in material science to recognize the various structures that electrodeposits exhibit and to understand how and why they form.

**T**he arrangement of atoms determines the structure of electrodeposits. Most electroplated metals are crystalline and the atoms are arranged in a regular three-dimensional pattern. The smallest atomic arrangement is called a unit cell. Copper, nickel, silver, gold, and the platinum-group metals have the most common unit cell—face-centered cubic (fcc), which is shown in the model, Fig. 1A. Iron and chromium have a body-centered cubic (bcc) structure. The hexagonal metals are cadmium, cobalt, and zinc.

Unit cells are the building blocks of larger, three-dimensional structures called crystals or grains. All unit cells within each grain are oriented the same way. In different grains of the same material only the cell orientation

differs. To designate orientation, a system for naming planes and directions has been established. The black balls in Fig. 1 D make up the front face of the unit cell, and these faces are referred to as  $\{100\}$  planes. The atom planes, which cut diagonally across a face, as shown by the black balls in Fig. 1 C, are designated as  $\{110\}$  planes. The cube-diagonal planes, one of which is represented by the black balls in Fig. 1 B, are called  $\{111\}$  planes. Several balls were removed from the figures to show these planes. There are many other crystal planes, but the three in the Fig. 1 models are most important.

The direction of crystals corresponds to atom rows. The cube edges are said to be in the  $\langle 100 \rangle$  direction (Fig. 2, left). In cubic crystals, a direction has the same digits as the cube plane perpendicular to it. For example, a  $\langle 100 \rangle$  cube edge is perpendicular to a  $\{100\}$  cube face.

Four methods are used to determine the structure of electrodeposits. Widely used to ascertain the spacing of atoms in a crystal and the orientation of unit cells are X-ray and electron diffraction. X-ray wavelengths are of the same order as the spacing of atoms. The wavelengths of electrons are shorter and therefore capable of resolving the details of atomic dimensions.

Transmission electron microscopy (TEM), together with electron diffraction, is the only way to measure the small grain size of deposits. Certain crystal defects that affect properties can also be observed by TEM.

Scanning electron microscopy (SEM) is used to observe surface morphology. Hills and valleys are completely in focus, even on rough surfaces. Although grain boundaries are usually valleys easily seen by SEM, electrodeposited surfaces exhibit other similar features often mistaken for grain boundaries. SEM should therefore not be used to measure the grain size of electrodeposits. Optical microscopy is the fourth method and is used to observe large structures.

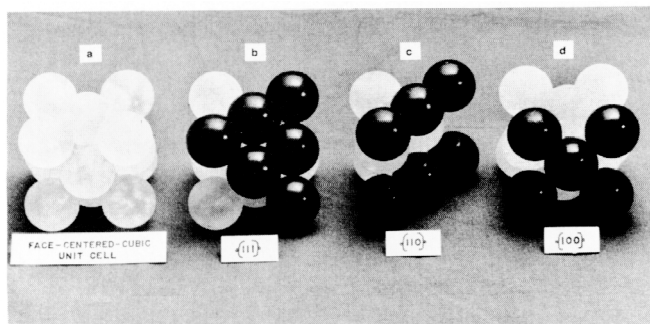


Fig. 1—Models of fcc unit cells. Black balls represent  $\{111\}$ ,  $\{110\}$ , and  $\{100\}$  crystal planes.

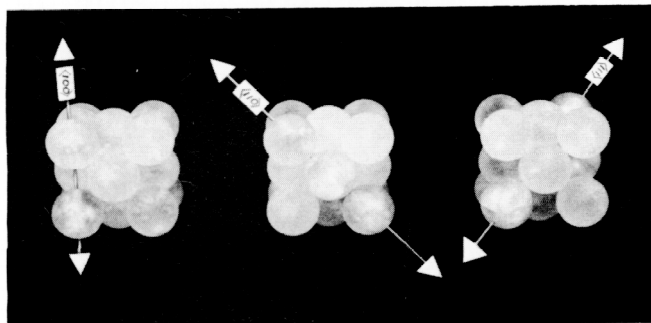


Fig. 2—Models showing (1-r)  $\langle 100 \rangle$ ,  $\langle 110 \rangle$ , and  $\langle 111 \rangle$  crystal directions.

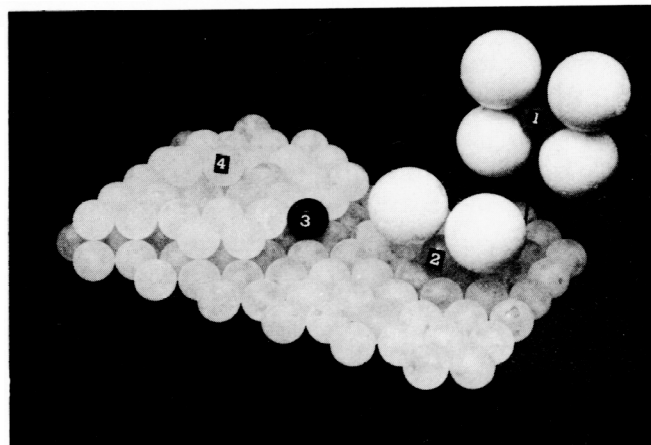


Fig. 3—Model showing incorporation of a metal ion into a deposit.

## Structure Development

Figure 3 shows how the atoms in a single grain become arranged. Ball No. 1 represents a metal ion near the workpiece (cathode) surrounded by ligands, which commonly are water molecules (the larger white balls). Ball No. 2 represents the next step in the development of the electrodeposit structure. The ion has picked up electrons and become an atom, which eventually will attach at a suitable location on the existing crystal arrangement. Such a place, called a kink site, is the end of an incomplete row of atoms and is exemplified by Ball No. 3. Ions can also wander in the plating solution until they are opposite a kink site and then land there directly. Atoms may encounter other atoms before finding a kink site. In this case, they start a new layer of atoms (Ball No. 4). If atoms meet and start a three-dimensional array that does not match the atoms beneath, a new grain is formed.

At the start of deposition, atoms may become attached to kink sites on the surface of the substrate. If this occurs, the atomic arrangement of the coating will be the same as that of the substrate, and the deposit is said to be epitaxial. A certain crystal plane and a direction of the deposit are parallel to a plane and a direction of the substrate. The planes and directions often have the same indices, but this is not a necessary condition for epitaxy. The intimate contact associated with epitaxial deposition usually provides good adhesion.

The metal atoms in the electrodeposit generally differ in size from those in the substrate. For example, electroplated nickel atoms are smaller than those of a copper substrate (Fig. 4). To fit in the valleys between the larger substrate

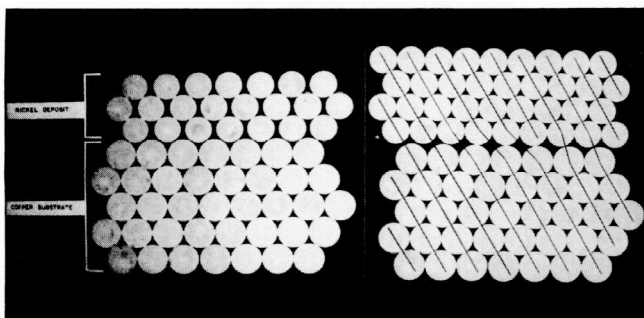
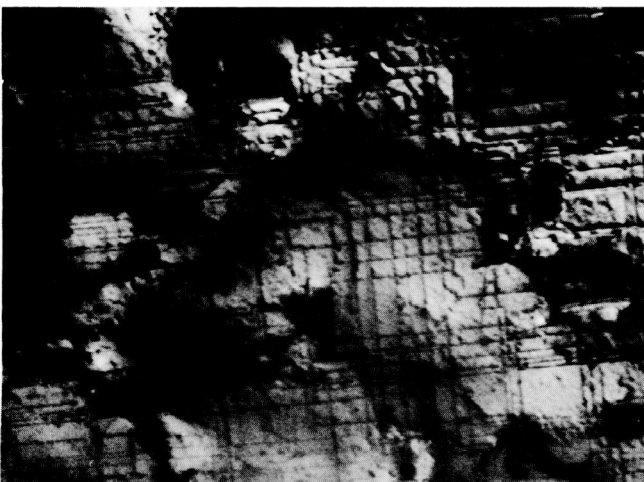


Fig. 4—Models of misfit and resulting dislocation in epitaxial deposition.



atoms, nickel atoms in the first layer of the deposit (Fig. 4, left) are spread apart. This is often the cause of high so-called misfit stress in thin epitaxial deposits. As the deposit becomes thicker, the atoms assume their own interatomic spacing (Fig. 4, right), and the stress is relieved. Then to compensate for the difference in interatomic spacing, an extra row of atoms has to be introduced periodically. In Fig. 4 (right) lines have been drawn through the rows of atoms in the deposit. The sixth line from the left does not continue into the substrate; the end of this extra row (in three dimensions) is a crystal defect called a dislocation. Dislocations play a dominant role in the determination of the mechanical properties and can be observed by TEM. The dark lines in Fig. 5 are dislocations.

Addition agents, impurities, and other species can affect the deposit structure. Side reactions during plating (e.g., hydrogen evolution) also can produce foreign species that alter the structure by blocking kink sites (Fig. 6, left). Thus, the bottom layer is prevented from spreading and the layers above can only spread to the edge. This leads to bunching (i.e., the development of multilayer shapes). An example of bunching is shown in Fig. 6 (right).

When such multilayer shapes are only slightly disoriented with respect to their neighbors, they are called crystallite and tend to have inclined sidewalls. When the inclinations are large, the crystallite are shaped like pyramids.

Figure 7 shows three-dimensional gold crystallites observed by TEM. They were epitaxially deposited on one grain of copper which was subsequently dissolved in nitric acid. The crystallite are the dark areas supported by an invisible carbon film. The sides of the crystallite average about 20 nm in length and consist of approximately 100 atoms. Many crystallite are seen joined to their neighbors but individual ones can still be discerned.

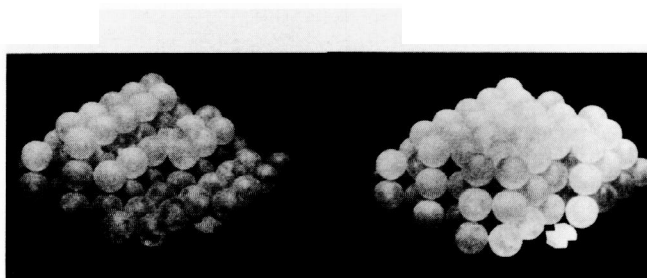


Fig. 6—Models of foreign molecule blocking kink site (left) and bunching (right). Two hexagons represent benzene rings of foreign molecule.

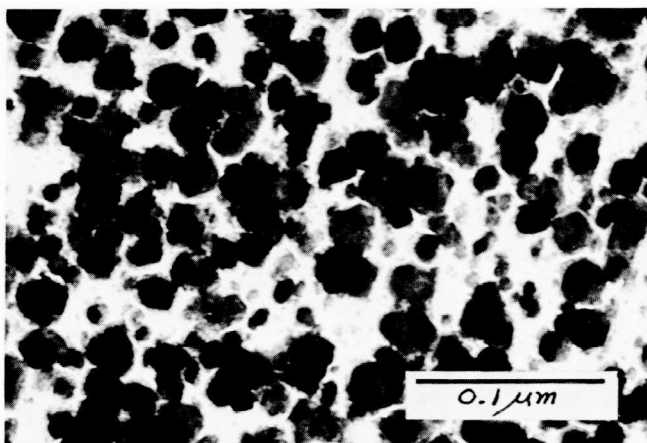


Fig. 7—TEM photo of three-dimensional gold crystallites.

Figure 8 illustrates the curvature caused by the coalescence of discrete, three-dimensional crystallite with inclined sides. If the substrate does not permit the layers of such a deposit to curve upwards, they are stressed in tension. Thus, crystallite coalescence can also cause internal stress within one grain of a deposit, in addition to that caused by the misfit.

The curvature due to the coalescence of crystallite with inclined sides can be accommodated when some vertical atom planes stop growing. In Fig. 9, the horizontal atom planes are curved because the middle vertical plane ends in the center. The end row of this vertical plane is a dislocation. Electroplated deposits usually contain more dislocations than metals produced by other means. Also, most dislocations in electrodeposits have a more complicated configuration than just the end row of an extra plane of atoms. The crystallite in front and back of those depicted in Fig. 8 can cause a perpendicular curvature that results in twisting of the extra atom plane. Therefore, the dislocation is not just a straight row of atoms.

The large number of dislocations present in electrodeposits can be seen by TEM (Fig. 10). Each little dark line is a dislocation. The spacing of the dislocations is

approximately the same as the size of the three-dimensional crystallite shown in Fig. 7. Therefore, these dislocations probably developed because of crystallite coalescence. The dislocations shown in Fig. 10 are much shorter than those caused by misfit and depicted in Fig. 5. The short dislocations extend from the top to the 'bottom of the specimen, which had to be very thin to be transparent to electrons. The misfit dislocations in Fig. 5, on the other hand, lay between the copper substrate and nickel deposit, i.e., essentially parallel to the sample surface. The misfit dislocations are straight because they are the end row of an extra plane of atoms and were not subject to twisting.

Another crystal defect frequently observed in electrodeposits is a twin. Twins can form when foreign species cause the atoms of the plated metal to be misplaced from their normal locations. In Fig. 11, a foreign atom has prevented the atoms from becoming attached to the atom plane. The misplacement is not large enough to accommodate an extra row of metal atoms. Figure 12 shows how such a misplacement leads to twinning. In Fig. 12A, four atom planes of the {111} type are shown in the normal position for an fcc crystal structure. Foreign species can cause the top plane to be misplaced as shown in Fig. 12B; the black balls emphasize this shift. As illustrated in Fig. 12C, another layer was also misplaced. Then, two layers were laid down in the normal position like the three on the

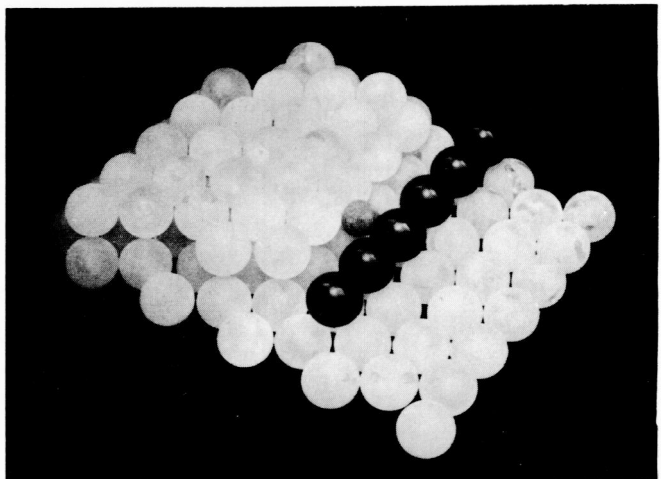
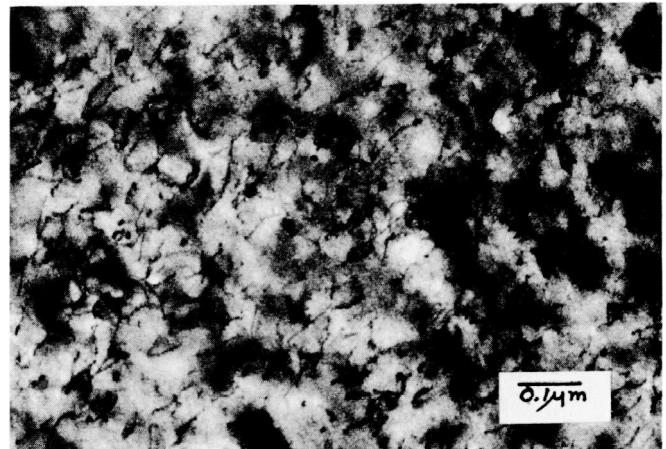
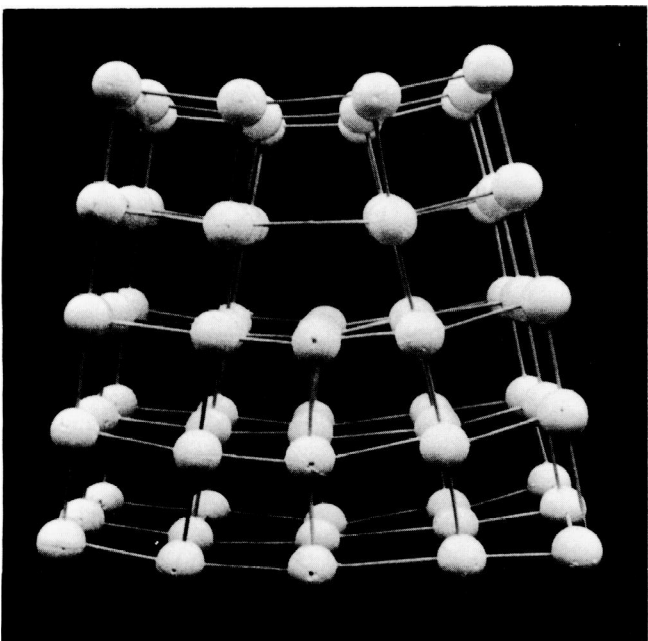
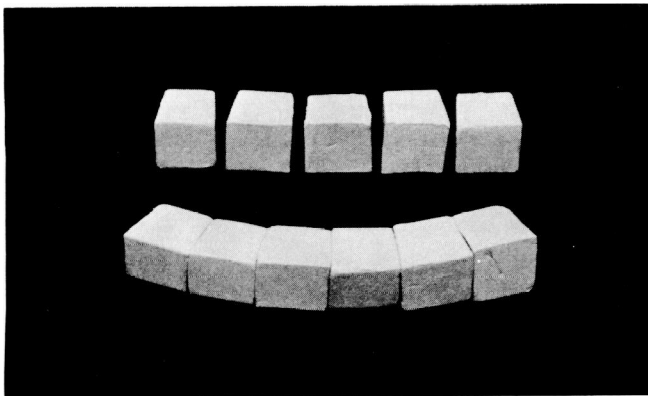


Fig. 11 —Model of misplacement due to foreign species. Little gray ball represents foreign atom, black balls, row of deposited metal atoms.

bottom. If mirrors were placed at the third and fifth layers (Fig. 12 D), the structure above a mirror would be the mirror image of that below it. The atom layers between the mirrors represent the twin. Actually, twins consist of many more atom planes than depicted in Fig. 12.

Figure 13 is a TEM photo of twins in an electroless copper deposit. The light bands in the dark background are the twins. The perfectly parallel boundaries of the twins correspond to the location of the mirrors in Fig. 12C. Twins increase deposit strength and hardness and play a role in the crystal orientation changes that lead to a loss of epitaxy.

### Grain Orientation

In electrodeposits, the grains tend to grow perpendicular to the surface. Growth parallel to the surface can only occur when not restricted by other grains. The growth of three grains is depicted in Fig. 14. In electrodeposits, atoms with a particular growth direction frequently grow faster than others. For example, in a plain Watts bath, grains with a  $\langle 100 \rangle$  direction perpendicular to the surface grow the fastest. Grains with different directions can be the ones that exhibit fast growth depending on the current density, pH, and composition of the plating solution. In some cases, all grains regardless of orientation grow at about the same rate.

The grains that grow the fastest can spread sideways because they are not impeded by the others. The faster-growing grains thus cover those less favorably oriented

(Fig. 14). However, the faster-growing grains can only spread sideways until they meet others of the same orientation. The deposit thus consists mostly of grains having the fastest-growing direction perpendicular to the surface. In Fig. 14, grains with the  $\langle 100 \rangle$  growth direction tend to make up most of the deposit surface, and the coating is said to have a preferred orientation.

Figure 15 is a surface view of a  $\langle 100 \rangle$  preferentially oriented deposit. A cube edge of the unit cells is shown perpendicular to the surface of most grains. However, the unit cells are shown randomly turned about a cube edge in different grains. This type of preferred orientation, which usually occurs in electrodeposits, is called a fiber axis. It is also frequently found in wires and fibers. Fiber axes are of particular importance in the electrodeposition of magnetic materials.

The fiber axis is usually found by using X-rays to determine which crystal plane is preferentially parallel to the surface. Then, as previously discussed, the direction with the same set of indices is the fiber axis for cubic crystals. Most investigators assume the crystal planes that most strongly diffract (i.e., coherently reflect) X-rays are the ones preferentially parallel to the surface. In the majority of cases, this assumption is correct. However, not all crystal planes diffract X-rays, and there is no reason such planes cannot be preferentially parallel to the deposit surface.

Because planes that do not diffract X-rays are preferentially parallel to the surface, sometimes the fiber axis is incorrectly reported. For example, a  $\langle 200 \rangle$  fiber axis is often reported in the literature because the  $\{100\}$  planes of cubic crystals do not diffract X-rays. However, if the  $\{200\}$  planes most strongly diffract X-rays, the  $\{100\}$

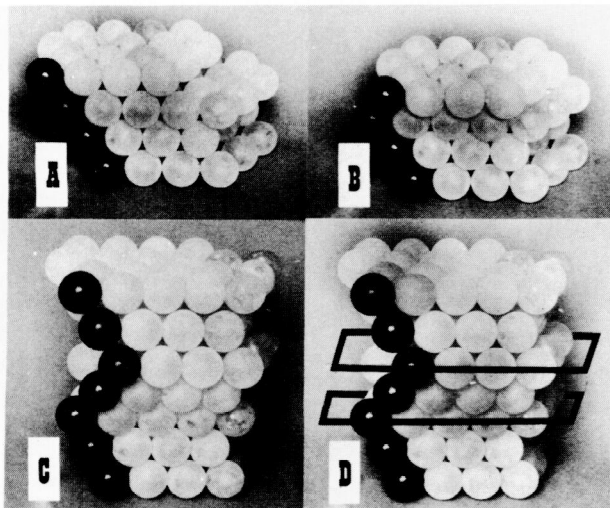


Fig. 12—Models of stages in formation of twin.

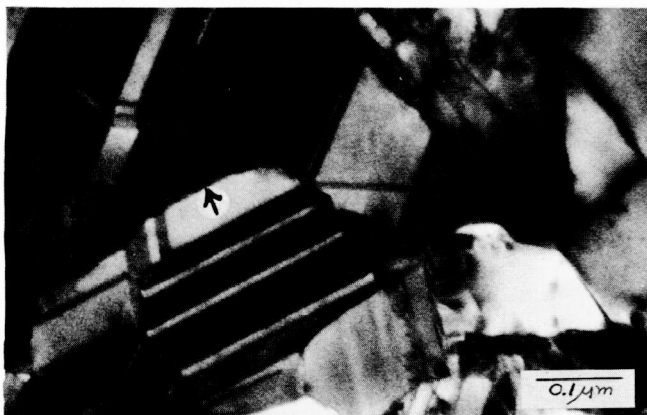


Fig. 13—TEM photo of twins in electroless copper.

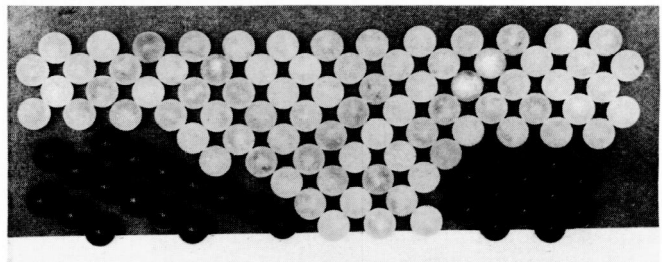


Fig. 14—Model of grain growth. Black balls on left are atoms growing in  $\langle 111 \rangle$  direction; white balls on right,  $\langle 110 \rangle$ .

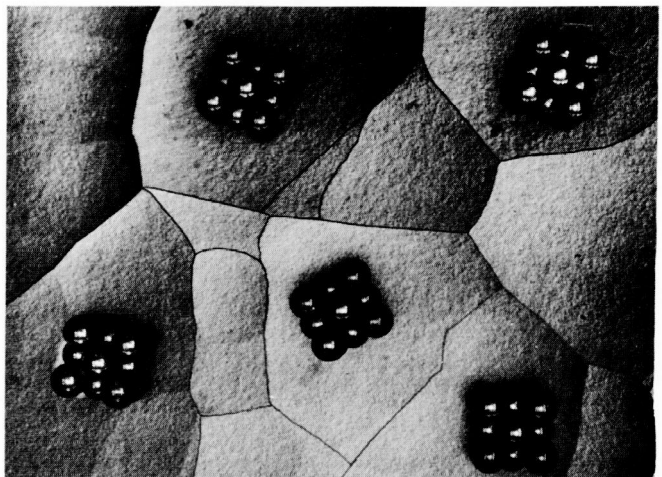


Fig. 15—Model of fiber axis.

planes, which are parallel to them, are also preferentially parallel to the surface. Because  $\{100\}$  planes have lower indices, a  $\langle 100 \rangle$  fiber axis should be reported, not a  $\langle 200 \rangle$ .

Another example of an incorrectly reported fiber axis is that of a deposit with a  $\langle 231 \rangle$  preferred orientation. The  $\{231\}$  planes of cubic crystals do not diffract X-rays. In this case, the  $\{111\}$  planes diffracted X-rays most strongly. The fiber axis was therefore incorrectly reported as  $\langle 111 \rangle$ .

When the deposit has a preferred orientation, the grains tend to be much longer than wide. The reason, as already discussed, is that they can only spread sideways until they meet others of the same orientation. Growth therefore has to be primarily into the plating solution. Consequently, the grains tend to have a columnar shape (Fig. 16).

### Foreign Substances

Foreign substances (e.g., addition agents) in the plating solution tend to limit the size of grains. Therefore, large grains are not usually observed in deposits plated in solutions containing growth-inhibiting substances. The cross sections of such deposits often exhibit a banded structure. Alternate light and dark layers parallel to the surface are brought out by etching. In Fig. 17, a cross section of a bright nickel deposit, an acid etchant preferentially attacked the dark layers. Differentiation of the layers resulted from variations in the amount of codeposited sulfur, which came from the addition agents. Periodic variations in the chemical composition, particularly in alloy deposits, and in grain size can result in the banded structure.

The surface structure of electrodeposits determines the brightness, which is an important property for decorative purposes. For a deposit to be specularly bright, the protrusions and depressions must not vary from the surface plane by more than the wavelength of visible light (about  $1\ \mu\text{m}$ ;  $40\ \mu\text{in.}$ ). The surface of a dull deposit (Fig. 18, left) has a roughness that far exceeds this value. The dull deposit consists of the ends of relatively large columnar grains that are often dome or pyramid shaped. The grain boundaries are deep depressions and there is essentially no planar area that can reflect light. Figure 18 (right) shows the surface structure of a semibright deposit. The grain size is not significantly different from that of the deposit on the left. However, the grain surfaces are much flatter and therefore more capable of reflecting light.

The surface of a bright nickel deposit is shown in Fig. 19 (left). Although this surface is by no means atomically smooth, it does not have any protrusions or depressions

larger than the wavelength of light and therefore is specularly bright. For grain boundaries not to be depressed deeper than the wavelength of light, the grains must be very small. However, a small grain size alone does not guarantee brightness. The surface shown in Fig. 19 (right) also has very small grains but the deposit has a hazy appearance as a result of the readily recognizable crevices. Because the crevices constitute only a relatively small fraction of the surface area, the remainder of which is flat, the deposit is neither really dull nor specularly bright.

Sometimes, crevices completely surround a group of small grains, which then resemble rounded mounds. Such deposits, although fine grained, are dull. The crevices surrounding groups of fine grains have been mistaken for grain boundaries. Such a mistake can be made easily when measuring grain size using a scanning electron microscope, with which it is impossible to obtain an electron diffraction pattern. To accurately determine the grain size of an electrodeposit that does not exhibit characteristic crystalline features, TEM should be used to obtain an electron diffraction pattern of the area thought to be one grain. If the area yields a single-crystal electron diffraction pattern, it is one grain. The grain size can then be determined with certainty.

### Mechanical Properties

The structural aspects discussed earlier explain why electrodeposits have certain properties. When a deposit is elastically deformed, the distance between the atoms

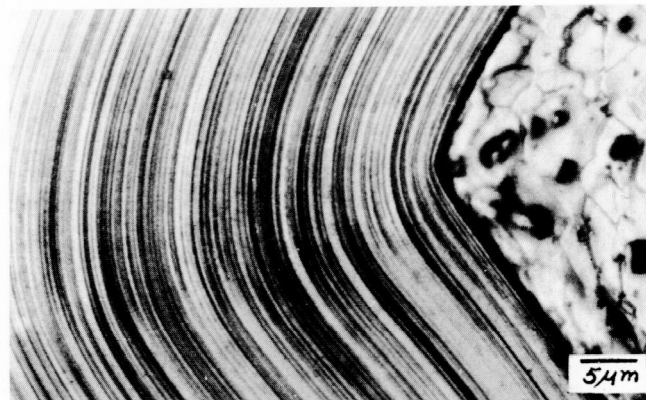


Fig. 17—Optical micrograph of cross section of nickel deposit showing banded structure.



Fig. 16—Optical micrograph of cross section of copper deposit.

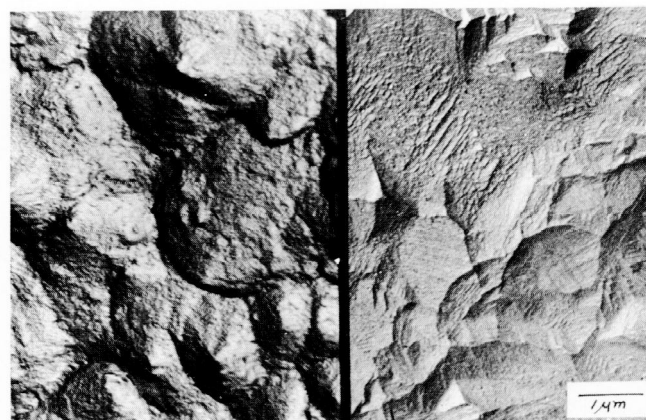


Fig. 18—TEM photos of replicas of dull nickel (left) and semibright deposit (right).



changes. However, the atoms do not change their positions relative to each other. Therefore, when the applied loads are removed, the atoms return to their original positions and no change in shape occurs. When a piece is plastically deformed, the atoms move relative to one another.

The main mechanism of plastic deformation in crystalline materials is slip. Atom planes slide over each other like cards in a deck. In fcc metals, the {111} planes are the ones that slide. However, a whole atom plane does not slide at once but moves one atom row at a time. This movement takes place by means of the dislocations previously discussed.

Figure 20 illustrates slip by means of dislocation motion. Two dislocations are indicated by arrows in Fig. 20A. They are the end rows of extra planes of atoms (Fig. 9). In Fig. 20, the large arrows represent the applied loads, under which the upper part of the atom plane moves to the right and the lower part to the left. In Fig. 20B, the dislocations at the boundary between the upper and lower parts have moved one atomic distance to the right because the lower part of the vertical atom plane has been positioned under the extra plane, making it a whole plane. Now the top part has become the extra atom plane. The dislocations have thus caused the top part to slip over the bottom part by the distance of one atom, while the atoms themselves have moved very little. In Fig. 20C, one dislocation has moved to the edge of the crystal. In Fig. 20D, a second dislocation has moved to the edge. Thus, each time a dislocation moves through a crystal, a permanent displacement takes place

(i.e., plastic deformation has occurred). Under the action of an applied plastic load, new dislocations are constantly being created. Therefore, there are always dislocations that can move through the crystals and cause more plastic deformation.

A second mechanism of plastic deformation observed in thin electrodeposits is twinning, in which the applied loads cause the atoms to move (Fig. 12). Dislocations are also involved in plastic deformation that occurs by twinning.

Because plastic deformation occurs by the movement of dislocations, the higher the stress required to move them, the greater are the yield strength and hardness. These two properties are a measure of the resistance of a material to plastic deformation. Anything that makes it more difficult for dislocations to move increases the yield strength and hardness. Foreign atoms or molecules in electrodeposits interfere with dislocation motion and, as previously discussed, can also cause twinning. The boundaries of grains and twins are obstacles to dislocation motion. The dislocations that develop due to crystallite coalescence generally cannot move easily and therefore impede the movement of others. Because electrodeposited metals contain more structural features that make dislocation motion difficult, they are usually stronger and harder than the same metals produced by other means.

If dislocations cannot move, the applied loads cause the part to fracture. Therefore, electrodeposit ductility, which is the degree of plastic deformation that can occur before fracture, is often lower than that of metals produced by other methods. Often, electrodeposits only appear to be brittle because the plastic deformation, although quite extensive, is limited only to a very small region of the tensile-test specimen.

It should be pointed out that while the structure of electrodeposits may appear to be well understood, further elucidation is needed. AESF-funded research must be credited for some of the advances to date.

#### Acknowledgments

The author is grateful to L. Gee, F. Chiang, and M. Parente for assisting in construction of the models, which were photographed by L. Gardella. Thanks are also due the members of the AESF Project 62/69 Committee for making valuable suggestions. This important work is continuing under AESF Research Project 69.

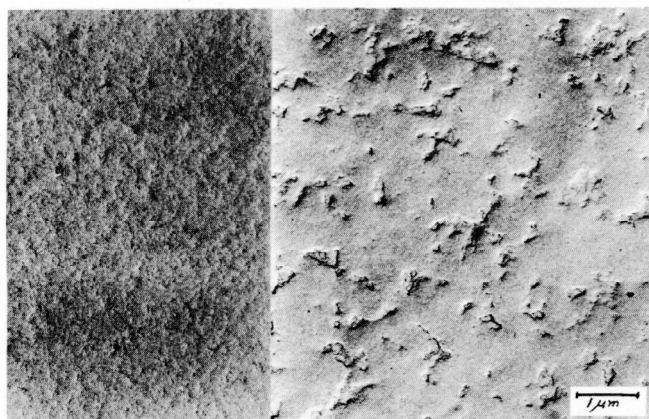


Fig. 19—TEM photos of replicas of bright nickel (left) and hazy bright deposit (right).

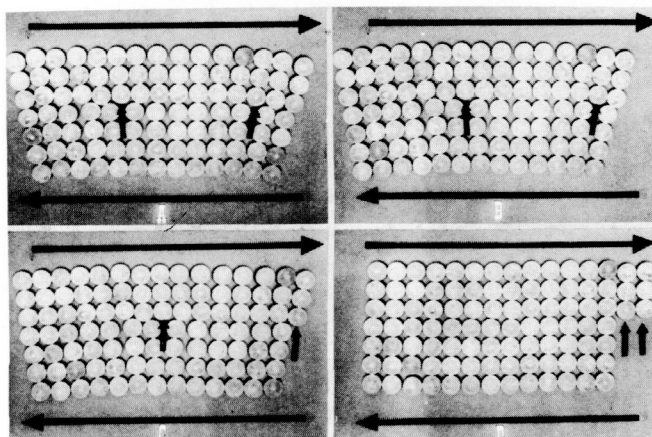


Fig. 20—Model of plastic deformation by dislocation motion.



#### About the Author

Dr. Rolf Weil is professor of Materials and Metallurgical Engineering, Stevens Institute of Technology, Castle Point Station, Hoboken, NJ 07030. He has served as director of three AESF research projects and written more than 50 technical papers. Dr. Weil is recognized for conducting the first investigation of electrodeposits using electron microscopy. He received BS and MS degrees at the Carnegie Institute of Technology, Pittsburgh, and earned his PhD at Pennsylvania State University. In 1981, he was honored with the AESF Scientific Achievement Award.