Analytically Speaking

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Characterization of Deposits, Coatings & Electroforms—The Use of TEM

Transmission electron microscopy (TEM) differs from scanning electron microscopy (SEM) in that the electrons pass through the specimen. The main disadvantage of TEM, therefore, lies in specimen preparation. The specimen must be a thin foil, about 100 nm thick, in order for the electrons to be transmitted. Thicker specimens must be thinned either by electropolishing or ion milling.

Advantages of TEM over SEM are better resolution and the ability to obtain diffraction patterns. The principal uses of TEM for deposits, coatings and electroforms are determination of the sizes and orientations of the grains, and the density and distribution of structural defects. The resolution of the TEM is high enough to image the atomic structure. Figure 1 shows the images of atoms and crystal planes in a sample of yttrium oxide. The planes of atoms are ~ 3 Å apart. The changes in the orientation of the planes of atoms in different tiny grains is clearly seen.

The contrast in the TEM of crystalline materials is primarily determined by the degree to which Bragg's law is obeyed. The electrons either pass through the specimen—*i.e.*, they are transmitted or diffracted if crystal planes are oriented in a particular area so that Bragg's law is obeyed. An aperture is placed below the specimen in such a way that either the transmitted beam or a diffracted one is allowed to pass through. If the transmitted beam passes through the aperture, the image is said to be a bright-field one. If a diffracted beam passes through the aperture, a so-called dark-field image results. In a bright-field image, therefore, in areas where Bragg's law is not obeyed, the electrons constitute the transmitted beam and can pass through the aperture. The image of this area therefore appears bright. Where there are crystal planes oriented for diffraction, the electrons are the diffracted beam that cannot pass through the aperture, so this area appears dark in the bright-field image. The opposite applies to a dark-field image.

Bend Fringes & Thickness Fringes

Figure 2 is a bright-field TEM of electrodeposited nickel, showing

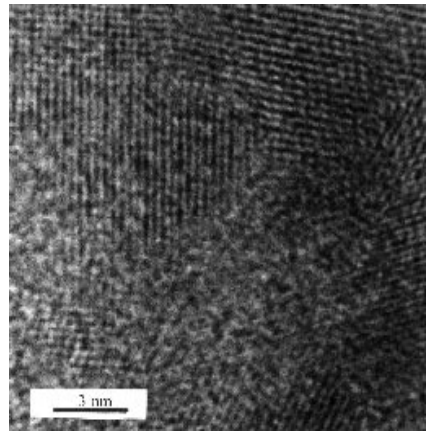


Fig. 1—Transmission electron micrograph showing atom rows in a crystal of yttrium oxide. (Photograph provided by J. Taylor of Stevens Institute.)

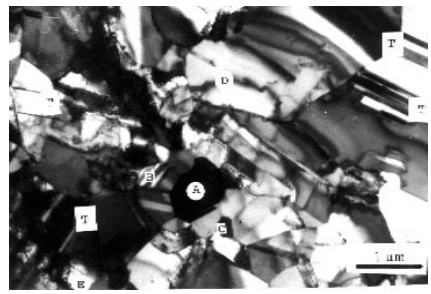


Fig. 2—Transmission electron micrograph of a nickel electrodeposit.

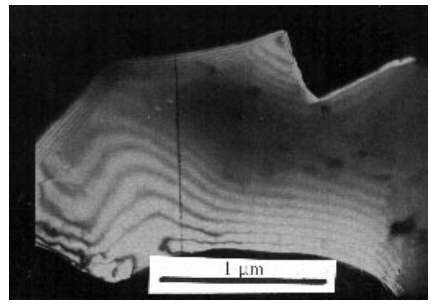


Fig. 3—Transmission electron micrograph showing thickness fringes at the edge of a piece of electroplated nickel.

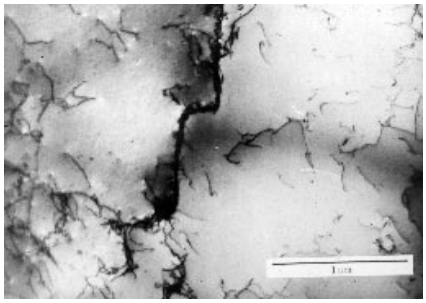
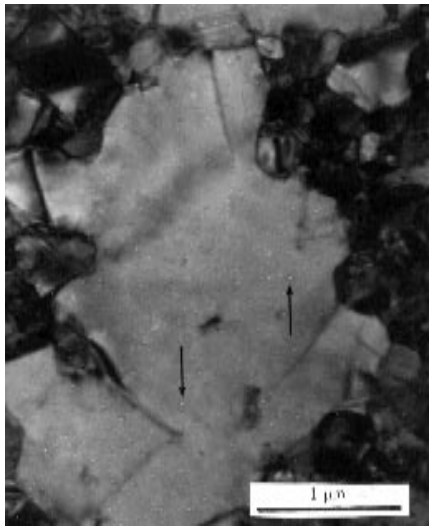


Fig. 4—Transmission electron micrograph showing dislocations in a copper electrodeposit.



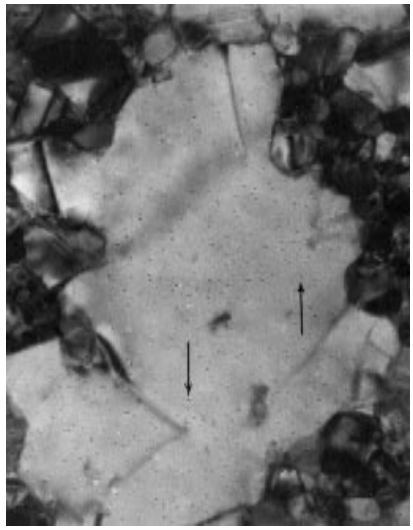


Fig. 5—Transmission electron micrograph obtained by defocusing, showing voids and molecules in a cobalt-hardened gold electrodeposit. (Photograph provided by Dr. Nakahara of Lucent Technologies.)

many of the structural features observed in this material. The area marked "A" is dark because crystal planes are oriented so as to obey Bragg's law. The electrons emanating from this area are diffracted and cannot pass through the aperture. If the aperture were placed to allow the diffracted electron to pass through, area A would appear light. The dark band in the area marked "D" is called a bend fringe. Because the specimen is very thin, it sags a little, and the crystal planes, therefore, are not exactly parallel. In the dark band, the crystal planes obey Bragg's law so that the electrons are in a diffracted beam, which again cannot pass through the aperture. Bend fringes can be easily identified because they move if the specimen is tilted. The ability to tilt the specimen is a feature of every TEM, so that any area can become oriented for diffraction. Bend fringes have no practical application.

Thickness fringes appear at area "C" in Fig. 2, although they are difficult to distinguish because they are very close together. Figure 3 shows them more clearly. Thickness fringes are sets of parallel, alternate dark and light bands. They are also

parallel to an edge of a hole where the specimen is wedge-shaped, or to an inclined grain boundary, as in Fig. 2. Thickness fringes can be used to estimate the thickness of the specimen.

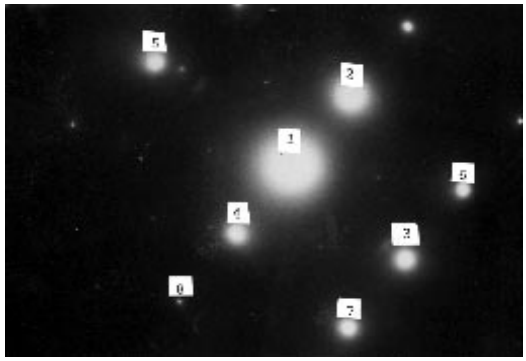


Fig. 6—Electron diffraction pattern of a single grain in a nickel electrodeposit.

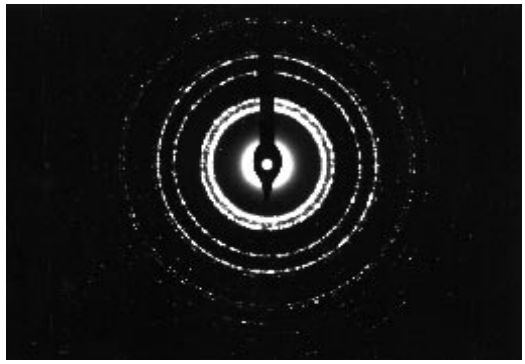


Fig. 7—Electron diffraction pattern of a polycrystalline silver vapor deposit.

Dislocations & Twins

The two structural defects most commonly observed in deposits, coatings and electroforms are also seen in Fig. 2. Dislocations that greatly affect the mechanical properties are shown in the area labeled "E." They are the fine, dark lines. Figure 4 shows dislocations at higher magnification. It can also be seen in Fig. 4 that dislocations form a low-angle grain boundary when they pile up. The dislocations can resemble the bend fringes seen in area D of Fig. 2. Dislocations can be readily distinguished from bend fringes, however, because they do not move when the specimen is tilted. The bands bounded by a set of parallel lines are shown in the area marked "B" in Fig. 2. They may contain sets of parallel lines, or they may not be seen, such as in the areas marked "T." Twins are caused by accidents during crystal growth, and tend to have a strengthening effect.

An application of the TEM that is uniquely suited to electrodeposits is the ability to observe tiny voids and inclusions of organic molecules. The molecules are generally the addition agents or their reaction products. The voids and molecules are made visible by slightly defocussing the image. Electrons travel faster through molecules composed of atoms of low atomic weight or the empty space of voids, than through the heavier metal. The objective lens normally combines the electron waves traveling at different velocities. However, by slightly defocussing the image so that the electron waves are not combined, the voids and molecules become visible. Figure 5 shows the structure of a cobalt-hardened gold deposit that exhibits the so-called polymer inclusions. The inclusions appear as small dots, several of which are indicated by arrows. In Fig. 5a, the dots appear lighter than the background; in Fig. 5b, the same dots are darker than the background. The dots change from dark to light as focus is passed. Figure 5a was overfocused by 3.9 μm, while Fig. 5b was underfocused by the same amount.

The Use of TEM For Determining Grain Size

Probably the widest application of the TEM to coatings, deposits and electroforms is in the determination of grain size. This procedure involves electron diffraction. The magnification is reduced so that the electron beams diffracted by the various sets of crystal planes in one grain become points in a photograph. An electron diffraction pattern of a single grain in a nickel electrodeposit is shown in Fig. 6. Figure 5a of Part III (which appeared in this column on p. 48 of the November issue of *P&SF*) illustrated how transmitted and diffracted beams originate and form spots on a film. It also showed that the angle between the transmitted and a diffracted beam is 2θ. In Fig. 6, the spot caused by the transmitted beam is the most intense, and is labeled No. 1. It is considered the origin and becomes the [000] beam. Spots caused by diffracted beams are labeled with the other numbers.

From a diffraction pattern such as that shown in Fig. 6, it is possible to determine the Miller indices of the crystal plane, which was perpendicular to the incident electron beam, as well as crystallographic directions in the plane. For the indexing procedure, Equation (1) is used:

$$(h^2 + k^2 + l^2) = (Ra_oK)^2 \qquad (1)$$

where h, k and l are the Miller indices of the planes that produced the spot, R is the distance between the origin and the spots caused by diffracted beams, a_o is the lattice parameter of the material, and K is a constant. The way to calculate K will be discussed later. The magnitude of R and the direction from the origin to a spot is a vector. The three indices of the vector, [hkl], are its components in the X, Y and Z directions of the coordinate system.

The indexing method consists of measuring the distance between the centers of the spots caused by the transmitted beam and the two nearest diffracted beams. The No. 2 spot is the one caused by the diffracted beam that is nearest to spot No. 1 (the origin). The distance between No. 2 and No. 1 is ~ 2.5 cm (this distance may not be the same when Fig. 6 is reproduced). The value of K is 1.966 x 10^7 cm^{-1} and a_o of nickel is 3.5239 x 10^{-8} cm. Therefore, by Eq. (1):

$$(h^2 + k^2 + l^2) = (2.5 \times 1.966 \times 10^7 \times 3.5239 \times 10^{-8})^2 \approx 3$$

Nickel has a face-centered cubic crystal structure, so the sum of the squares of the Miller indices of the planes that produced spot No. 2 are of the {111} family, because the sum of the squares is 3. Because the Miller indices are digits, calculating the sum of their squares by Eq. (1) beyond the decimal point has no meaning. The distance between spot No. 1 and No. 3, the next-nearest one, was 4.1 cm. If this value of R is substituted into Eq. (1), then $(h^2 + k^2 + l^2)$ equals about 8. The Miller indices of the planes that produced spot No. 3, therefore, are of the {220} family.

This discussion will be continued in next month's column. **P&SF**