

Analytically Speaking

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Characterization of Deposits, Coatings & Electroforms-Part IV

A nother application of X-rays for deposits, coating and electroforms is the *measurement of macrostresses*. Macrostresses—often called stresses or internal stresses are the ones that can cause distortions of parts or cracking in chromium deposits, for example. They are referred to as macrostresses to distinguish them from microstresses, which will be discussed later.

Methods of Measurement X-rays measure the macrostresses remaining after deposition. Other methods, such as a spiral contractometer, generally measure the macrostresses during deposition and often as a function of thickness.

The macrostresses of concern in deposits are parallel to their surfaces. The spacing between the crystal planes parallel to the surface, therefore, is decreased if the macrostresses are tensile, and increased if they are compressive. According to Braggs law, the value of (2θ) —*i.e.*, the position of the counter where a peak occurs—is changed from what it would be if there were not stresses.

If the interplanar spacing designated by (d_o) in a stress-free deposit were accurately known, the strain would be calculated from the value of (d_s) , the interplanar spacing of the stressed deposit. The value of (d_s) could be calculated from the (2θ) position by Braggs law. The strain would then be $[(d_s - d_o)/d_o]$, and the macrostress would be the strain multiplied by the modulus of elasticity.

For the types of materials discussed here, however, the value of the interplanar spacing in the stress-free condition is never known with sufficient accuracy, because other factors—such as codeposited hydrogen—change it. So this simple method cannot be used for deposits.

The method that must be used is based on the fact that the strains in various directions are related by Poisson's ratio. The determination of the macrostresses is made by obtaining two (2 θ) values of only one peak. One value of (2θ) is obtained from the crystal planes that are parallel to the surface of the deposit. A second value is obtained from the same planes, but inclined to the surface in other grains. The value of $(2\theta_n)$ is determined with the specimen in the usual position where the rotation of the holder and the counter are coupled. Then the Xrays diffracted by crystal planes parallel to the surface enter the counter, as previously discussed.

The second value, $(2\theta_w)$, is obtained when the specimen holder is decoupled and rotated by the angle (ψ) , which is usually 45°, leaving the position of the counter unchanged. Then the X-rays reflected by planes inclined at the angle (ψ) to the specimen surface in other grains enter the counter. In order to accomplish the decoupling, a special specimen holder is required. A peak with a value of (2θ) as close to 90° should be selected for the greatest accuracy. The closer the peak is to 90°, the larger is the change of the value of $(\theta_n - \theta_w)$ for a given macrostress. Because peaks close to 90° generally have low intensities, an X-ray tube should be selected with a target whose value of the mass absorption coefficient of its K_{α} radiation for the material of the deposit is as small as possible. The macrostress (σ) can be calculated by:

$$\sigma = \frac{E \cot\theta \left(2\theta_{n} - 2\theta_{\psi}\right)}{2 \left(1 - \nu\right) \sin^{2}\psi}$$
(1)

where E is the modulus of elasticity and (v) is Poisson's ratio. The value of the angles must be in radians.

The X-ray method is the only one that determines the macrostresses nondestructively if the part is not distorted. It is useful to study changes in the macrostress with time after plating. Many deposits exhibit such changes because of hydrogen diffusion. It is sometimes difficult to obtain an accurate value of the macrostresses by the X-ray method because, as will be discussed later, microstresses (which are also frequently present in deposits) cause peaks to become broad. Twins cause peaks to become assymetric. Both these factors make it somewhat difficult to obtain an accurate value of the peak maxima, which yield the values of (2θ) used in the calculations.

Determining Microstrains & Particle Sizes

Another use of X-rays is the determination of microstrains and particle sizes. Microstrains differ from macrostrains in that they change sign-*i.e.*, from tensile to compressive over small areas of a deposit. Macrostresses have the same sign over the entire surface. The reason microstrains and particle sizes are considered together is because both cause diffraction peaks to be broadened. Particle size, determined by Xrays, is the size of regions between defects, and is generally much smaller than the grain size. Only in very finegrained deposits are particle and grain sizes the same.

There are computer programs available for most X-ray equipment to separate the microstrain from the particle size. These programs also include the means for correcting the two other factors that cause the peaks to be broadened. One of these factors is the degree to which the X-ray beam is focused in the instrument. To determine this so-called instrumental broadening, a large-grained, wellannealed sample of the same metal is needed, or one having the same crystal structure and a similar lattice parameter can be employed.

The index of peak broadening generally used is the so-called halfwidth (B). It is the width of the diffraction peak in radians at half the maximum intensity, as illustrated in the figure. The half-width of the peaks of the deposit designated by (B_d) is corrected for the half-width (B_1) , because of instrumental broadening by the equation:

$$B_{st}^2 = B_d^2 - B_1^2$$
 (2)

where (B_{st}) is the half-width of the socalled Stokes-corrected peak that is used in all subsequent calculations. The Stokes correction is usually performed by the computer program.

A second factor that can cause peaks to be broadened is that there are actually two wavelengths of K_{α} radiation, caused by a small difference in the energy of electrons in the L shell. There is a small energy difference, therefore, depending on which electrons in the L shell replaced knocked-out electrons in the K shell. The two different resulting wavelengths are called $K_{\alpha 1}$ and $K_{\alpha 2}$. There are also actually two peaksone resulting from diffraction of $K_{\alpha l}$ and one of $K_{\alpha 2}$ radiation. In most deposits, the two peaks overlap, resulting in broadening. The separation of the two peaks also increases with increasing values of (θ) , so that the broadening increases as well. It is therefore necessary to use only the half-width of the stronger $K_{\alpha 1}$ peak when calculating the microstrains and particle size. The separation of the $K_{\alpha 1}$ peak from the combined one is accomplished by what is known as the Rachinger correction. It is based on the equation:

 $I(2\theta) = I_{\alpha 1}(2\theta) + \frac{1}{2}I_{\alpha 1}(2\theta + \Delta 2\theta_{\alpha 1\alpha 2}) \quad (3)$

where $[I(2\theta)]$ is the profile—*i.e.*, the variation of the intensity with (2θ) of the Stokes-corrected peak; $[I_{\alpha 1}(2\theta)]$ is the desired peak profile, only as a result of the $K_{\alpha 1}$ radiation and

 $[(\Delta 2\theta_{\alpha 1\alpha 2})]$ is the difference in the maxima of the peaks as a result of $K_{\alpha 1}$ and $K_{\alpha 2}$. The Rachinger correction is also usually performed by the computer program.

The microstrains and particle sizes are calculated from the Stokes and Rachingercorrected half-width (B_c). It is necessary to assume a distribution of the microstrains that can either be a Cauchy or a Gaussian one. If a Cauchy distribution is assumed, the microstrain (ε) and the particle

diameter (D) are calculated by:

 $(B_c \cos\theta) / \lambda = 1/D + (4\epsilon \sin\theta) / \lambda$ (4)

Again, the computer program is generally used to calculate micro-



Fig. 1—Diffraction pattern of an electroless nickel deposit. Also shown is the half-width (B).

strain and particle size. The microstresses are the microstrains multiplied by the modulus of elasticity.

It is also possible to plot $(B_c \cos\theta/\lambda)$ vs. $(4\sin\theta/\lambda)$ for several peaks. The intercept of the graph is then (1/D)

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Fig. 2—Optical micrograph of a copper deposit showing columnar grains and twins.

and the slope is (ϵ). If the points of such a plot do not lie on a straight line, it means that the particles are not symmetric. Such would be the case if the particles were columnar. Then only the corrected half-widths of a peak, and that of a second-order one of the same set of planes, should be used in the graphs. If there is a <100> fiber axis, for example, the particle size perpendicular to the surface could be obtained by plotting the corrected half-widths of the {200} and {400} peaks. The determination of the particle size of a powder is much simpler because there are no microstrains. The half-width of only one peak is needed. If a peak at a low value of (2θ) is selected, the separation of the $K_{\alpha 1}$ and the $K_{\alpha 2}$ peaks is very small, so that the Rachinger correction is usually not needed. The peak only has to be corrected for instrumental broadening by Eq. (2). The particle size (D) can be calculated by the

formula:

$$D = 0.9\lambda/(B_{st}\cos\theta)$$
 (5)

There have been relatively few studies of deposits in which microstrains and particle sizes were determined. The microstrains provide an indication of the defects that are present. Because microstrains are related to hardness, they can be used to provide a means of determining the hardness for very thin deposits where the indention method is not applicable (unless a nanohardness tester is available). The particle size can be used to determine the grain size of very fine-grained deposits.

The particle size of electroless nickel deposits decreases with the amount of the codeposited alloving element, phosphorus or boron. As the particle size decreases, the peaks become increasingly broad. Because no second-order peak is observed in Fig. 1, it is not possible to calculate the particle size and microstrain. It is likely, however, that the broadening of the peak is mostly the result of small particle size. In this case, calculating the particle size by Eq. (5), a value of ~ 100 nm is obtained. Because the peak was a result of diffraction from {111} planes, it is evident that there was a strong fiber axis with these planes being parallel to the surface. When the particle size approaches atomic dimensions, the deposit is considered to be no longer crystalline, but amorphous. Then only one very broad peak is observed in the intensity vs. (2θ) pattern. Such a broad peak would resemble the apparently weak one occurring between 72° and 90° .

Determination of the twinning probability is another application of X-rays. Twins are frequently observed in electrodeposits. The regions between a set of two parallel lines seen in Fig. 2 are twins. A twin boundary is characterized by the fact that the crystal lattice on one side is the mirror image of that on the other one. Twins are most prevalent in facecentered cubic deposits. Twin boundaries can increase the yield strength of materials in a way similar to grain boundaries, but probably to a lesser degree. The effect of twin boundaries on the strength of electrodeposits has not been investigated.

Twins affect the peaks by causing them to become asymmetric. In that case, the (2θ) value of the center of gravity (CG) of the peak—a vertical line drawn on the peaks of the diffraction pattern so that the areas on each side are equal—does not coincide with the (2θ) value, where the intensity is a maximum.

The twinning probability (*i.e.*, the ratio of the average width of twins to the size of grains) can be calculated from the asymmetry of the peak. When the deposits are face-centered cubic, the two peaks having the smallest (2θ) value on the diffraction pattern—namely, the {111} and $\{200\}$ —are used in the calculation. The centers of gravity and the points of maximum intensity are determined. The twinning probability (β) can then be calculated from the difference $[\Delta CG(2\theta)]$ in the value of (2θ) between the CG and the point of maximum intensity of the {111} and {200} peaks by the formula:

$$[\Delta CG(2\theta)]_{111} - [\Delta CG(2\theta)]_{200} = (6)$$

 $\beta [11 \tan \theta_{111} + 14.6 \tan \theta_{200}]$

The constants, 11 and 14.6, permit the values of (2θ) to be in degrees. If (β) is 10⁻³, for example, and the average grain diameter is 10 μ m, the twins would be 10 nm wide.

Twins can be caused by growth accidents and by mechanical deformation. The deformation-fault and growth-fault probabilities can be determined from X-ray patterns. In this case, the peak shape has to be expressed in terms of a Fourier series. The probabilities can then be calculated from the Fourier coefficients. The method is described in a paper by A.S. Fieze, R. Sard and R. Weil, which appeared in the *Journal of the Electrochemical Society*, Vol. 115 (1968), p. 586. *Pase*

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