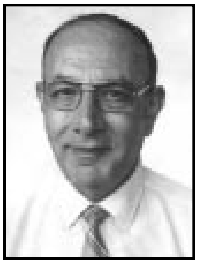

Analytically Speaking

Dr. Rolf Weil
Professor Emeritus
Stevens Institute of Technology
Hoboken, NJ 07030

Characterization of Deposits, Coatings & Electroforms—Part III

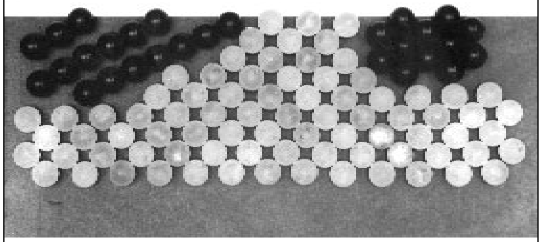

Fig. 1—Model of faster-growing grains covering slower-growing ones.

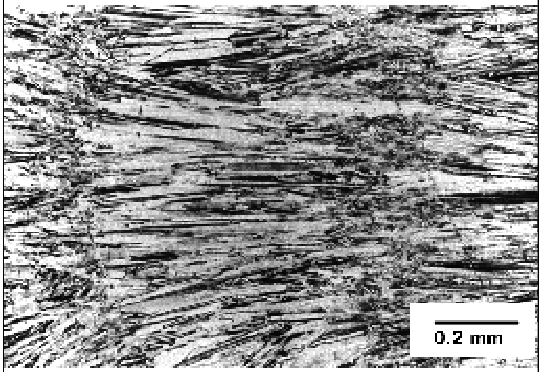

Fig. 2—Optical micrograph of a copper deposit showing columnar grains and twins.

In the previous two columns (Parts I & II), the applications of X-rays for determination of the chemical composition and identification of compounds were described. Some basic aspects of X-rays, which will be referred to again, were also discussed.

X-ray Methods

Preferred Orientations

The preferred orientations that many deposits exhibit are generally determined by means of X-rays. Preferred orientations originate because certain crystals, which in solid materials are usually called *grains*, grow faster than others. The faster-growing grains have a certain crystallographic direction perpendicular to the substrate. This phenomenon, called *epitaxy*, occurs if the substrate is free of soils or oxides, and if the deposition rate is relatively slow. In other cases, deposition may begin with the formation of many small, randomly oriented grains (*i.e.*, having many different crystallographic orientations perpendicular to their surfaces).

In both cases, the grains having a certain crystallographic direction perpendicular to their surfaces often grow outward (away from the substrate) faster than the others. One reason why they grow faster is that some directions just naturally do so. In other instances, however, hydrogen, basic substances or the products of reactions involving addition agents are adsorbed to a lesser degree on the faster-growing grains.

Figure 1 illustrates that the grain represented by the white balls grew outward further than the ones shown to consist of the black balls. It is also illustrated that the faster-growing grains spread laterally, so as to cover the slower-growing ones. The faster-growing grains can spread sideways until they encounter those of the same orientation. In this way, the deposit will consist mostly of grains having the faster-growing, preferred orientation. The preferentially oriented grains, by growing outward, are essentially unhindered from the columnar structure, and are often seen in the cross section of deposits (see Fig. 2).

The type of preferred orientation that results from the faster outgrowth of certain grains is called a *fiber axis* or texture, because it is similar to what is observed in a wire. In a wire, the preferred direction is parallel to its length, while in a deposit it is perpendicular to the surface. In both cases, however, the directions that are perpendicular to the preferred one are more randomly distributed, as illustrated in Fig. 3. Here, the face of the unit cell, a plane of the {100} family is illustrated to be parallel to the surface of most grains. On the sides of the unit cells, however, the <001> directions are not parallel to each other in the different grains, and therefore more randomly distributed.

This randomness is characteristic of a fiber texture. A sheet texture differs in that a certain direction lying in the surface also tends to be aligned. Often this alignment occurs in the rolling direction. The determination of a fiber axis by means of X-rays is much simpler than that of a sheet texture, which involves pole figures. (This will not be described further, because it requires special instrumentation and is rarely used for the materials discussed here.) A pole figure can be used to determine a fiber axis and the degree of its alignment.

The instrumentation used to determine if a fiber texture is present was shown in Fig. 1 of Part I. The specimen is placed in specimen chamber B. Monochromatic K_α X-rays are directed at the specimen. A chart of intensity entering the counter vs. the (2θ) positions where peaks occur, which is called a diffraction pattern, is obtained. X-rays are said to diffract if the reflected beams are in phase. If a strong fiber texture is present, the intensity of certain peaks in the diffraction pattern will usually be very high. It may be recalled that the intensity is proportional to the number of grains having planes with the same interplanar spacing parallel to the surface. This number is called

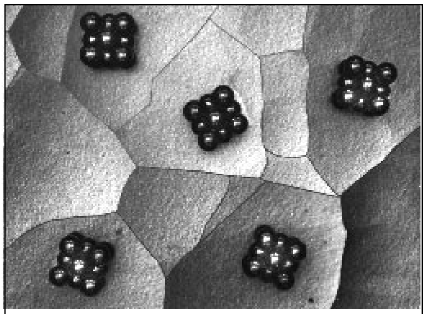

Fig. 3—Model of a deposit exhibiting a fiber axis, showing that directions parallel to the surface are random.

Relative Intensities Of Diffraction Peaks of Nickel

Peak	Rel. intensity	Peak	Rel. intensity
{111}	100	{222}	7
{200}	42	{400}	4
{220}	21	{331}	14
{311}	20	{420}	15

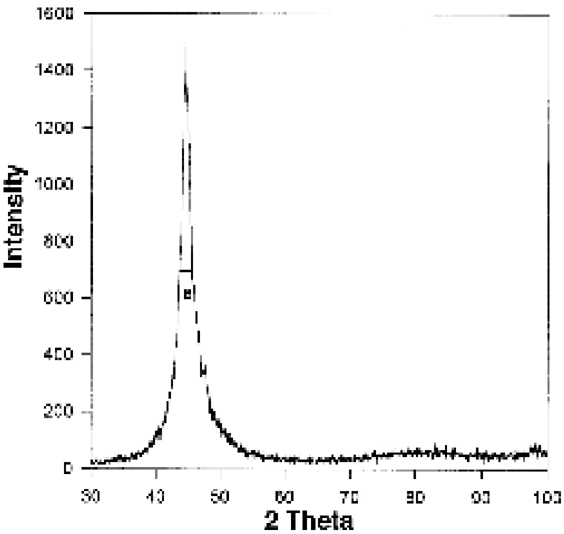

Fig. 4—Diffraction pattern of a <100> oriented nickel deposit.

the *multiplicity factor*. For the identification of compounds, it was necessary that there be an equal number of grains having all the different planes parallel to their surfaces. There should be six or a multiple of six grains, for example, with a {100} plane parallel to their surfaces as there are six faces of a cube. So, for a randomly oriented sample, the multiplicity factor is six for {100} planes. The multiplicity factor for {200} planes is also six, because they are parallel to the {100} planes. Tables of multiplicity factors for the different planes in cubic crystals can be found in most crystallography texbooks.

The intensities relative to the most intense peak, which is set equal to 100, of the different crystal planes of randomly oriented nickel are listed in the table. The relative intensities of the peaks can be calculated approximately from the product of the square of the structure factor (the sum of the X-ray waves reflected by atoms in the unit cell when a certain set of crystal planes diffracts the X-rays), the multiplicity factor and a function of (θ) called the *Lorentz polarization factor*. For face-centered-cubic crystals, the structure factor is zero, in which case there is no peak unless all the Miller indices of the diffracting planes are either all odd or all even. The number zero is considered even. There are therefore no peaks for {100} and {110} planes, because their indices are mixed.

According to Braggs law (Equation 1 of Part I), therefore, the smallest value of (2θ) where a peak occurs is that corresponding to the value of the interplanar spacing (d) of the {111} planes. The next peak would be that belonging to {200} planes. For body-centered-cubic crystals, the structure factor is not zero if the sum of the Miller indices is even. Again, there would not be a {100} peak. The peak with the smallest (2θ) value would be that corresponding to the (d) value of {110} peaks and the next one would again be that belonging to {200} planes, because the sums of the Miller indices are even numbers. The relative intensities, such as shown in the table, can also be obtained from the JCPDS file. It can be seen from the table that the most intense peak in randomly oriented nickel is that belonging to the {111} planes. Such is the case for most face-centered-cubic metals.

If a fiber axis exists, so that most grains have a {100} plane parallel to their surfaces (as is often the case in nickel electrodeposits), there are more grains with a plane of this family parallel to the surface than predicted by the multiplicity factor. The {200} peak is then much more intense than the other peaks. As nickel is face-centered-cubic, there is no {100} peak. Other peaks are much less intense than if the nickel deposit were randomly oriented, because there are fewer planes with other indices parallel to the surface. Figure 4 is a diffraction pattern belonging to a nickel deposit exhibiting a fiber texture. It can be seen that the {200} peak in Fig. 4 is much more intense than that belonging to the {111} planes. It therefore appears that relatively few grains had {311} planes parallel to their surfaces. Apparently, there were not grains with other index planes parallel to their surfaces.

When one peak is much more intense than the other ones, it is quite certain that a fiber axis exists. Then the direction with the same indices as the set of planes that caused the intense peak is the fiber axis. Many authors of technical papers have called the fiber axis of nickel <200>. The <100> direction, however, is also perpendicular to the {200} planes. The convention is to name the fiber axis by the smallest set of indices, so even though there is no {100} peak, the fiber axis should be called <100>.

It is sometimes difficult to determine if a fiber axis exists or what its indices are. Such is the case if no very strong peak, such as that seen in Fig. 4, is observed. If the relative intensi-

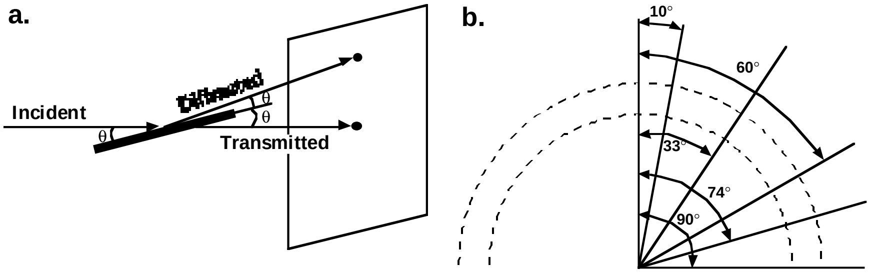

Fig. 5—Schematic representations of (a) diffracted and transmitted beams, and (b) film showing fiber axis.

ties are different from those predicted by the JCPDS file, and especially if some peaks are absent, it is an indication that there is a fiber axis. It is possible that the fiber axis is the direction perpendicular to a set of planes where the structure factor, and consequently the intensity of the peak, are zero. Such would be the case if the indices are mixed for a face-centered-cubic metal or the sum of the indices is odd for a body-centered-cubic one. Then the peak of a set of second-order (indices multiplied by 2) planes, where the intensity is not zero for cubic metals, could be more intense than predicted by the JCPDS file. If the <120> direction were the fiber axis, for example, the peak belonging to {240} planes could be more intense. This method cannot always be used. The second-order peak could occur at a value of (2θ) greater than 180°. In some cases, a peak occurring at a large value of (2θ) is inherently so weak that it cannot be determined if its intensity is indicative of a fiber axis.

There is a method employing film, rather than the diffractometer chart, by which the fiber axis can always be determined. The experimental setup for this method is illustrated in Fig. 5a. The incoming X-ray beam should be perpendicular to the fiber axis. In the case of a deposit, it has to be bent slightly so that the beam passes through the apex. The film, which is placed behind the sample (as shown in Fig. 5a), will show semicircles as illustrated in Fig. 5b. Ordinarily there would be circles, but the sample shields half of them. If a fiber axis exists, the semicircles will show small arcs of higher intensity, as illustrated in Fig. 5b. This pattern represents that of a copper deposit taken with Cu K_α X-rays of wavelength 0.542 nm. As can be seen in Fig. 5a, the distance between the spots on the film of the transmitted and diffracted beams is ($D\tan2\theta$), where (D) is the specimen-to-film distance. The spots diffracted in different directions from the same set of planes generate the semicircle. So the quantity, ($D\tan2\theta$) is its radius. The inner semicircle of Fig. 5b has a radius of 2.8 cm. As D=3 cm, θ=21.5°. Because copper is face-centered-cubic, the first semicircle belongs to the {111} planes. Similarly, for the outer semicircle, which has a radius of 3.6 cm and belongs to {200} planes, the value of (θ) is 25.1°. The angles between the centers of the more intense arcs and the vertical direction—designated by (δ)—are 33° and 74° on the {111} semicircle and 10° and 60° on the {200} one. The angles, the fiber axis and the direction perpendicular to the set of planes that produce the semicircle must be calculated by:

$$\cos\rho = \cos\theta \text{ x } \cos\delta \text{-----------3}$$

where (ρ) is the calculated angle. The values of (ρ) are calculated to be 39° and 75° for the angle between the fiber axis and the <111> direction, and 27° and 63° with <100>, which, of course, is also perpendicular to <200>. From a table of angles between directions that are listed in any crystallography textbook, it is found that the angles between the <120> and the <111> directions are 39° and 75°. The angles between the <120> and <100> directions are 27° and 63°. Therefore, <120> is the fiber axis. The <120> direction also makes the angle 90° with <100>, but in most cases this higher-intensity arc is obscured by the specimen. Reflection high-energy electron diffraction (RHEED), which will be discussed along with electron microscopy in a subsequent column, can also be used in a way similar to the X-ray film method to determine the fiber axis. It was also previously pointed out that a pole figure can be used to determine the fiber axis.

The practical value of knowing that there is a fiber axis without actually establishing its indices is that it indicates the presence of a columnar-grain structure. This fact, however, can also be established by examining the cross section metallographically. Columnar grains can be detrimental for the mechanical properties, primarily because their boundaries tend to be weak. There is essentially no effect on the mechanical properties because they depend on orientation. As was seen in Fig. 2, the directions parallel to the surface of a deposit tend to be randomly oriented when there is a fiber axis. The mechanical properties parallel to the surface—which are the important ones—therefore tend to be averaged over the different grains. Certain fiber axes are also related to the brightness of deposits.

Many technical papers erroneously list the fiber axis as the indices of the most intense peak, when they are not the smallest digits (*e.g.*, <200> instead of <100>). Also, in some papers where there was a doubt about the fiber axis, the second-order peaks were not examined nor the film method applied. One purpose of this series of columns is to prevent such errors in the future. ***P&SF***