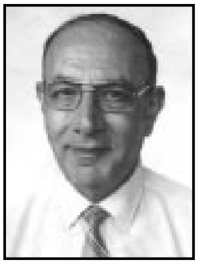

Analytically Speaking

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Characterization of Deposits, Coatings & Electroforms—Part II

The identification of crystalline compounds or phases present in deposits, coatings or electroforms is based on a different principle than the methods for fluorescent analysis (discussed last month in Part I). For reference, the two equations noted in Part I were as follows:

Equation 1

Braggs Law, which states:

$$2d \sin\theta = n\lambda \quad (1),$$

where d is the spacing between the reflecting crystal planes, λ is the wavelength of the X-rays and θ is the angle. The value of n can usually be taken as unity.

Equation 2

Absorption, which obeys the equation:

$$\ln I/I_o = -(\mu/\rho)\,\rho t \quad (2),$$

where μ/ρ is the mass absorption coefficient listed in tables for all elements when they absorb K_α radiation. The density is ρ and the foil thickness is t.

Identification of Compunds

In fluorescent analysis, the d spacing of Eq. 1 was kept constant, and the variation of the wavelengths λ of the characteristic radiation with the 2θ value of the peaks was calculated. For the identification of compounds, the wavelength must be kept constant, and the variation of the λ spacing with the 2θ value of the peaks must be determined. It has been pointed out that, because of the three variables in Braggs Law, either d or λ must be kept constant and its value known.

The identification of compounds is based on the fact that the d spacings and the relative intensities of peaks are unique for each compound or phase. To understand the method of identifying compounds, a knowledge of some basic concepts of crystallography is necessary. A crystal can be thought of as consisting of a regular three-dimensional array of points, called a *lattice*. The same pattern of one or several atoms, called the *motif* or *basis*, is associated with each lattice point. The smallest arrangement of lattice points with their associated motif is called the *unit cell*, which can be thought of as the building blocks of the crystal.

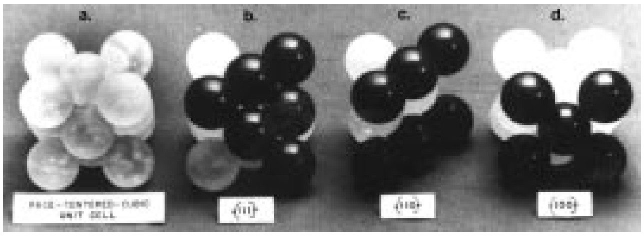

Fig. 1—Models showing the fcc unit cell (a) and family of crystal planes: (b) the {111}, (c) the {110}, and (d) the {100}.

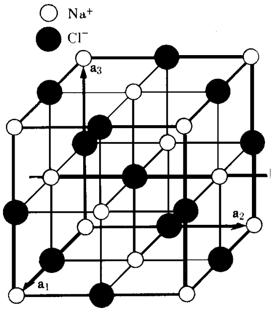

Fig. 2—Model of the sodium chloride unit cell.

Most electroplated metals, such as copper, nickel, silver, gold and the platinum group, have the face-centered-cubic (fcc) unit cell shown in Fig. 1a. The motif for these metals is a single atom. There are lattice points at the eight corners and in the center of each face, each occupied by an atom in this case. The lattice points are located at the centers of the atoms. Because each corner is shared by eight unit cells, only one-eighth of the eight corner atoms is in the unit cell. Similarly, because two unit cells share a face, only half of the atoms in the six faces are in the unit cell.

The dimensions of the unit cell are called the *lattice parameters*. Iron and chromium have a body-centered-cubic (bcc) unit cell, with single atoms at the corners and one in the center. Cobalt, zinc and cadmium have a hexagonal unit cell. Many compounds (*e.g.*, sodium chloride) also have cubic lattices, so that more than one atom is associated with each lattice point. As shown in Fig. 2, the sodium ions (represented by open circles) are located on the lattice points, and the chloride ions (represented by filled-in circles) are halfway between the sodium ions, where there are no lattice points. So the motif consists of a sodium and a chloride ion.

It is convenient to name the planes in a crystal. The so-called Miller indices are named by the reciprocals of the intercepts of the crystal planes in a coordinate system in which the lattice parameters are the units of measurement. If a plane passes through the origin of the coordinate system, the origin must be moved one unit. The front face of a cube, for example, has intercepts of 1 with the Z axis, and infinity with the X and Y axes because it is parallel to them, and the reciprocals are (100). The regular brackets signify a definite plane. The (100) plane of the fcc lattice is shown by the black balls in Fig. 1d. Because all faces are identical in cubic

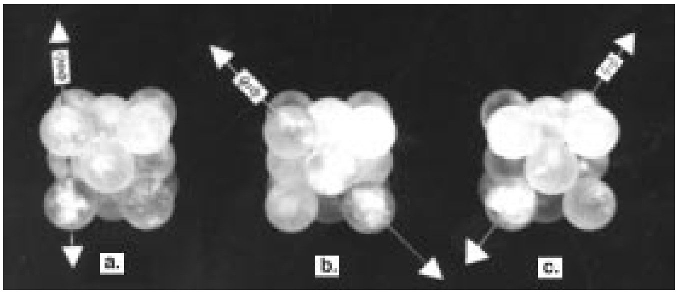

Fig. 3—Models showing crystal directions: (a) <100>, (b) <110> and (c) <111>.

crystals, one generally speaks of *families of planes* that are designated with different brackets, such as {100}. A family consists of all planes having the same three-digit indices. The face-diagonal planes are {110}, and are shown by the black balls for the fcc lattice in Fig. 1c. The body-diagonal planes with the indices {111} are shown by the black balls in Fig. 1b for fcc crystals. For cubic lattices, the directions that have the same three-digit indices as the planes are perpendicular to them. One direction of each of the <100>, <110> and <111> families is shown in Fig. 3a, 3b and 3c, respectively. The triangular brackets denote a family of directions (*i.e.*, all directions having the same three-digit indices).

As previously discussed, the identification of compounds is based on the conversion of the 2θ value, where a peak is recorded by the counter into d spacings via Braggs Law (Eq. 1). A single wavelength, namely that of K_α, must produce the peak, and the only radiation that actually has to be eliminated is K_β. Other wavelengths are too weak to be of significance, and form the background. It was mentioned previously that a filter can eliminate the K_β radiation. Another way is to use a monochrometer, which is a curved crystal that reflects the K_β so that the peaks it produces are not recorded by the counter.

The d spacing of crystal planes depends on the lattice parameters and the Miller indices. The smaller the magnitudes of the Miller indices, the larger the d spacing. In cubic crystals, the d spacing is inversely proportional to the square root of the sum of the squares of the indices. The {100} planes, therefore, have the largest d spacing, followed by {110} and {111}. The peaks produced by {100} planes would therefore occur at the smallest 2θ position of the counter.

The intensity of a peak depends on the sum of the X-ray waves reflected by the atoms or ions in the unit cell, and on the Miller indices of the reflecting planes. The intensity also depends on a function of θ and on how many crystal planes have the same d spacing. The identification of compounds therefore requires there be the same number of all different planes parallel to the surface of the specimen, so that they can reflect X-rays into the counter. This condition can only be satisfied if the specimen consists of very small, randomly oriented crystals. Some deposits satisfy this condition; most do not, and the material must then be ground into a fine powder.

No two compounds or phases have the same value of d spacings and order of decreasing intensities. A file of approximately 30,000 X-ray patterns of crystalline materials has been compiled by the Joint Committee on Powder Diffraction Standards (JCPDS), and is available on index cards and computer diskettes. In the JCPDS file, the materials are listed first according to the values of the d spacings of the most-intense peak, and then according to the d spacings of peaks of decreasing intensity. If the most intense peak occurred, for example, at a 2θ position of the counter that converted to a d spacing of 2.40 Å; the second to a d spacing of 1.70 Å; the third to a d of 1.45 Å; the fourth to 1.39 Å; the fifth to 1.07 Å, and the sixth to a d of 0.98 Å, etc., the compound would probably be calcium oxide. It could also be another compound, such as silver scandius or rhodium tarbius. Other possibilities can readily be ruled from the chemical analysis. In most modern equipment, it is not necessary to actually perform the identification steps (*i.e.*, convert to d spacing and list them in order of intensity). Computer programs perform all the calculations, compare them to the JCPDS file, and then list the possible compounds.

The application of the above procedure would probably be only to CVD coatings, because most vapor and electrodeposits are not compounds. In some cases it may only need to be determined if a certain compound is present. An example would be annealed electroless nickel, when the presence of Ni_3P would have to be determined. In this case, the d spacings of Ni_3P would be obtained from the JCPDS file and converted to 2θ values. The presence of peaks at the values on the output of the counter would suffice to show that the deposit contained Ni_3P.

The same procedure could be followed to detect the presence of oxides. The limitations of the procedure are that the compounds must be present in sufficient quantities and must be crystalline, so it is not possible to detect most organic compounds. A procedure to detect small quantities of crystalline compounds will be described in a future column, in conjunction with electron microscopy. ***P&SF***