

Analytically Speaking

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Characterization of Deposits, Coatings & Electroforms-Part I

Editor's Note: This is a new monthly column on analytical methods. Topics covered will include analytical equipment, measurement methods and specific applications. Dr. Weil's practical approach, in layman's terms, is aimed at taking the fear out of using sophisticated equipment.

E ssentially the same methods are used to characterize electroplated, electroless, vapor deposited and chemically vapor deposited (CVD) coatings, as well as electroforms. Scanning electron microscopy is the method most frequently employed for the materials discussed here. Transmission electron microscopy and optical microscopy also have applications. The more recently developed scanning tunneling and scanning force microscopy, also known as atomic force microscopy, do not require samples to be kept in vacuum, and are therefore applicable to in-situ studies in electrolytes. Auger electron spectroscopy and X-ray photoelectron spectroscopy, or electron spectroscopy (for chemical analysis), have special uses. The characterization of the mechanical properties is important, especially for electroforms and deposits used in printed circuits. Various characterization methods, underlying principles, experimental techniques and their applications to coatings, deposits and electroforms, will be discussed.

Part I of this month's column deals with the use of X-rays for chemical analysis, thickness measurement and identification of compounds, as well as some general aspects of X-rays that are applicable to later discussions.

X-ray Methods

Probably the widest application of Xray methods to deposits, coatings and electroforms is *fluorescent analysis* for the determination of chemical composition. The method is based on how X-



Fig. 1—Typical X-ray unit. (Photo courtesy of Rigaku International Corp.)

rays are generated, which occurs when electrons or photons knock out electrons in the shells close to the nucleus of atoms. The knocked-out electrons are replaced by ones from shells farther from the nucleus. The farther electrons are from the nucleus, the greater their energy, so when an electron from a farther shell replaces one from a closer shell, the excess energy is given off as X-ray photons. The energy difference between shells is unique for any given element, and the resulting X-rays are called characteristic radiation. Because the energies or wavelengths, which are inversely proportional to the energies of the characteristic X-rays, are different for each element, they can be used to identify the element (e.g., for chemicalanalysis). Because the characteristic Xrays are generated close to the nucleus, their wavelengths are independent of valence or the state of the material (i.e., solid or liquid, elemental or compound).

Tables and computer programs are available that list the wavelengths of these characteristic X-rays for each element. The process by which knocked-out electrons are replaced by ones of higher energy (emitted as Xrays) is called *fluorescence*. When this is used to determine chemical composition, it is known as *fluorescent analysis*.

There is a system of naming the characteristic X-rays. If an electron is knocked out of the K shell, which is the one closest to the nucleus, and is



Fig. 2—Schematic of X-ray paths.

replaced by one from the next-closest shell (the L shell), the X-rays are designated K_{α} . The letter refers to the shell of the knocked-out electron, and the subscript to the number of shells between it and the one from which the replaced electrons came. So α refers to the next-closest shell, β to the second-closest, etc. If an electron is knocked out of the L shell, for example, and replaced by one from the N shell (two shells farther from the nucleus), the X-rays would be called L₈.

Typical X-ray equipment is shown in Fig. 1. For fluorescent analysis, however, it must be modified from this design. The unit consists of the X-ray tube (A), the specimen holder (B), and the counter (C). The tube contains a tungsten filament that, when heated, gives off electrons by thermal emission. The electrons are attracted to a piece of metal (the target) by applied potential.

It is important to note that electrons from the filament knock out electrons in the K shell of the target, which are replaced by ones from the L and M shells, producing K_{α} and K_{β} X-rays. The wavelengths of the K_{α} and K_{β} radiations are characteristic of the target material (usually copper). For longer wavelengths, a chromium target is used. A molybdenum target produces X-rays of shorter wavelengths than those of copper. The potential applied between the filament and the target determines the intensity of the emitted beam. Because the filament and target are sealed in a vacuum, it is only possible to change targets by changing tubes.

As shown in Fig. 1, the position of the tube is fixed in the X-ray unit; the chamber holding the specimen rotates. As shown in Fig. 2, crystal planes parallel to the surface of the specimen make the angle θ with the emitted X-ray beam. Slits and collimators in front of the tube control the divergence of the beam, which is reflected at the angle θ by the crystal planes of the specimen parallel to its surface. The reflected beam then makes the angle 2θ with the incoming one. The counter moves on a circular track and is coupled with the rotation of the specimen. When the specimen rotates through the angle θ , the counter rotates through the angle 2θ , with respect to the incoming beam. In this way, the X-rays reflected by the surface of the specimen enter the counter. X-rays reflected by crystal planes inclined to the surface do not enter the counter when its rotation is coupled with that of the specimen. The data obtained consist of peaks (where the intensities of the X-rays entering the counter are above background) and the 2θ positions where they occur.

In the unit shown in Fig. 1, the track on which the counter moves is horizontal. Some units have a vertical track. Because of the reflected X-rays that do not enter the counter, it is necessary to shield the specimen. The surface of the specimen also must be at the exact center of the circular track on which the counter moves.

For fluorescent analysis, the wavelengths of the characteristic radiation produced in the sample must be determined. The conversion of the 2θ positions of the counter to wavelengths can be accomplished with Braggs Law, which states:

 $2d \sin\theta = n \lambda$ (1), where d is the spacing between the reflecting crystal planes, λ is the wavelength of the X-rays and θ is the angle (shown in Fig. 2). The value of n can usually be taken as unity.

Because there are three variables in Braggs Law—d, θ and λ —it can only be solved if one of the quantities is constant and its value known. A single crystal, called the *analyzer crystal*, is placed in specimen chamber B (Fig. 1). A lithium-fluoride crystal is often used because it can be cleaved so that a single set of planes is parallel to the surface, reflecting the X-rays into the counter. The sample for analysis is placed in the beam path (not shown in Fig. 1). Some X-ray units can be converted for this type of chemical analysis by providing a way to place the sample in the X-ray beam. There also are units specially built for fluorescent analysis.

For fluorescent analysis, characteristic X-rays of the elements present in the sample must be produced. The X-ray photons emanating from the tube must have a definite energy or wavelength to knock out electrons from the K shell, for example, in sufficient numbers to produce peaks of relatively high intensity. It is only possible, therefore, to obtain strong characteristic X-rays from a single element. Also, the target of the tube must be selected to produce X-rays with the correct wavelength.

The fluorescent analysis method described here is called *wavelength* dispersive. The other method is called energy dispersive. In the wavelength dispersive method, the characteristic Xrays from the sample are reflected by the analyzer crystal into the counter at the appropriate 2θ positions. Most Xray units have computers that convert the 2θ positions of the peaks into the wavelengths of the element's characteristic radiations present in the sample for chemical analysis and identification. With appropriate standards, the quantity of each element can be determined from the intensity of the peaks, yielding a quantitative analysis. High-intensity peaks are needed for this analysis.

Fluorescent analysis can be applied to coatings, deposits and plating solutions. It has one severe limitation it is not possible to analyze elements of low atomic number, such as hydrogen and carbon. This can be a disadvantage if the presence of organic compounds or of gas-filled voids is to be determined in electrodeposits. The inability to analyze for boron is also a disadvantage for some electroless deposits.

The measurement of the thickness of thin foils by X-rays is based on some of the same principles as wavelength dispersive analysis and on absorption, which obeys the equation:

ln I/I_o = - ($\mu \rho$) ρt (2), where μ / ρ is the mass absorption coefficient listed in tables for all elements when they absorb K_a radiation. The density is ρ and the foil thickness is t. The quantities I and I_o, whose natural logarithm is substituted in Eq. (2), are obtained as follows.

A piece of metal with a small window cut out is placed in front of the tube. The counter is set at the 2θ , at

which K_{α} -characteristic X-rays from the tube are reflected. This position is calculated from Eq. (1) by substituting the d spacing of the analyzer crystal planes, which are parallel to the surface, and the λ of the K_{α} radiation. This setting is necessary because the mass absorption coefficients, which vary with wavelength, are only listed for K_{α} radiation. The intensity of the X-rays passing through the window is I. When the foil is placed in front of the window, the intensity of the X-rays is I. With these two intensity measurements, as well as the density and mass absorption coefficient of the material, the thickness t can be calculated by Eq. (2).

Another phenomenon related to absorption, as well as fluorescence, is used to filter out undesirable X-rays. When X-rays emanating from the tube have the right energy to knock out electrons from the K shell, for example, in material anywhere in the path to the counter, these photons are preferentially absorbed. The wavelength at which the preferential absorption by a material occurs is called the *absorption edge*. The practical application of this phenomenon is in the production of Xrays of one wavelength (i.e., monochromatic radiation). It is possible to filter out the K_{β} , leaving only K_{α} radiation, by selecting a material so that the K_{β} photons have just the right energy to knock out electrons in its K shell and are then preferentially absorbed. The K absorption edge of the material in the X-ray path should be just slightly longer than the wavelength of the K_β photons. The wavelength of copper K_β radiation, for example, is 0.1392 nm; the K absorption edge of nickel is 0.1488 nm. Nickel, therefore, is a suitable material to filter out K_B radiation emanating from tubes with copper targets. A thin foil of the filter material is usually placed in front of the X-ray tube. PASF

About the Columnist Dr. Rolf Weil is professor emeritus at Stevens Institute of Technology, Hoboken, NJ. He has served as director of the AESF research projects and has 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, PA, and a PhD at Pennsylvania State University. In 1981, he received the AESF Scientific Achievement Award.