

Analytically Speaking

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## Characterization of Deposits, Coatings & Electroforms—The Use of SEM

The main advantages of scanning electron microscopy (SEM) over optical ones are better resolution and depth of focus. The superior depth of focus of the SEM permits the examination of rough surfaces, such as fractures. Even such rough surfaces as dull electrodeposits would be wholly in focus. Because it is often difficult to distinguish crevices surrounding nodules from the boundaries of grains, great care must be exercised if their size is to be determined by SEM.

Advantages & Disadvantages Figure 1 shows a scanning electron micrograph of electroless nickel. It illustrates that the features resembling grams are, in fact, nodules. Even if there are structural features—such as the lines seen in Fig. 1 that appear to extend across grains—it is still difficult to determine the actual grain size. It is best, therefore, not to determine the grain size of deposits by SEM.

The principal disadvantage of the SEM is that the samples are in a vacuum. In situ observations of electrodeposition or corrosion cannot be made. Such observations are possible by optical microscopy. The surfaces of non-metallic materials have to be coated with a very thin film of a conducting material, usually gold. Otherwise, charges develop that can obscure the structure. This coating can be avoided, and organic materials such as plastics, which would distort in the electron beam, can be examined if a very low accelerating voltage is used.

Recently developed scanning electron microscopes, in which the electrons are produced by field emission, permit the use of low accelerating voltages. A scanning



Fig. 1—Scanning electron micrograph of electroless nickel showing nodules often mistaken for grains.

electron microscope, however, is much more expensive than an optical microscope.

Operation of the SEM As implied by the name, the SEM uses electrons rather than visible light for illumination. The wavelength of electrons is several orders of magnitude smaller than that of photons in the visible range. The resolution, therefore, is not limited by the wavelength, and the quality of the lenses determines the resolution. For the examination of most deposits, the resolution of an SEM is adequate.

Contrast is determined by the mode in which the SEM is operated. The two main modes use back-scattered and secondary electrons, respectively. In the back-scattering mode, the incoming electrons are reflected by the surface of the specimen. Contrast is achieved primarily by how much energy the electrons lose when they are reflected. The smaller the atoms that reflect them, the more energy the electrons lose. As an analogy, when a ping-pong ball hits a bowling ball, it does not lose any energy—it only changes direction. It cannot transfer



*Fig.* 2—*Scanning electron micrograph of grains in a copper electrodeposit.* 



Fig. 3—Scanning electron micrograph of the same area seen in Fig. 1 showing phosphorus distribution.

any energy to the bowling ball because it cannot move the bowling ball. If a ping-pong ball hits a tennis ball, however, the latter is moved a little, so the former loses energy.

If only back-scattered electrons with energies greater than a certain value are imaged, structural features consisting of small atoms will appear darker than those consisting of mostly large atoms. The reason for the contrast, therefore, is that only the electrons back-scattered by the large atoms are imaged. An example would be annealed electroless nickel containing Ni<sub>3</sub>P particles. Because the phosphorus atoms are smaller than the nickel atoms, the  $Ni_3P$  particles would appear darker than the nickel matrix. So if the desired contrast depends on atomic weight, the SEM should be operated in the back-scattering mode.

In most cases, the morphology (*i.e.*, the protrusions and depressions) needs to be viewed, so secondary electrons should be imaged. When an electron scans a specimen in the SEM, other electrons are emitted. These secondary electrons are much less energetic than the ones that cause them to be emitted. So only those secondary electrons emitted near the surface cannot escape out of the material and be imaged. The closer to the surface the secondary electrons are emitted, the brighter the image.

The contrast depends, therefore, on the length of the path to the surface. The greater the path length, the fewer secondary electrons are imaged and the darker the region appears. The path length of an inclined structural feature, for example, is greater than that of one that is parallel to the surface. Figures 1 and 2 were both produced in the secondary-electron mode.

Most SEMs are equipped with a means to perform chemical analysis. Essentially, this method is the same as that discussed in the past four "Analytically Speaking" columns, whereby the electrons knock out other ones in the lower shells of the atoms. When electrons from shells farther from the nucleus take their place, the energy difference is emitted as characteristic X-rays.

As discussed earlier, the elements present in a sample can be identified from the wavelengths of their characteristic X-rays. The main difference between this fluorescent-analysis method and that attached to an SEM lies in the size of the area that can be analyzed. Because the electron beam in an SEM can be focused on a small area of the specimen, it is possible to chemically analyze very small structural features, such as a small codeposited particle. The limitation of the earlier method—the inability to analyze elements of low atomic number, such as hydrogen—also applies to the SEM attachment.

The characteristic X-rays can also be imaged in the SEM. It is therefore possible to determine how a given element is distributed. In Fig. 3, which represents the same areas as those shown in Fig. 1, characteristic X-rays of phosphorus were imaged. By careful analysis, it may be seen that the crevices in Fig. 1 contain more phosphorus than other areas.

A disadvantage of the SEM is that it is not possible to obtain regular diffraction patterns. It is therefore not possible to determine crystallographic information, such as the directions of the fine lines in Fig. 2 or the orientation of a given grain. It is possible to obtain a type of diffraction pattern called a bitter pattern—from large grains, but these patterns are very difficult to obtain and to interpret. **PASF**