Modern Microscopy on the Light Side
Analyzing Chemical States and Phases
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As an industrial consulting laboratory specializing in small particle, thin film, and surface analysis, instrumental techniques to solve problems involving contamination, failure analysis, processing control, and materials research are used on a daily basis. In many cases, elemental analysis for samples is sufficient to pinpoint problems and suggest solutions. However, some cases require a more detailed understanding of chemical states and phases in small particles and films than that typically obtained from light and electron microscopy and x-ray microanalysis.

The chemical states and phases in crystalline particles and thin films can be analyzed with several techniques found in many laboratories, including polarized light microscopy, x-ray diffraction, and electron diffraction. In combination with elemental analysis, these techniques oftentimes provide a very detailed understanding of the chemistry of particles and films. However, amorphous particles and thin films and surface treatments require different techniques for chemical state analysis.

Applications requiring chemical state determination in small, amorphous particles and thin films include the measurement of metal oxidation states, important in catalysis and mineralogy; thin film chemical bonding, particularly in electronics; carbon bonding, for surface treatment analysis; and, characterization of particle chemistry, for a variety of uses. Although many wet chemical and instrumental analysis techniques exist for bulk crystalline and amorphous samples, small particles and thin films require techniques with high spatial and depth resolution. Three techniques useful for the chemical state analysis and the imaging of particles and thin films are x-ray photoelectron spectroscopy (XPS or ESCA), Auger electron spectroscopy (AES), and electron energy loss spectroscopy (EELS). In many cases these techniques are used solely for elemental analysis, but all three spectroscopies measure electronic transitions that are sensitive to the chemical environment of the target atoms. Changes in chemical state and environment are manifested as changes in peak position and peak structure. Although the changes are often small and subject to substantial peak overlap, quantitative chemical state information can be obtained by curve fitting or multivariate analysis techniques.

XPS is perhaps the best developed of the techniques, with extensive databases and theoretical models for peak positions and structure. XPS is surface sensitive, with photoelectron elastic escape depths of 5-40 Å. An important advantage of XPS is that nonconductive samples can be analyzed with no major problems; thus, XPS has been widely used for polymer and mineral samples. New small area and imaging systems greatly extend the capabilities for the techniques for small samples and particles.

AES is used extensively in surface science and in some AEM instruments, but primarily for elemental analysis. Although many species exhibit AES chemical shifts equal to or greater than XPS, the complicated structure of AES spectra and the use of derivative spectra have prevented the widespread use of AES for chemical state analysis. With newer systems using electron-counting data collection and improved spectral processing routines, AES can be just as useful as XPS for chemical state determination on many samples. AES has the same surface sensitivity as XPS, and excellent spatial resolution and imaging capabilities, particularly with field emission sources.

EELS, performed in a TEM or STEM, is similar to XPS, but involves the measurement of energy lost by electrons passing through a thin sample. Thus, EELS is less surface sensitive than XPS or AES, which can be an advantage in the analysis of particles that might have surfaces altered by oxidation or other processes. Spatial resolution can be as good as or better than AES, depending on the sample. The near-edge structure of edge profiles can be treated by a variety of methods to obtain bonding information, particularly for transition metals. Improvements in data reduction methods should lead to a greater use of EELS for chemical state determination.

Two recent examples from our laboratory that required instrumental measurement of chemical states involved the analysis of bonding in a mixed metal nitride thin film and the quantitative determination of iron oxidation states in clay particles. In the first case, a protective nitride film, containing aluminum and other metals, on a vanadium alloy substrate was analyzed by XPS. Although elemental analysis showed nitrogen in the film, the manufacturer was not certain that under his deposition conditions he was producing the desired aluminum nitride film. Measurements of the aluminum photoelectron and Auger peak energies showed that the film was primarily aluminum nitride and confirmed that the client's process was working correctly.

The second example was a research project designed to determine the feasibility of quantitative measurement of Fe(II)/Fe(III) ratios in clays and other silicate minerals. Iron oxidation state ratios are important in controlling clay properties such as brightness and swelling. Although several techniques, including XPS and EELS, were shown to be able to measure iron oxidation states in clays containing several wt% iron, EELS proved most useful, due to its superior spatial resolution, probing depth, and sensitivity. Further refinements could allow EELS to complement Mössbauer and other bulk techniques for quantitative transition metal oxidation state determination in clays and other minerals.

These examples illustrate that chemical state determination by high spatial and depth resolution instrumental techniques can be used to answer a variety of questions beyond the realm of elemental analysis, even for amorphous samples and ultrathin films. Improvements in source brightness and spot size, multichannel detectors, and data reduction strategies will increase the ease and applicability of chemical bonding analysis by electron emission and energy loss spectroscopies.
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