



ANALYTICAL SERIES

Auger Electron Spectroscopy (AES) and Sputter Depth Profiling for Characterization of Metal Substrates and Pretreatment Coatings

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This article is the third in a series focusing on surface analysis techniques for studying the surface composition of solid materials in automotive paint operations. In a previous issue (Vol. 8, No. 2, pp 42-55, February 2011), x-ray photoelectron spectroscopy was described. This article provides an overview of the Auger electron spectroscopy technique and includes examples of its use for studying coatings. A subsequent issue will detail secondary ion mass spectroscopy (SIMS). Together, these complementary methods can be used to resolve the majority of technical issues that concern the surface chemistry of solid materials.

INTRODUCTION

Auger electron spectroscopy (AES) is a surface sensitive analysis method for determining the elemental composition of solid materials. It involves the measurement of electrons that are emitted from the solid as atoms relax from an excited state. From these measurements, one can determine what elements are present as well as their concentrations.^{1,2} This type of information is similar to what can be learned using x-ray photoelectron spectroscopy (XPS). However, there are several important differences that make each technique unique. AES is not as powerful as XPS in determining the chemical state of the surface elements; it typically only provides elemental composition information. However, AES can be focused to a very fine probe which can be used to determine the composition of sub-micron

sized regions.^{3,4} In this way, localized variations in elemental composition on a sub-micron scale can be determined. The small analysis area capability of AES makes it well suited for depth profiling experiments by combining it with ion sputtering. These experiments can be used to determine the composition of thin films and for examining buried interfaces.⁵

While several variations of AES exist, the most common method employs a focused electron beam to excite the specimen. Since electrons carry a negative charge, insulating specimens, such as organic coatings, are difficult to examine as the specimen becomes electrically charged. Fragile materials can be damaged by electron bombardment which alters the elemental composition of the surface. Therefore, AES is not commonly used to characterize organic paints and coatings. However, it is extremely useful for studying defects at the surface of metals and in inorganic pretreatment coatings.^{6,7} As such, most applications of AES in the coatings industry involve the study of substrates and base materials to ensure they are adequately prepared prior to coating.

THEORY

The process for generating Auger electrons begins with an electron beam transferring energy to an atom in the solid causing an electron to be ejected from a core energy level^{1,2} (see the schematic diagram in *Figure 1*). This atom is left in a high energy state and it relaxes by

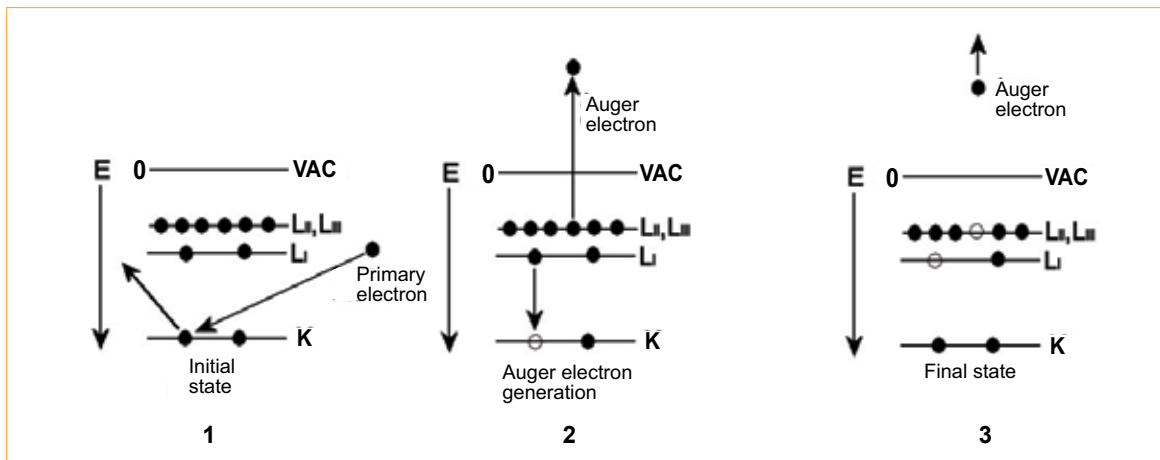


Figure 1—Schematic of the Auger electron generation process. Each image represents the energy levels of an atom in the solid. The dark circles are electrons and the open circles are vacancies. In panel one, the initial state, an incoming primary electron transfers energy to an electron in the K shell, ejecting it from the solid. In panel two, an electron from the L_{II} shell fills the vacancy in the K shell and an additional electron from the L_{III} shell is ejected into the vacuum. In panel 3, the final relaxed state of the atom is shown with the Auger electron (that we measure in this experiment) traversing through the spectrometer.

filling the core level vacancy with a valence level electron. Additional excess energy then leaves the atom by one of two mechanisms. In the first mechanism, the energy can leave as an X-ray photon, which is the basis for energy dispersive x-ray spectroscopy, the popular elemental analysis method used in scanning electron microscopes (SEM). In the second mechanism, excess energy can be transferred to another valence electron, the Auger electron, which gains enough energy to leave the atom. The process is named after the French scientist, Pierre Auger, who discovered this effect.⁸

The energy imparted to the Auger electron is dependent on the position of the electron energy levels involved. It is unique for each element and is governed by the following equation:

$$E_{KLL} = E_K - E_L - E_L \quad (1)$$

where the energy level labels are those shown in *Figure 1*. Thus, measurement of an Auger electron's energy will give the identity of the atom that emitted that electron. This is commonly done by comparing the energy of the Auger line to values from look-up tables that were generated with known compounds.⁹

One important aspect of the Auger process is that the energy of the emitted electron is completely independent of the excitation. This can be easily seen in equation (1) in that the excitation beam energy is not included. This feature allows the analyst wide latitude in choice of the excitation source used to probe the sample. X-rays, ions, positrons, and electrons have all been used to excite samples and generate Auger electrons. In fact, Auger peaks are commonly observed in XPS spectra. However, due to the ease in generating, focusing, and directing electron beams, most

AES experiments are performed using electron excitation.²

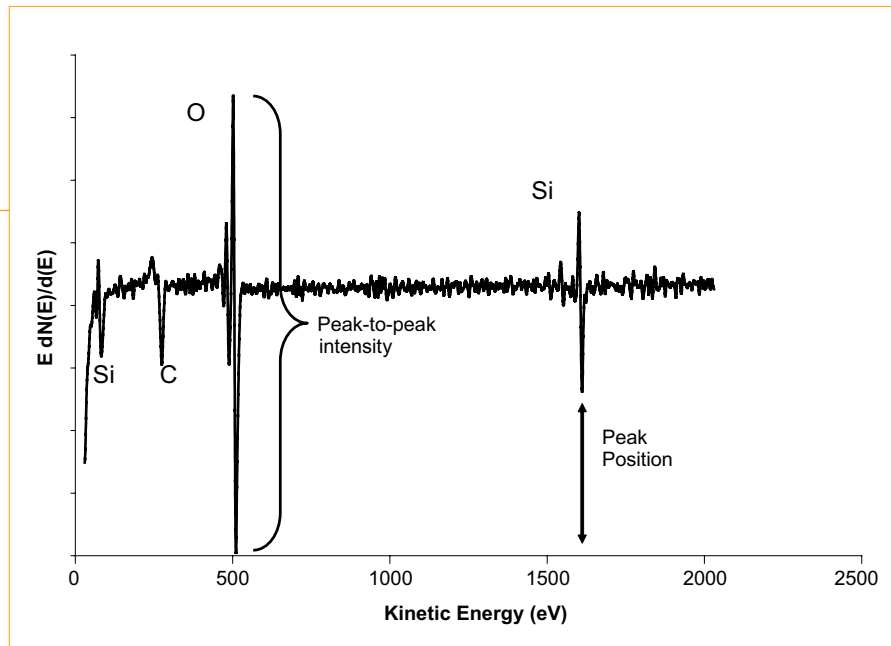
Auger electrons typically have energies in the 50–2200 eV range and a spectrum is shown as a plot of electron intensity as a function of electron energy. Electrons in this energy range can only penetrate short distances in solid materials before suffering energy-losing collisions. Hence, only Auger electrons that are generated in the outer 1–2 nm of the surface can escape the solid where they can be measured.¹⁰ This makes the technique very surface sensitive. For example, a human hair is approximately 80 μm in diameter which is over 10 million times larger than the Auger sampling depth.

The numbers of emitted Auger electrons from a given chemical element are proportional to the concentration of that element at the sample surface. Therefore, comparing peak intensities gives a semi-quantitative measure of the concentrations of surface elements. Results are typically presented in atomic percent, normalized to 100% of the detected elements.⁹ AES can detect all elements in the periodic table except for hydrogen and helium as these elements do not have enough electron energy levels to generate Auger electrons.

ANALYSIS METHODS

The electron excitation source is a versatile probe that can be focused and directed at small regions to give an analysis of sub-micron sized areas. It can also be rastered over large areas to give an average surface composition of the specimen. Use of this probe for excitation does have some drawbacks, however. Detection of the Auger electrons is difficult as scattered primary electrons from the excitation source contribute to a large background in the spectrum. Historically, this problem is dealt

Figure 2—An AES survey scan of silicon dioxide. Peak position shows what element is present and peak-to-peak intensity is proportional to how much of a given element is present.



with by viewing AES spectra as the first derivative of the electron intensity¹¹ (see *Figure 2*). When viewed this way, peak positions in the spectrum are measured from the negative excursion of the derivative peak and intensities are measured from the largest positive excursion to the largest negative excursion, which is called the peak-to-peak intensity.

One of the most useful features often employed with AES in characterizing thin films and buried interfaces is a technique called sputter depth profiling (SDP). In SDP, the AES experiment is combined with an ion sputtering source which is used to remove thin layers of material from the sample. This exposes sub-surface regions to AES analysis. By alternating ion sputtering and AES analysis, the changes in elemental composition as a function of depth into the sample can be followed.⁵

Ion sputtering occurs when energetic ions, usually noble gas ions, are directed at a solid surface. Through ballistic effects, energy is transferred from the ions to the surface resulting in atoms from the solid acquiring enough energy to leave the sample. Over time, this process exposes successively deeper layers in the solid to the surface where they are characterized by AES. The elemental composition at a given depth is determined from the peak-to-peak intensity of the AES data. These compositions are then plotted as a function of sputter time.

A typical example of an AES depth profile is shown in *Figure 3*. The elemental composition is shown on the y-axis and the sputter time (which is proportional to sputter depth) is shown on the x-axis. The elemental composition at the surface is at the left edge of the graph and how the com-

position changes in successively deeper layers is shown as the graph progresses from left to right.

Ideally, one would like the sputter process to peel layers successively, much like removing layers one at a time from an onion. In reality, the sputtering process leaves behind a damaged surface with layers somewhat intermixed. Thus, the interface between layers is somewhat indistinct from this intermixing. The sputtering process also can alter the elemental composition somewhat as some elements may sputter more easily than others. This artifact is called preferential sputtering. Finally, while there is a proportional relationship between sputter time and depth, different materials sputter at different rates which can vary by over a factor of 10. Thus, calibration of the depth scale in this experiment requires standards of known thickness that consisted of the same or very similar compositions as the material being measured. Despite these artifacts, AES and SDP are very good at making relative comparisons between samples with different surface compositions.

ANALYSIS EXAMPLES IN PAINT TECHNOLOGY

The small area and thin-film analysis capabilities make AES an ideal method for characterizing metal substrates and their interactions with pretreatment/conversion coatings. Often the first step in painting metals is a chemical treatment to passivate the material. This treatment replaces the surface oxide that is present on most metals with a more chemically stable material. This coating pro-

cess is often referred to as a metal pretreatment or conversion coating.

An example of using AES to characterize metal substrates is shown in *Figure 4* which is a photograph of a galvanized steel panel used for construction of body panels on an automobile. This panel has several dark stains that interfere with the vehicle coating process. AES depth profiles from a stained region and an unstained region are shown in *Figure 5*. The data from the unstained region consists of a thin carbon-containing film that disappears after a few cycles of ion sputtering. This carbon contamination layer is often referred to as adventitious carbon as it collects on the surface of all metal specimens exposed to the environment, unless special precautions are taken. Beneath this layer is a thin region containing zinc oxide, as zinc and oxygen are the only elements present in significant concentrations. This layer is removed from the surface after a short (less than one minute) amount of sputtering, indicating that it is an extremely thin layer. Most metals will oxidize in air (gold is one exception) unless protected by a coating, so the presence of a thin zinc oxide film is expected.

In contrast, the depth profile from the stained region shows an oxygen signal that stays high for a significantly longer period of ion sputtering. This shows that the stain is a thick layer of zinc oxide. Based on these results, it was deduced that the panel was contaminated with a corrosive material that resulted in growth of a significantly thick zinc oxide film. Thick oxides are known to interfere with subsequent painting processes such as the zinc phosphate pretreatment coating and/or electrocoat deposition. This oxide stain results in uneven deposition of the zinc phosphate and electrocoat layers, causing a defect called mapping.¹² In mapping, this

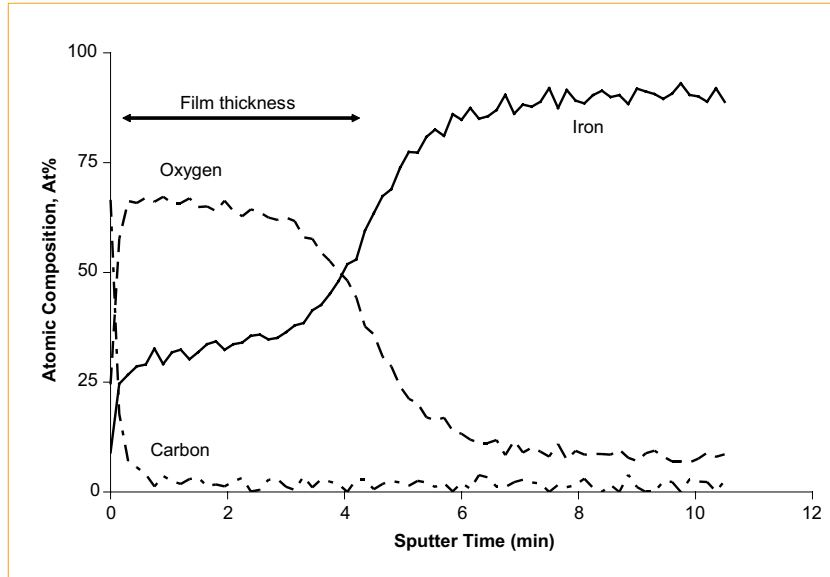


Figure 3—A sputter depth profile through the surface oxide layer on a steel panel.

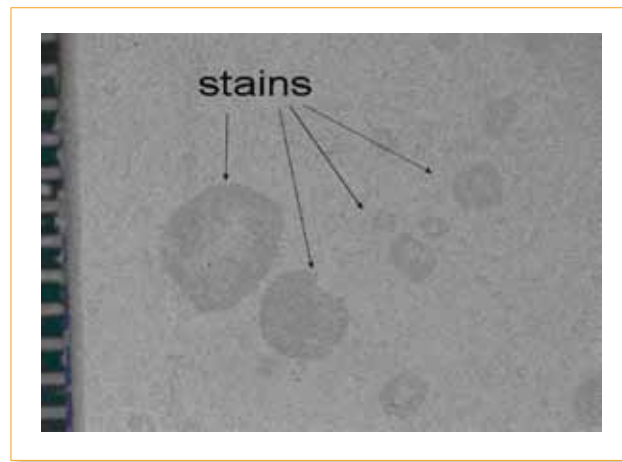


Figure 4—A reflected light micrograph of stains on a galvanized steel panel. The scale at left is 1 mm/division.

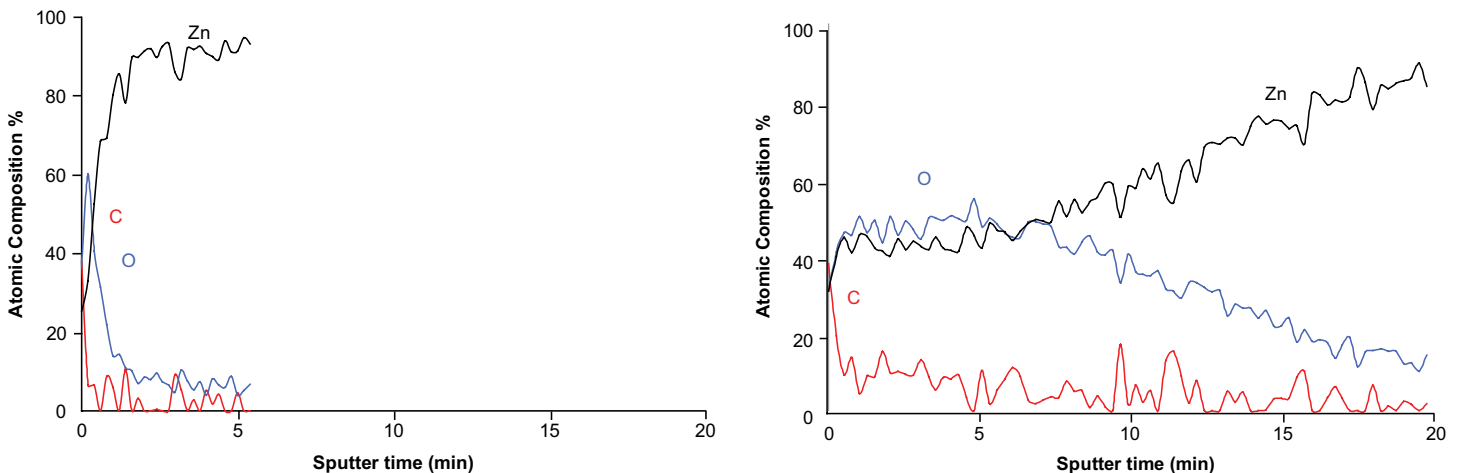


Figure 5—Sputter depth profiles of an unstained region (left) and a stained region (right) from the galvanized steel panel shown in *Figure 4*.

Figure 6—SEM image (top) and iron AES map (bottom) from a zirconium oxide coating on a CRS substrate. The light regions on the AES map show regions of high relative iron concentration.

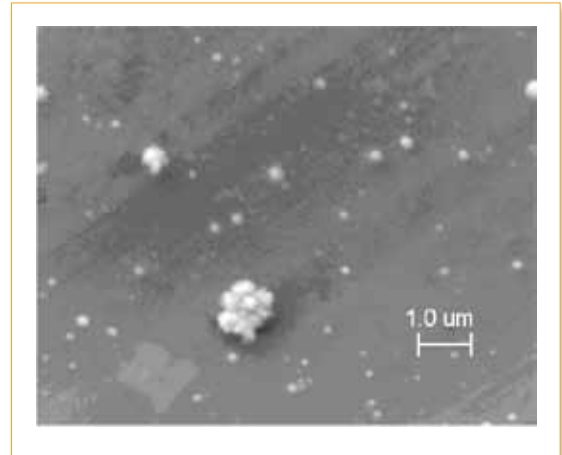
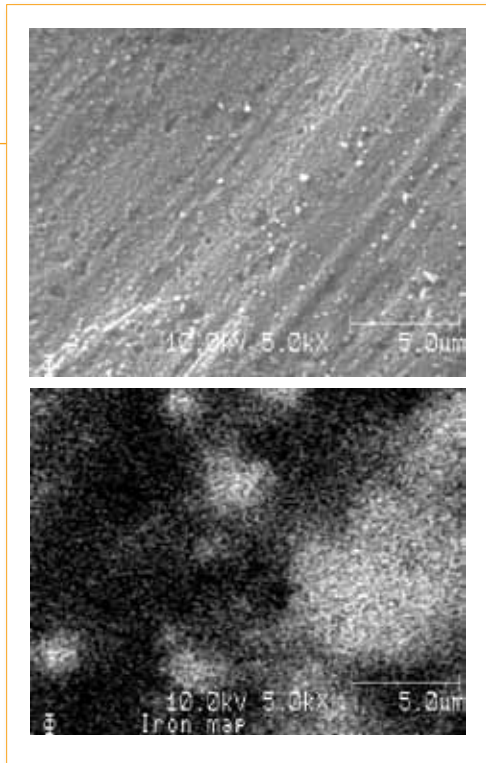


Figure 8—SEM image of the zirconium oxide coating on aluminum 6111.

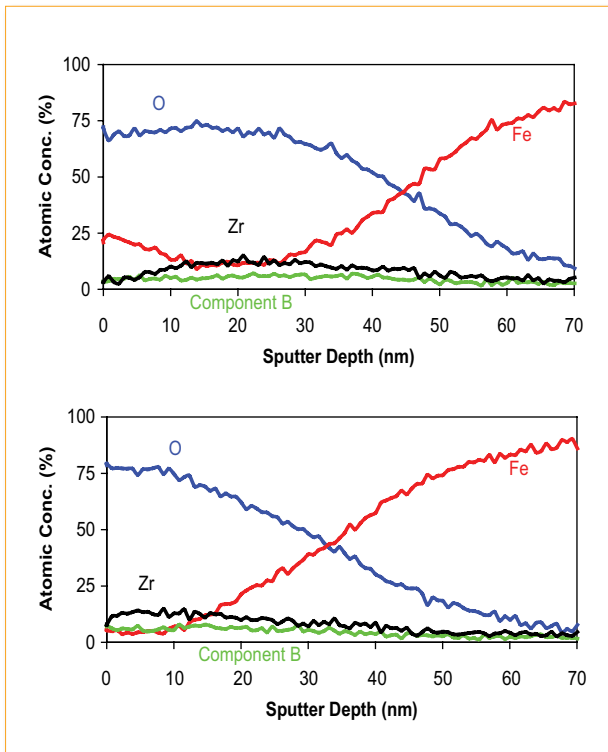


Figure 7—Sputter depth profiles from the CRS panel. The top profile is from the iron-containing region and the bottom profile is from the iron-free region. These correspond to light (top) and dark (bottom) regions in the iron elemental map shown in Figure 6. Component B is a proprietary additive in the zirconium oxide formulation.

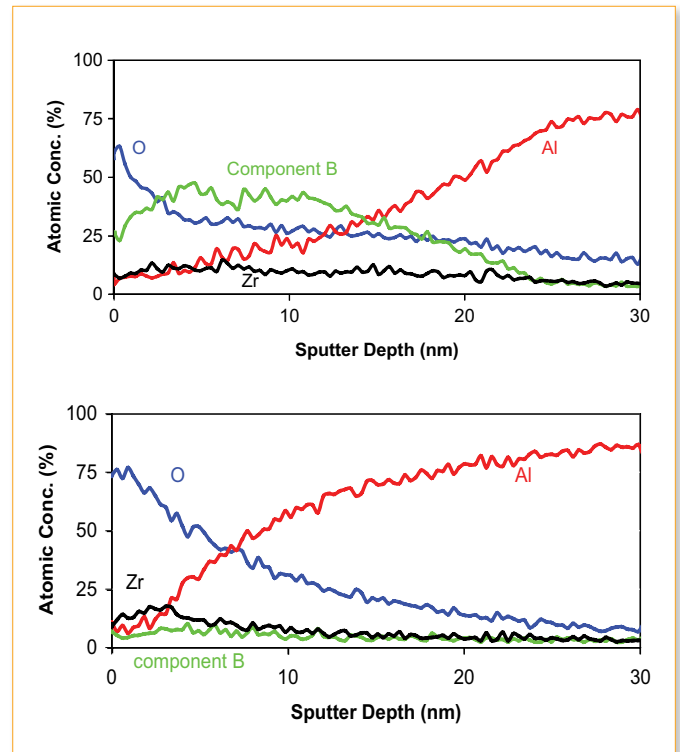


Figure 9—Sputter depth profiles from the zirconium oxide film on aluminum 6111. The top profile is from a nodule region and the bottom profile is from regions between nodules.

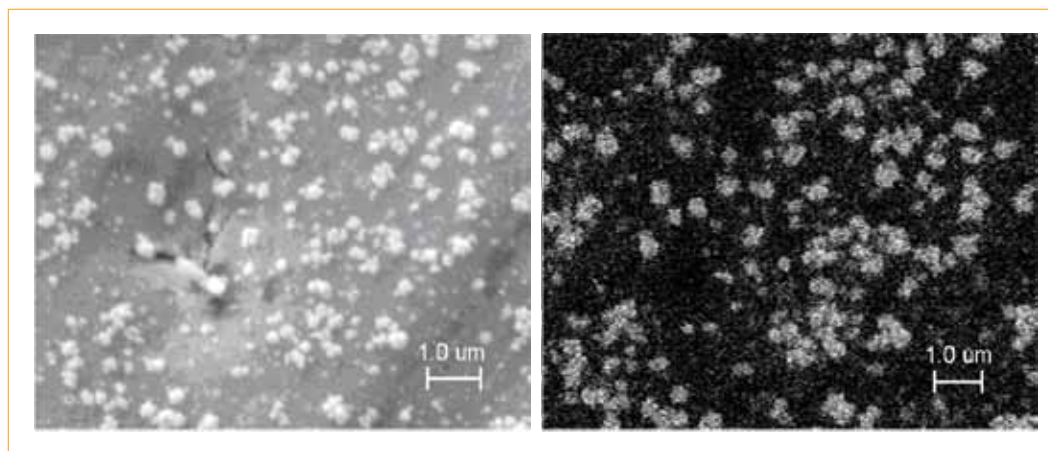


Figure 10—A secondary electron image (left) and the corresponding Auger map for major component B (right) for a zirconium oxide film deposited on aluminum alloy 6111.

uneven coating propagates through all the paint layers resulting in a ridge or “map” that is visible in the final paint job. Hence, metal with stains of this type are unacceptable for construction of car bodies.

Recently, the automobile industry has been investigating the use of zirconium oxide-based pretreatment films to replace the current zinc phosphate-based pretreatment technology.¹³⁻¹⁵ Traditionally, the quality of the zinc phosphate coatings is characterized using SEM-EDS methods. However, these new zirconium oxide-based coatings are so thin that they cannot be easily detected. The high spatial resolution, surface, and thin-film analysis capabilities of AES make it an ideal method for characterizing thin films such as zirconium oxide-based pretreatments.

The SEM image and a corresponding AES iron elemental map of a zirconium oxide pretreatment film on cold-rolled steel are shown in *Figure 6*.⁷ The film appears as a collection of small round particles in the SEM image. However, the size distribution of particles is not uniform. The bright white spots on the iron elemental map are regions of high iron signal at the surface of the panel. Note that these regions are localized and do not correspond to any visible feature on the SEM image.

Depth profiles from the iron-containing and iron-free areas show that there are two distinct regions found on this surface (see *Figure 7*). The regions that show iron in the elemental map have a bi-layer structure with an iron oxide film on top of the zirconium oxide coating. It is likely this surface iron oxide layer formed by redeposition of iron onto the panel after the zirconium oxide film had formed. The other regions on the CRS panel only contain the single zirconium oxide layer. This type of bi-layer structure would be extremely difficult to discern using SEM-EDS analysis methods. The films are so thin that the sampling depth of SEM-EDS would be greater than the layer thicknesses, meaning significant signal would come from the iron substrate. Separating the iron signal of the surface film from that of the


substrate, while trivial with AES, would be an extreme challenge with SEM-EDS.

Another example of the utility of AES for characterizing these materials concerns the coating formation on an aluminum alloy substrate.¹⁶ A representative SEM image of the coating on aluminum alloy 6111 is shown in *Figure 8*. The surface is decorated with large circular nodules that are well defined and separated from other particles on the surface. The rest of the surface is relatively featureless with a few small circular particles spread randomly on the surface.

Depth profiles from each region are shown in *Figure 9*. Regions between the nodules are covered with a relatively thin zirconium oxide coating as shown in *Figure 9*, bottom. The nodules are significantly thicker and are composed of a mixture of zirconium oxide and a second element from the coating bath, labeled major component B (MCB); see *Figure 9*, top. The content of MCB in these nodules is significantly greater than the zirconium oxide amount. The AES elemental map and SEM image in *Figure 10* confirm a one-to-one correspondence between these raised nodules and the selective deposition of MCB.

SUMMARY

AES is an extremely useful tool for the coatings industry that is able to yield detailed information specifically regarding the preparation of metal surfaces for coating and inorganic corrosion protective conversion layers that are often the first coating step. The high surface sensitivity of AES allows for characterization at the near surface where the environment may impose chemical changes that can be radically different from the bulk material content. The high spatial resolution of AES allows for excellent imaging capabilities and the ability to identify surface defects with high precision. Sputter depth profiling greatly enhances the characterization capability of AES by providing elemental composition

information as a function of depth. In all, the high surface sensitivity at high resolution coupled with depth profiling give AES a unique ability to provide spatially resolved chemical information that cannot be attained with other images techniques such as SEM which probe considerably deeper into a material surface. 

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