Applications Note

A Complimentary Spectroscopic Characterization of a Corroded Tinplate Sample with XPS and AES

Overview

A corroded tinplate sample was analysed by XPS and AES techniques using the Kratos AXIS Supra$^+$ to gain an insight into the extent and mechanism of corrosion. XPS was firstly used to analyse the composition of the surface and from this, characterize the Sn 3d and Fe 2p oxidation states. The corroded area was then examined using SEM to pinpoint significant positions for further analysis with AES. The resulting data indicates the position at which corrosion is initiated and examines the extent of this corrosion across an area of the surface.

Introduction

Both X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) are important surface analysis tools. While XPS can be used to analyze the chemical state of surface elements, AES can examine the elemental distribution of microdomains. The ability to utilize XPS and AES techniques coincidently at a specific analysis location is a significant advantage of the Kratos AXIS spectrometers.

Tinplate consists of a low-carbon containing steel sheet coated with a thin layer of tin metal. This coating greatly improves the corrosion resistance and brightness of steel and has therefore been widely used in industries such as food canning, electronic devices and chemical paints. Unfortunately, this material is still susceptible to corrosion under certain conditions, with pitting corrosion found to occur at specific areas on the surface. In this applications note, the extent to which a tinplate surface has corroded is studied using XPS and AES.

Experimental

The surface analysis of a corroded tinplate material was performed using the state-of-the-art Kratos AXIS Supra$^+$ spectrometer, where high resolution XPS spectra were acquired over a small energy range for each particular element. The instrument was also configured with a 10 keV field-emission electron source for Auger Electron Spectroscopy (AES), Scanning Auger Microscopy (SAM) and Secondary Electron Microscopy (SEM).

The field-emission electron source employs a beam of electrons as a surface probe. Since the probe electrons can be focused to diameters < 0.5 µm, high spatial resolution analysis

can be performed. By rastering the focused electron beam synchronously with a video display, using SEM techniques, one can produce images and element distribution maps of the surface. The ability to pinpoint exact areas for analysis makes AES especially suited to investigate small features, such as the corroded area on this sample surface.

As a result of an electronic rearrangement within an atom, Auger electrons are emitted from the surface. These electrons are characteristic of each element present at the surface. Only those electrons that emerge from the topmost atomic layers contribute to the spectrum, therefore giving rise to the high surface specificity of this technique. AES detects all elements except hydrogen and helium to a sensitivity better than 1 atomic percent.

Results and Discussion

Surface analysis of the corroded sample using XPS reveals both Sn and Fe present in the survey spectrum. High resolution spectra of the Sn 3d and Fe 2p regions were acquired to examine their chemical states in more detail. As can be seen from Figure 1a, there are two chemical states observed in the Sn 3d region, where the major chemical state is assigned to SnO_2 (486.5 eV) and the minor to elemental/metallic Sn (484.9 eV). Figure 1b shows the Fe 2p region and reveals the presence of Fe_2O_3 oxide (710.4 eV) on the surface. This detection of Fe indicates the breakdown of the tin coating due to corrosion.
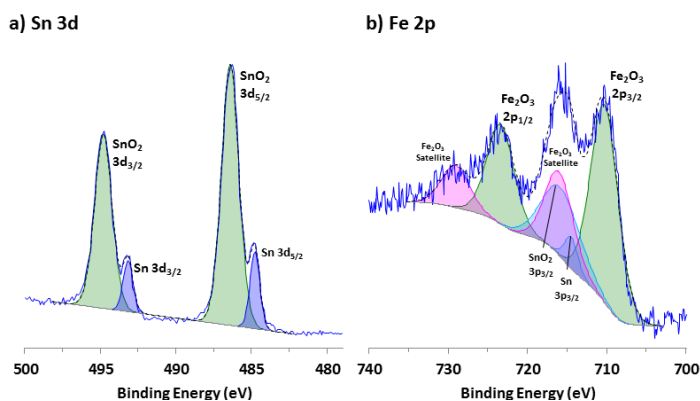

Figure 1. XPS spectra for the a) Sn 3d and b) Fe 2p regions.

Figure 2a shows a SEM image of the corrosion area detected by the secondary electron detector. The image reveals that there are different morphological areas on the surface of the tin plate, which are labelled #1 - #5. AES was performed at all of these locations to analyze the extent of surface corrosion.

Figure 2b displays the differentiated Auger spectra at each individual position. The absence of Fe at sites #1 and #2 indicates that corrosion at these positions is minimal. There is however an increase in carbon content at site #3 which implies that there are more foreign pollutants present. The presence of Fe is also

visible at this site, with the Fe content further increasing from positions #4 to #5. This implies that position #3 is slightly corroded, whilst positions #4 and #5 are severely corroded.
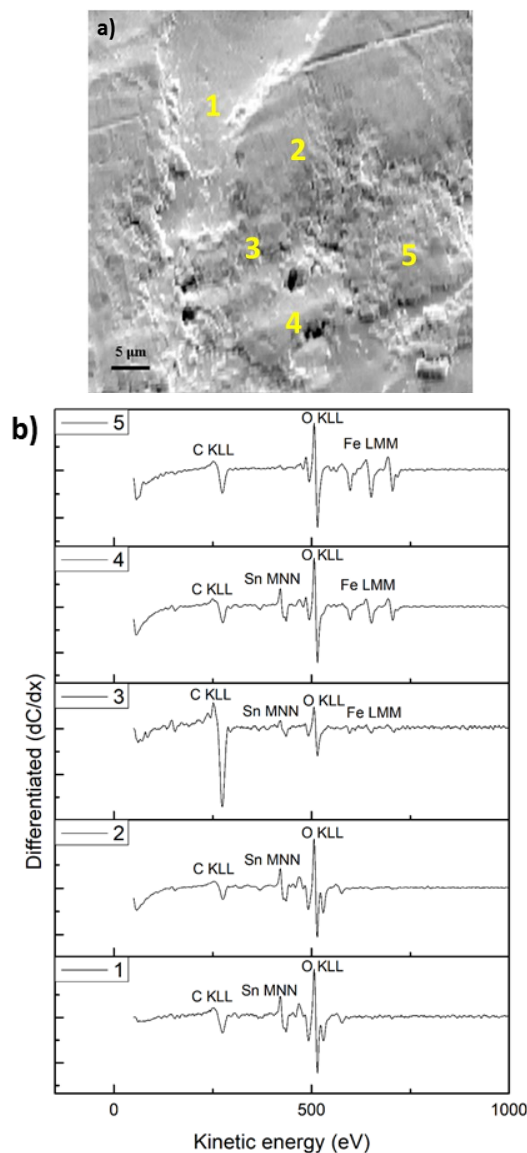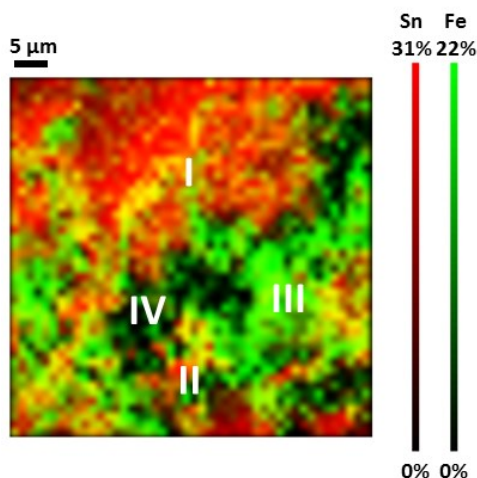

Figure 2. a) SEM picture of the corroded tinplate sample and b) differentiated Auger spectra of the labelled positions.

In order to further characterize the Sn and Fe content of the corroded structure, the surface was analyzed using Scanning Auger Mapping (SAM). The resulting Auger map for the corroded areas (displayed in Figure 3) shows the surface can be divided into four regions. Analysis of this Auger map indicates that slight corrosion has occurred at region I, region II is a corroded semi-naked region, region III is completely Sn free and region IV is a contaminated attachment region. In agreement with the Auger spectrum, this Auger map also shows that there are more pollutants at position #3/region III.

Since the electrode potential of Fe is lower than that of Sn, Fe is relatively easy to corrode in comparison to Sn. It can

therefore be speculated that corrosion starts from region III, after which, electrochemical corrosion occurs between the Fe layer and the Sn layer. As elemental Fe gradually forms Fe_2O_3, the coated Sn layer is delaminated which results in the exposure of the steel substrate. The corrosion area in turn gradually expands, resulting in a largely corroded area.

Figure 3. Overlaid Auger maps of Sn (red) vs. Fe (green).

Conclusions

The structure of a corroded tinplate sample was analyzed by XPS and AES, which infers the corrosion initiation point and corrosion growth process. The results show that the AXIS Supra$^+$ spectrometer can effectively analyze the elements present and their distribution within a microscopic area. This combination of these techniques is extendable to many other industries and research fields.

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