

Corrosion Analysis in Metallurgical Samples: A PHI 710 Multi-technique Approach

Overview

The annual cost of corrosion in developed countries is estimated to reach 3-4% GDP.¹ Understanding corrosion mechanisms is of critical importance in the effort to mitigate corrosion and its effects on the strength and permeability of materials. To date, studies of the initial stages of corrosion using advanced surface characterization techniques are scarce.² Key challenges in the investigation of corrosion mechanisms include lack of surface sensitivity, chemical characterization limitations, and poor spatial resolution. Here, a carbon steel sample containing defect sites in the form of inclusions of unknown chemical composition is analyzed using a PHI 710 Multi-Technique Scanning Auger Nanoprobe. Rapid location of the inclusions is achieved followed by ultra-high lateral resolution (~ 8 nm) chemical imaging. In situ depth profiling of the inclusions further allows nano-volume analysis and corrosion site characterization.

Sample Measures

The PHI 710 Multi-Technique Scanning Auger Nanoprobe is a true UHV electron microscope equipped with surface sensitive Auger electron spectroscopy (AES) and optional energy dispersive x-ray spectroscopy (EDS), electron backscatter diffraction (EBSD), and focused ion beam (FIB). A carbon steel sample containing inclusions of unknown chemical composition was analyzed using a Physical Electronics 710 Scanning Auger Nanoprobe. These inclusions were found to be initiation sites of corrosion.

Results

An inclusion on the surface of the carbon steel was located by SEM and analyzed by EDS, which showed Mn, S, and Fe present at the center of the particle (Figure 1, left and center). In addition to Mn, S, and Fe, Auger spectroscopy also detected 6 atomic percent of copper (Figure 1, right). The presence of copper in MnS inclusions had not previously been detected by EDS and was totally unexpected. Note that AES electrons originate from the top ~ 5 nm of the sample surface, while EDS electrons originate from much deeper within the sample (a few to several microns).

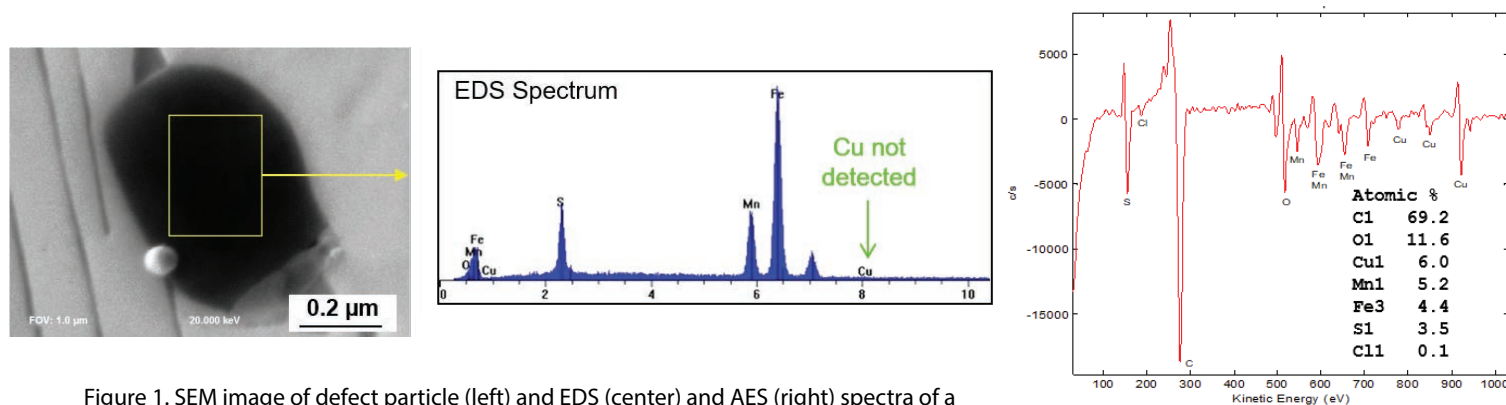


Figure 1. SEM image of defect particle (left) and EDS (center) and AES (right) spectra of a region of interest taken from the particle (yellow).

Auger elemental mapping confirms that the Mn, S, and Cu are located only within the defect particle and not in the surrounding Fe substrate (Figure 2). The AES map of Fe, together with the Fe detected in the particle from the AES spectrum, confirm that the defect particle consists of a small, but finite amount of Fe, which is not obvious from the EDS data alone.

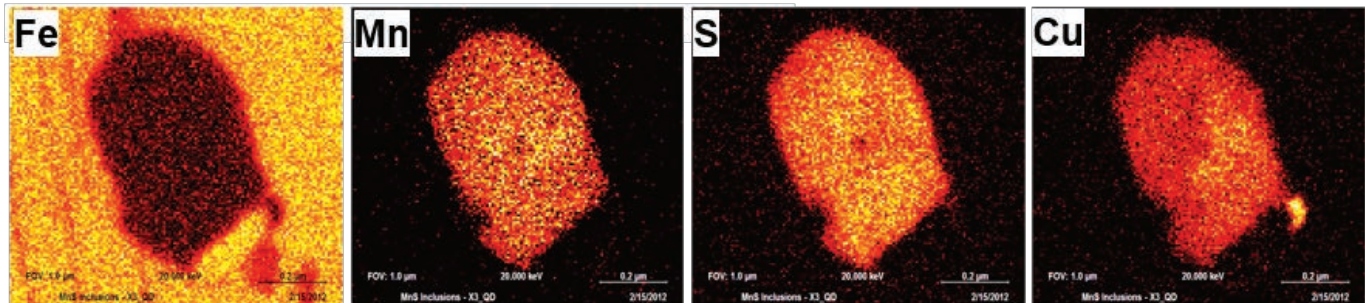


Figure 2. Auger elemental maps of defect particle. Field of view is 1 µm.

An Auger depth profile on the particle (Figure 3) shows the thickness of the Cu to be ~5 nm. The profile indicates that the Cu may be present as CuS on the surface of the MnS particle.

A second MnS inclusion on the carbon steel was rapidly located by SEM/EDS and subsequently mapped with AES (Figure 4). AES maps show that S diffuses some distance away from the inclusion, but that Mn does not spread. In-situ EBSD maps show the orientation of Fe grains and strain fields at the same region and help predict where localized corrosion will take place when the surface is exposed to a corrosive environment.

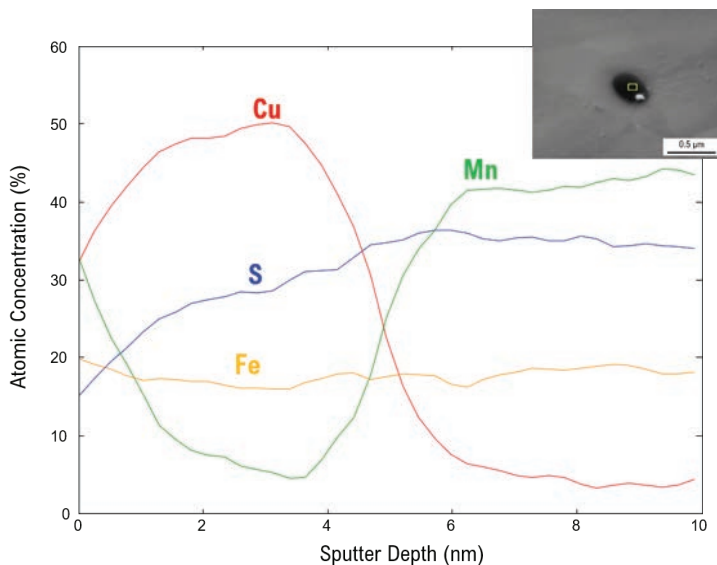


Figure 3. AES depth profile of MnS inclusion. The depth profile data was acquired from a region of interest on the particle (inset, yellow).

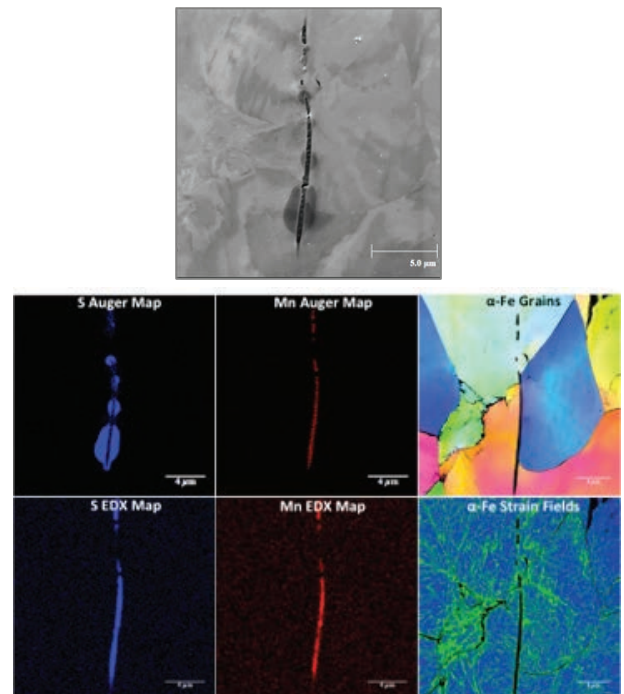


Figure 4. SEM image (top) and corresponding AES, EDS, and EBSD maps of the inclusion site (bottom).

Conclusion

Corrosion analysis is readily achieved using a multi-technique Auger instrument. The combination of SEM, AES, EDS and EBSD available on a single UHV system allows for the rapid analysis of defect particles or inclusions in metallurgical samples. Here, EDS was used to rapidly locate MnS particles on the carbon steel surface. AES analysis further revealed the presence of a ~5 nm CuS layer on top of the MnS particle. At a second defect site, EDS quickly detects Mn and S and AES shows a different distribution of S at the sample surface compared to the bulk S signal seen in EDS. Furthermore, EBSD is used to identify grain boundaries and strain present at the inclusion site without breaking vacuum.

References:

- [1] Renner, F., Stierle, A., Dosch, H. et al. Initial corrosion observed on the atomic scale. *Nature* 439, 707–710 (2006).
- [2] Dwivedi, D. and Lepková, K. and Becker, T. 2017. Carbon steel corrosion: a review of key surface properties and characterization methods. *RSC Advances*. 7 (8): pp. 4580-4610.

Acknowledgement:

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