

Wednesday Afternoon, November 12, 2014

Applied Surface Science

Room: 316 - Session AS+BI+MC-WeA

Practical Surface Analysis I

Moderator: Alexander Shard, National Physical Laboratory, Christopher Szakal, National Institute of Standards and Technology (NIST)

2:20pm **AS+BI+MC-WeA1 The Application of XPS to Study Corroded Stainless Steel Surfaces**, *Helen Brannon, S.J. Coultas, J.D.P. Counsell, S.J. Hutton, A.J. Roberts, C.J. Blomfield*, Kratos Analytical Limited, UK, *J. Morrison*, The University of Birmingham, UK

The corrosion of structural materials in contact with hot, pressurised water, which is heavily dependent on the condition of the exposed surface, is a common problem in nuclear power processes. This side reaction is undesirable due to the reduced heat transfer efficiency which is caused by the deposited oxide layers.

X-ray photoelectron spectroscopy (XPS) is demonstrated as a quantitative surface analysis technique which can be used to determine the type of corrosion chemistry that occurs.

Stainless steel (316L) substrates containing 70% Fe, 18% Cr, 8% Ni and 2% Mo (as well as a low concentration of impurities) are suspended in water at 300 °C for 1000 hours. A metal oxide double layer is found to develop over time on the stainless steel surface: the top layer is a mix of magnetite (Fe₃O₄) and Nickel Ferrite (NiFe₂O₄) and the bottom layer is a mix of magnetite and chromite (FeCr₂O₄) (below is the base metal).

A high energy, medium sized argon gas cluster source is shown to be advantageous compared to a conventional monatomic argon ion source when depth profiling such layered structures, causing reduced structural and chemical damage from the ion beam sputtering process.

Data acquisition at small analysis areas gives well resolved spectra, revealing the multi-layered oxide structures produced from the corrosion process.

[1] Depth profiling of the Passive Layer on Stainless Steel using Photoelectron Spectroscopy, Wendy Fredriksson, Uppsala University

[2] Applied Surface Science, 257, (2011), 2717–2730

[3] The Radiochemistry of Nuclear Power Plants with Light Water Reactors, By Kark-Heinz Neeb

2:40pm **AS+BI+MC-WeA2 Molecular Characterization of Lubricant Degradation Produced in a Tribological Wear Test Using TOF-SIMS and Scanned Microprobe XPS Imaging**, *Gregory Fisher, S.S. Alnabulsi*, Physical Electronics Inc., *T. Le Monge*, Ecole Centrale de Lyon - LTDS, France, *J.S. Hammond*, Physical Electronics Inc.

Scanning Auger microscopy (SAM) and x-ray photoelectron spectroscopy (XPS) are today the most widely used surface analysis techniques for quantitative elemental and chemical analysis in tribology. Modern SAM instrumentation allows the elemental and chemical analysis of features at spatial resolutions down to 10 nm while modern scanning x-ray microprobe XPS instrumentation can provide even more complex chemical state surface characterization at a sub-10 μm spatial resolution. The use of a scanned x-ray microprobe enables chemical state imaging at a low x-ray fluence to minimize disturbance of the surface chemistry. Notwithstanding the aforesaid capabilities, the elucidation of molecular chemistry and lubricant degradation that occurs via tribological wear remains intractable by SAM and XPS analysis alone.

This study focuses on the application of time-of-flight SIMS (TOF-SIMS), with supporting XPS analysis for quantification, to determine the molecular decomposition and metal-organic reaction products of lubricants used in bio-diesel fuel. The test specimens were produced on a reciprocating cylinder-on-flat tribometer to simulate the piston / cylinder contact geometry and dynamics that are typical of internal combustion engines. The lubricant used in the bio-diesel fuel consists of C₁₈ fatty acids at a concentration in the high part-per-million (ppm) range. The TRIFT mass spectrometer of the PHI nanoTOF provides an advantage for this study in that the wear track topography is effectively decoupled from the molecular characterization and imaging. The HR² imaging mode of the PHI nanoTOF, simultaneously achieving a spatial resolution < 400 nm and a mass resolution of ≈ 10,000 m/Δm, is an important asset in molecular identification and imaging.

3:00pm **AS+BI+MC-WeA3 Surfaces and Interfaces of Real-World Products: What Do We Really Need to Know and What Are The Best Ways to Find Out?**, *Anna Belu, L. LaGoo, W. Theilacker*, Medtronic, Inc.

INVITED

Real world components and products come in many shapes, sizes and materials, and their surface properties are critical for performance in many areas including adhesion, biocompatibility, corrosion, lubricity, and welding. Surface analysis tools are often employed to gain a fundamental understanding of surface properties of products in development, as well as to evaluate properties of surfaces and interfaces of products that are not performing as specified. This presentation will discuss best practices for analysis of real world samples in an industrial, mainly R&D, environment.

The culture of industry is typically fast paced with the goal being to get product into the hands of consumers as soon as possible. In this environment, the surface analyst is faced with the challenge of providing high quality information from a variety of materials and issues in a short amount of time. The requestor often wants a simple answer and is unaware that the analyst progresses through a series of questions such as What is the issue? What are the best tools to find the answer to the issue? Are the tools up to the task? Is the lab up to the task? What types of results are necessary? What types of samples are helpful? What is the most efficient way to obtain the data? Is it OK to use one tool and analyze one point on one sample? What are efficient ways to analyze data? Do the results solve the problem? This presentation will discuss the consideration that goes into providing high quality data in a short amount of time and include several examples of surface analysis from real world products.

4:20pm **AS+BI+MC-WeA7 Forensic XPS Surface Characterization of Cosmetic Trace Evidence**, *Brian Strohmeyer*, Thermo Fisher Scientific, *R. Blackledge*, Independent Consultant

X-ray photoelectron spectroscopy (XPS) has a long distinguished history of providing important information on the surface chemistry of a wide variety of materials including: catalysts, ceramics, coatings, fibers, glass, metals, oxides, polymers, powders, semiconductors, thin films, and many others. In addition, studies involving the use of XPS have addressed numerous complex materials problems in a multitude of diverse fields such as: adhesion science, chemical surface treatments, corrosion, electronics, medical devices, oxidation, solar cells, and so on. Despite its many advantages and unique capabilities as a surface analytical technique, XPS has not been widely used in forensic science for the examination of specimens gathered at the scene of a crime. The main reasons for the lack of forensic studies involving XPS are: 1) the lack of standard forensic XPS methods and standard samples for comparison to real world samples; and 2) the historical long analysis times (hours per sample) and large analysis areas (several square millimeters) compared to other common forensic techniques such as Raman microscopy and scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM/EDS). Advances in XPS instrumentation over the last decade have now improved analysis times to minutes per sample and analysis areas down to the range of tens to hundreds of micrometers. Also, recently developed argon cluster ion sources now allow "soft" depth profiling of organic and polymeric species with minimal ion beam damage, thus preserving the chemical state information available from XPS. XPS, therefore, has increased potential for new forensic science applications involving the surface characterization of trace evidence materials. Previous work has demonstrated the potential of XPS for revealing unique surface chemical information for gunshot residue (GSR) and textile fibers. This presentation will describe the use of XPS for forensic characterization of cosmetic materials such as hair chalks, shimmer, and glitter. These types of cosmetic materials have a high probability of transfer and retention if a victim struggles with an assailant during an abduction or sexual assault and could help support an association between an assailant, a victim, and a specific crime scene in a specific case circumstance. XPS is an excellent technique for characterizing residues of these cosmetic materials.

4:40pm **AS+BI+MC-WeA8 Industrial Applications of Surface Analysis**, *William Stickle, M.D. Johnson, G.A. DeHaan, J.A. Burgess*, Hewlett Packard

Using surface analysis has been a mainstay of industrial research and corporate analytical labs for more than thirty years. The applications of surface chemical analysis in an industrial setting range from the investigation of the composition and chemistry of buried interfaces of single molecule memory devices created in the R&D lab to the routine analysis of plasma treated polymer surfaces on the production line. Some analyses are performed to provide a 'yes' or 'no' answer to question such as 'Has the oxide been removed?' or 'Was the surface plasma treated?'. Other analyses

are much more complicated and often require the application and correlation of several analytical methods. This correlation between techniques often occurs in the characterization of, for example, fab processes where a process may be characterized by x-ray photoelectron spectroscopy to understand the chemistry; but then the analysis needs to correlate to the information obtained by Auger electron spectroscopy or ToF SIMS which are the techniques of choice when the process is scaled to dimensions where XPS is not practical. Further, simple data processing, such as calculating atomic concentrations, is often not the end of the analytical story. Examples of using numerical methods such as linear least squares fitting or the application of Tougaard backgrounds to clarify an analysis will also be discussed. More detailed analyses can also be achieved by applying modeling methods such as SESSA or using simple overlayer models to describe a material. This presentation will cover these different aspects of surface chemical analysis in an industrial laboratory with practical examples of using XPS, AES and ToF SIMS for process characterization, materials development and failure analysis.

5:00pm AS+BI+MC-WeA9 Peter Sherwood Mid-Career Award Talk: Chemical Analysis of Cells and Tissues with Imaging ToF-SIMS, Lara J. Gamble, B. Bluestein, D. Graham, University of Washington INVITED

The ability to image cells and tissues with chemical and molecular specificity could revolutionize our understanding of biological processes. It would increase our understanding of chemical changes in cells and tissues as a function of an applied stress or as a result of disease, and enable tracking the spatial distribution of metabolites and lipids. Chemistry of tumor microenvironments, lipid metabolomics relationship to cancer, delivery of nanoparticles to cells, and tissue repair could be visualized on a cellular and sub-cellular level. The sub-cellular resolution mass spectral imaging capability of ToF-SIMS holds the potential to achieve this possibility. ToF-SIMS analysis of biological samples from 2D images of tissue biopsies to 3D images of nanoparticles in cells will be presented including multivariate analysis of the ToF-SIMS image data. The ToF-SIMS images are also combined with optical images of the same samples (same slices and serial biopsy slices). This combination of images allows researchers to visualize a molecular map that correlates with specific biological features or functions. The potential to combine the ToF-SIMS images with other techniques will also be discussed.

5:40pm AS+BI+MC-WeA11 Characterization Strategies for the Detection of Carbon Nanotubes within an Epoxy Matrix, Justin Gorham, J. Woodcock, W.A. Osborn, J. Heddleston, K. Scott, National Institute of Standards and Technology (NIST)

Carbon nanotubes (CNT) have been widely incorporated into composite systems due to the enhanced properties that they add to new and existing products, especially with respect to mechanical strength. X-ray photoelectron spectroscopy (XPS), in conjunction with SEM and Raman spectroscopy, has been employed in efforts to characterize several CNT: epoxy composite systems. This characterization approach was applied to composite systems with (1, 4 and 5) CNT weight percentages. Additionally, imaging XPS results will be presented to provide further insight into the dispersion quality on the micron scale. Challenges associated with overlapping spectral features, charging and a variety of other considerations regarding the surface and the bulk of the sample will be discussed.

6:00pm AS+BI+MC-WeA12 Measuring Schmutz: Accounting for Adventitious Carbon Contamination in X-ray Absorption Spectra of Carbon-Based Materials, Filippo Mangolini, J.B. McClimon, J. Hilbert, R.W. Carpick, University of Pennsylvania

Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy is one of the most powerful weapons in the surface-analysis arsenal, since it provides insights into the local ordering, bonding configuration, oxidation state, and hybridization of the elements present in the near-surface region (information depth: ~5 nm). NEXAFS analyses are commonly performed under the assumption of chemical and structural homogeneity within the nanometer-depth scale probed. Unfortunately, this does not hold for the vast majority of solid surfaces due to the presence of complex surface and near-surface structures (*e.g.*, natural oxides, contamination) and can lead to large errors when analyzing elements that are simultaneously present in multiple layers. This is particularly challenging for carbon-containing materials previously exposed to air, as their carbon K-edge NEXAFS spectra are a convolution of the spectrum of the material under investigation and that of the adventitious carbon contamination. While analysis methods for determining the composition and thickness of each layer in a multilayer system without applying any destructive technique have been developed for X-ray photoelectron spectroscopy, no corresponding methodology has ever been reported for NEXAFS spectroscopy.

Here, we present a novel, non-destructive, and generally-applicable method for accounting for the contribution of thin overlayers (with thickness

smaller than the information depth) from NEXAFS spectra of two-layered systems (constituted by a substrate covered by a surface layer) to give the corrected NEXAFS spectrum of the substrate. The new methodology is applied to NEXAFS data acquired on air-exposed hard carbon-based materials (ultrananocrystalline diamond and hydrogenated amorphous carbon) and allowed for the removal of the contribution of adventitious carbon contamination from the as-acquired spectra to give the intrinsic photo-absorption NEXAFS spectra of the materials under investigation. The results demonstrated that, in the case of amorphous carbon-based materials, significant errors, between 5% and 20%, could be introduced in the computation of the fraction of carbon atoms in different hybridization states if the contribution from the carbonaceous contamination layer is not removed from the as-acquired NEXAFS spectra. We also extract information about the composition and bonding found in the contamination layer.

The development of this novel methodology has important implications for the thorough investigation of the near-surface region of carbon materials as well as of the phenomena occurring in them in response to different energetic inputs (*e.g.*, temperature, mechanical stress).

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