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Time of flight-secondary ion mass spectrometry (TOF-SIMS) is a highly sensitive technique capable of identifying both inorganic and organic components of a sample with a detection limit in the ppm-ppb range [1]. Combined with its extreme surface sensitivity of 1-2 nm [2] and an imaging spatial resolution of 1 µm or less [1], this technique is invaluable in coatings research conducted at PPG. However, for complex coatings systems produced in the real world, this ultra-high sensitivity can sometimes be a detriment to sample analysis. Trace contamination, charging, surface roughness, and other factors can all influence the data, and therefore sample preparation becomes critically important. In addition, the surface sensitivity restricts the ability to analyze the bulk coating without additional preparation. This paper will address some of these challenges, exploring the effects of different sample preparation methods of coatings systems on the corresponding TOF-SIMS data.

In order to understand the effect of sample preparation on TOF-SIMS data collection, two different sample preparation techniques were compared on a single coating system. The coating system was chosen because it contained predominantly inorganic components and was a single layer on a metal substrate, with the exact composition and distribution of the components unknown. When first analyzed with X-ray photoelectron spectroscopy (XPS), the major elements in the coating of interest were confirmed, but trace elements present could not be determined. TOF-SIMS, however, has a much lower limit of detection than XPS [1], and therefore was used to identify these elements. The initial TOF-SIMS result indicated that a small amount of an additional Group 1A metal was indeed present at the coating surface. In order to understand the distribution of this metal throughout the layer, careful sample preparation was required, and multiple methods were investigated.

The first method involved the formation of a crater in the surface of the coating using a 4 keV Ar\(^+\) ion beam while the sample was compucentrically rotated. The net result was the formation of a crater with sloping sidewalls approximately 4.5 mm in total length, as shown in Figure 1a. This method effectively stretches the coating layer by approximately 1000:1, allowing for easier depth profiling analysis. A TOF-SIMS linescan was then performed along the coating surface, down the sidewall of the crater, across the bottom of the crater (at the substrate surface) and then mirrored on the other side. This linescan revealed that there was variation in the amount of the Group 1A metal present within the coating, with more of the metal accumulating at the coating surface, shown in Figure 1b-d compared to the major element within the substrate. However, crater formation with an ion beam can increase the surface roughness as well as cause sputtering and migration of material, and therefore it was difficult to determine if these variations were real. Therefore, a second sample preparation method is currently being investigated to see if the results are reproducible.
The second method involved cross-sectioning a small piece of the coating system and then vertically mounting the piece in epoxy. This epoxy mount, with a 1 inch diameter, was then ground and polished using an auto-polisher and a series of sandpapers with increasingly smaller grit size. The grinding and polishing step creates a smooth surface along the cross-section, which greatly reduces or eliminates any influence that surface roughness would have on the results. However, it also introduces potential artifacts, such as contaminants left behind by the grinding and polishing process, as well as the potential for charging caused by the epoxy mount. These parameters and others are currently being explored to understand their influence on the TOF-SIMS results and determine the true distribution of this Group 1A metal throughout the coating.

TOF-SIMS can be a powerful tool for analyzing components of a coating system with very high sensitivity, and developing the correct sample preparation methods would allow for analysis of real-world complex coating systems. Understanding the distribution of trace elements and small organic molecules throughout a coating stack allows for better understanding of these systems, informing future design for corrosion resistance, higher adhesion, and long-term durability.

References:


Figure 1. a) Illustration of the sample after crater formation, showing the direction of the linescan for TOF-SIMS analysis. b, c) TOF-SIMS linescans showing the raw signal intensity of a Group 1A metal and the major element found in the substrate along the crater formed in the coating layer. The blue box indicates the location of the crater. d, e) The corresponding raw signal intensity maps for the Group 1A metal (d) and the substrate (e).