

Characterization of Zirconium Oxide-Based Pretreatment Coatings

Part 2 – Challenges in Coating Aluminum Body Panels

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ABSTRACT

The pretreatment of aluminum sheet material in preparation for further paint application can be challenging due to the presence of a thick oxide layer. The composition of the oxide layer is primarily aluminum oxide, but it may also contain magnesium that is typically dispersed unevenly throughout the oxide layer. Zinc-phosphate systems remove much of the oxide layer on aluminum, but questions remain on the extent of removal of the oxide layer by zirconium oxide-based pretreatments and how these oxide layers may affect the zirconium oxide-based pretreatment deposition on aluminum.

Several methods have been used to characterize the coating of zirconium oxide-based pretreatments on aluminum. Scanning electron microscopy at very high magnification reveals a coating on aluminum that is significantly different in morphology than the same coating chemistry on steel substrates. Auger electron spectroscopy allows for further analysis of the coating, revealing a significant amount of inhomogeneity in the coating and often the presence of oxide layers under the coating. Although X-ray fluorescence has been a useful tool to characterize the coating on steel substrates, the technique is challenging on aluminum due to small amounts of zirconium in the aluminum substrate. This paper will discuss the variability in the pretreatment coating technology, the effects of oxides, aged material, and contamination on coating deposition and corrosion behavior.

INTRODUCTION

Automotive companies are continually evaluating their production systems looking for changes that can improve efficiency, save money, and reduce their environmental footprint. The metal pretreatment system is one area where an attractive alternative to the existing system has been identified as outlined in Part 1 of this report¹. Replacing the zinc phosphate pretreatment system with one based on zirconium oxide will result in a simpler assembly line with fewer stages, reduced energy consumption, and will produce less waste. However, customers demand that any changes to the production system will not compromise the performance of the finished product.

During initial characterization of zirconium oxide pretreatment coatings, it became clear that film deposition was significantly different depending on the substrate that was being coated¹. Of particular concern were aluminum 6111 substrates as the zirconium oxide films were extremely thin on this material. Maximum coating thickness on this substrate was in the 10-20 nm range even on carefully prepared laboratory panels. With such a small amount of material deposited on aluminum 6111, it is possible that small perturbations in the process will significantly alter the quality of the zirconium oxide film.

In an effort to determine the key processing parameters required to successfully coat aluminum 6111 with zirconium oxide, detailed characterizations were performed on coatings deposited using a variety of conditions. Multiple methods were employed for characterization including high resolution SEM, Auger electron spectroscopy (AES), sputter depth profiling, and

x-ray fluorescence (XRF). Changes in the zirconium oxide deposition as a result of substrate variability, processing time, and bath contamination were examined.

RESULTS AND DISCUSSION

COATING DEPOSITION

Base Alloy

Coating metals with thin films requires a detailed understanding of the surface oxide films that are present and how these oxides affect film deposition. For example, zinc phosphate is a "true" conversion coating that strips the surface oxide and replaces it with a crystalline phosphate-mineral deposit. Oxide scales that are too thick may not be completely removed during deposition, which will alter or in some cases prevent crystal deposition. Initial evidence suggests that zirconium oxide deposits on aluminum in different ways depending on the nature of the metal oxide that is present. The nature of that oxide is also important for determining the amount of coating that deposits as well as coating adhesion. Thus, a detailed characterization of the surface oxides on aluminum is important in determining how zirconium oxide deposits on this material and ultimately the corrosion performance of this coating.

The surface of aluminum alloys quickly form stable aluminum oxides when exposed to air. Removal of this oxide is ideal for coating deposition. Unfortunately, the oxide can continue to grow as the alloy ages resulting in a surface that is more difficult to coat than fresh metal. Thus, careful control of metal inventory is important for aluminum sheet used in the auto industry. Also, these surface oxides can be mechanically folded back into the sheet when rolled and stamped making it more difficult to remove. In addition, Al 6111 contains magnesium which tends to surface segregate during aging. This results in a mixed aluminum/magnesium oxide that has different characteristics than either oxide alone.

Figure 1 shows an SEM image of an aluminum alloy 6111 prior to a zirconium oxide coating. The contrast differences in the image are the result of thickness non-uniformities in the surface oxides. These are illustrated in the AES sputter depth profile in Figure 2. The surface of this metal sample is rich in magnesium oxide as a result of surface segregation of this metal. Beneath this layer is the aluminum oxide film. The slow decrease in oxygen signal at deeper layers is caused by regions of varying oxide thickness within the AES analysis area. At these depths, the oxide layer has been removed in thin regions but is still present in neighboring thick regions. These regions of thickness variations observed in the depth profile correspond to the areas of different contrast in the surface SEM image.

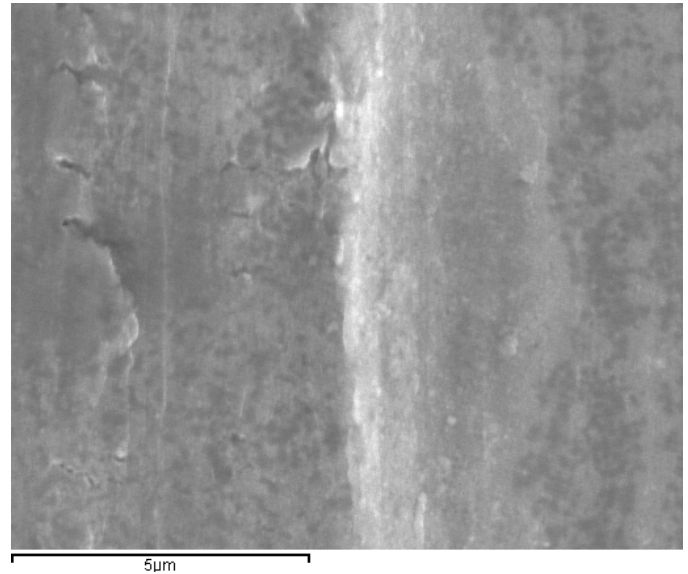


Figure 1: SEM image of aluminum alloy without zirconium oxide pretreatment.

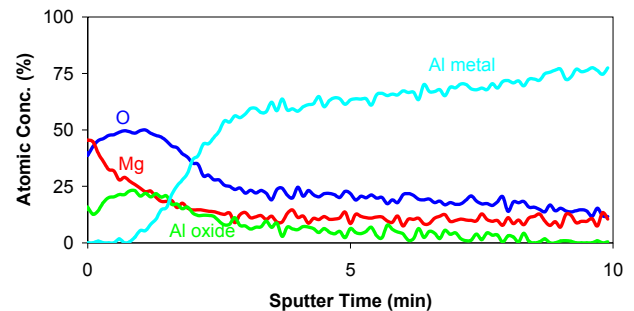


Figure 2: AES sputter depth profile of the native oxide on aluminum 6111 alloy.

Aluminum Alloy with Zirconium Oxide Coating

Characterization of the metal oxide surface was followed by characterization of a lab-applied zirconium oxide coating. The following figures show an SEM and two AES sputter depth profiles of a typical zirconium oxide coating on aluminum alloy 6111 (see Figures 3-5). The SEM image shows a surface that is decorated with small nodules that form during the coating deposition. These nodules vary in size from approximately 1 μm to much less than 0.1 μm. The darker regions between these nodules have a thin zirconium oxide layer on top of the aluminum alloy. This coating is mainly zirconium oxide in composition as shown in the depth profile in Figure 4. The nodules are made primarily of a second component with lesser amounts of zirconium oxide and are significantly thicker than the zirconium oxide coating found in regions between the nodules as shown in the AES sputter depth profile Figure 5. This second component is one of the constituents of the zirconium oxide deposition bath.

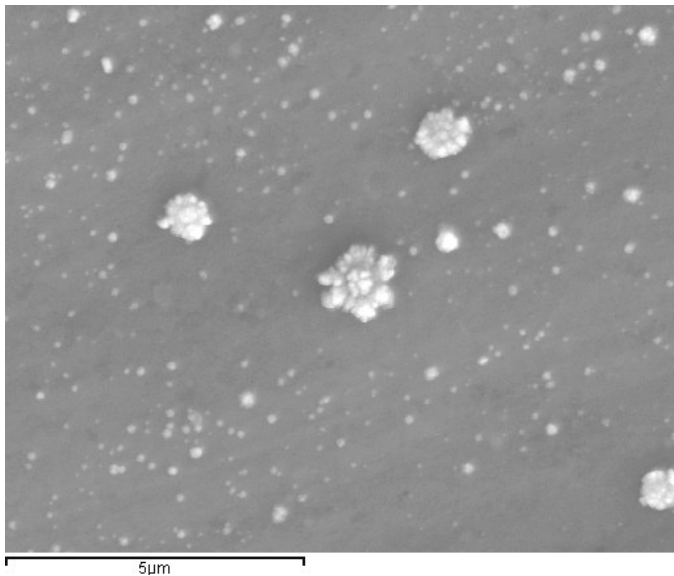


Figure 3: Zirconium oxide coating on aluminum 6111.

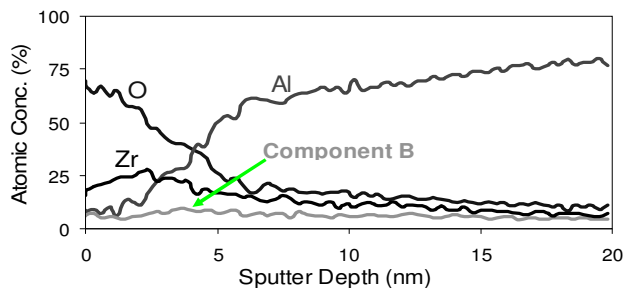


Figure 4: AES measurement of area between nodules on an Al 6111 panel treated with zirconium oxide.

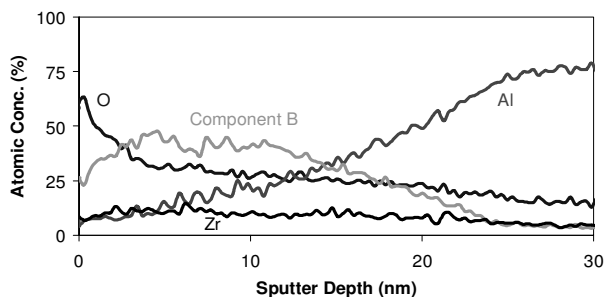


Figure 5: AES of a nodule on an Al6111 panel treated with zirconium oxide.

The nodular structure of the film formed on Al 6111 is problematic for characterization methods with limited spatial resolution such as x-ray photoelectron spectroscopy (XPS) and XRF. With these methods, a critical assumption is made that the film composition is uniform in the analysis area. This leads to an overestimation of the film thickness as the signal from the much thicker nodules strongly contribute to the final result¹.

More detailed AES profiles from regions between the nodules showed large variation in film composition from

location to location. The variation in coating during the depth profiles usually fell into three scenarios. 1) A thin zirconium oxide layer which transitioned directly into the aluminum alloy. An example of this condition is shown in Figure 6. 2) Zirconium oxide mixed with an aluminum oxide on the surface of the base alloy. An AES sputter depth profile pertaining to this scenario will exhibit zirconium oxide with or on top of an aluminum oxide then a transition to the base metal alloy (see Figure 7). 3) The third scenario exhibited an oxide containing aluminum and magnesium on the surface of the base alloy with little zirconium deposition (see Figure 8). Thus in some regions the zirconium oxide film appears to be a conversion coating (scenario 1), while in others it appears as a deposit on the existing oxide (scenario 2). Of most concern however, are regions with significant magnesium oxide present on the surface as these regions show little zirconium oxide film deposition.

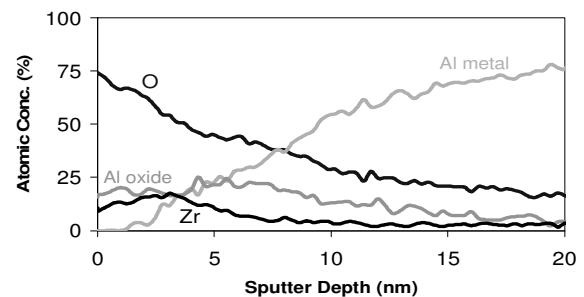


Figure 6: AES sputter depth profile of scenario 1, zirconium oxide deposition on aluminum metal.

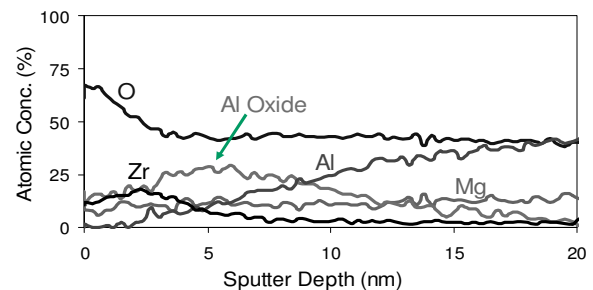


Figure 7: AES sputter depth profile of scenario 2, zirconium oxide deposition on aluminum oxide.

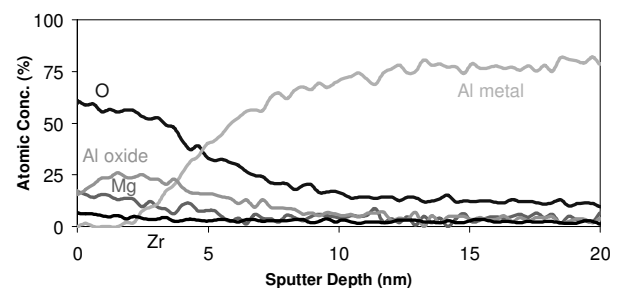


Figure 8: AES sputter depth profile of scenario 3, poor zirconium oxide growth on mixed aluminum-magnesium oxide.