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EVALUATION OF ALTERNATIVE METHODS FOR SURFACE PREPARATION AND DEPOSITION OF CERIUM-BASED CONVERSION COATINGS ON ALUMINUM ALLOYS

By

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ABSTRACT

This thesis investigates alternative surface preparation and deposition methods for cerium-based conversion coatings (CeCC) on high strength aluminum alloys. Cerium-based conversion coatings are being investigated as a more environmentally friendly replacement for chromium-based conversion coatings. Currently, the alloys are immersed in strong alkaline and acidic solutions to prepare the aluminum surfaces for conversion coating, in which immersion may not be suitable for all situations. Alternatives to this method were investigated, including wipe application of solution, ultrasonic processing in deionized water, and abrasive blasting with alumina. Al 7075-T6 test panels were prepared using each of these methods and compared to a conventional alkaline chemical immersion process. Coatings were evaluated using Auger depth profiling, electrochemical response, and corrosion performance. A CeCC was produced by spray deposition. The chemical wipe method produced the surface most similar to the chemical immersion method. Both of these methods had an uncoated total impedance value near 4 $k\Omega\text{-cm}^2$. However, the immersion panel coating was approximately 125 nm thick after one spray while the wipe prepared panel coating was approximately 75 nm thick after the spray. Both coatings provided similar protection in corrosion testing.

An alternative deposition method using a brush was investigated on Al 2024-T3. Prior to deposition, the panels were prepared using an acidic chemical immersion method. The CeCC was deposited using the brush-based method or the spray-based method. These methods were compared using coating thickness, morphology, and crystalline phases in the coating. Brush-based coatings were thinner than spray-based, but they had a similar surface morphology. Spray deposited coatings were about 400 nm thick after three deposition cycles, while brush deposited coatings were approximately 275 nm thick after five cycles. Cerium phosphate, a phase previously shown to improve corrosion resistance, was detected in spray coatings after treatment in a 85°C phosphate solution but not in brush-based coatings. Brush-based deposition provided some corrosion protection but not as much as a spray applied coating, likely due to the absence of the formation of cerium phosphate.

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SECTION

1. INTRODUCTION

Weight is a limiting factor for aircraft. Since an engine can lift a limited amount of mass, a lighter airplane can carry more cargo and is more fuel efficient than a heavier airplane. However, lightweight aircrafts have to withstand the forces of flight. Therefore, lightweight, high strength structural materials are required for aviation. [1]

Aluminum alloys can provide high strength while retaining the light weight. Aluminum has low intrinsic strength; it is a soft and malleable metal. However, with the addition of alloying elements, aluminum can be strengthened using strain hardening or precipitation of secondary phases during heat treatment. Strain hardening increases the number of dislocations in the material, to the point at which they begin to impede dislocation movement and formation. Impeding dislocation movement makes additional plastic deformation more difficult and the material stronger. The solubility of most alloying elements in aluminum decreases with temperature; heat treatable aluminum alloys are those that can be solution treated, quenched, and then precipitate second phase particles during subsequent heat treating. Further heat treating may be at room temperature (natural aging) or at an elevated temperature (artificial aging). The size of the precipitates depends on aging time, alloy composition and other factors, and range from nanometers to microns in length. If precipitates are evenly distributed throughout the material, they impede dislocation movement and increase strength.[2] Aluminum 2024 and 7075 are heat treatable alloys commonly used in aerospace applications. Al 2024 contains 4.4% copper, 1.5% magnesium, and 0.6% manganese, while Al 7075 contains 5.6% zinc, 2.5% magnesium, 1.6% copper, and 0.23% chromium. [3]

Due to the presence of precipitate phases, these high strength aluminum alloys are highly susceptible to corrosion. Aluminum and its alloys form a thin, passive oxide film on the surface which retards further oxidation. The oxide layer present on aluminum alloys is not uniform, and may break down, exposing the underlying metal. Breakdown of the oxide layer is usually caused by ion attack, typically a chloride ion. The exposed metal will reform the oxide layer in air, but the chloride ion will continue dissolving the reformed layer. The passivation and oxidation cycle forms a pit, and the pit accelerates the reaction by concentrating the chloride in the small site. [4] Heat treatable aluminum alloys are especially vulnerable to pitting corrosion, as they contain intermetallic particles that form galvanic couples with the aluminum matrix. Al 2024 contains many different intermetallics, such as $CuAl_2$ and Al_2CuMg. [5] Al 7075 contains zinc-rich intermetallic particles such as $MgZn_2$ and $Al_2Mg_3Zn_3$, among others. [6] Copper and zinc intermetallic particles are electrochemically more noble than the surrounding aluminum matrix, creating potential cathodes of a small galvanic cell. The cathodic sites greatly increase the rate of corrosion of the aluminum alloy as the more active sites increase the probability of pit formation. [7]

1.1 ALUMINUM SURFACE TREATMENTS

A number of different surface treatments have been shown to improve the corrosion resistance of aluminum alloys. Examples include clad aluminum, anodizing, organic coatings, and conversion coatings.[8] Clad aluminum is produced when a high-strength alloy core has a more corrosion resistant metal bonded to the surface. Anodizing is electrochemically growing the oxide layer to provide a more resistant film. Organic coatings such as paints and primers are one of the most commonly used coatings. Organic coatings provide a physical barrier layer to corrosion; corrosion inhibitors can also be incorporated for more active protection. Chemical conversion coatings, a thin chemically altered layer on the aluminum surface, are often used to provide secondary corrosion protection and to increase the adhesion of organic coatings to the aluminum. The standard aerospace coating system consists of a primer containing a corrosion inhibitor applied over a conversion coating, with a topcoat to provide the required weather resistance. [7]

Clad aluminum is one potential method of corrosion protection. [9] The core material is protected by addition of a more anodic surface layer. This surface layer is bonded to the core metal by roll bonding. Most metals can be roll bonded, and cladding is used on many metals. Alclad aluminum is a special case of cladding, with one aluminum alloy clad to another. Strong, high strength aluminum alloys can be clad with weaker but pure (or low alloy content) aluminum to produce a material with the strength of the core metal and the corrosion resistance of the pure aluminum outer layer. The clad material should be anodic to the core metal to prevent galvanic corrosion of the alloy. A problem with alclad is that the low concentrations in the cladding will cause diffusion of alloying elements out of the core and into the cladding during heat treatment. [9]

Anodizing is the process of forming an oxide layer on a metal by placing it at the anode of an electrochemical cell. The anodic potential causes the aluminum to oxidize and produce a thicker oxide layer. The properties of the thickened layer depend on the conditions used in the anodizing cell. Two types of oxide can be formed, porous or barrier. Porous films are the most common, which are ~10-100 μm thick and produce a wide range of properties, including better paint adhesion. A barrier film is a thin, continuous layer that passivates the surface and is difficult to penetrate. [10]

Organic coatings, or paints, can be tailored for specific purposes. Paints owe their versatility to their variable composition, including binders to form cohesive films, thinners to promote flow, fillers or pigments to change the properties of the final coating, and additives to change the properties of the liquid coating. A wide variety of components and the relative amounts can be adjusted to alter the final properties of the coating. For corrosion prevention on aircraft an undercoat, or primer, that contains a corrosion inhibitor is used. This layer usually is also engineered to provide better adhesion to the topcoat. The topcoat provides the desired appearance qualities and weatherability for the system. [11]

Conversion coatings are thin (100 to 3000 nm), chemically reacted layers on the surface of the substrates. Conversion coatings are formed by applying a solution that causes controlled oxidation or dissolution of the substrate and the deposition of a surface layer. Examples of conversion coatings include phosphate coatings and chromate coatings. Conversion coatings are very complex systems, involving many different chemical reactions. Surface preparation is critical, as an unclean or passive surface may deposit a different coating or resist deposition altogether. Conversion coatings have a wide variety of applications, from friction reduction to corrosion protection, as well as secondary benefits like increasing the adhesion of organic coatings. Conversion coatings are usually porous, so a sealing step is typically used. [12]

Chromates have traditionally been used as a corrosion inhibitior in conversion coatings. [13] Chromate coatings are very effective corrosion inhibitors that exhibit a self-healing capability. Chromate conversion coatings and primers contain both trivalent

(Cr^{3+}) and hexavalent (Cr^{6+}) chromium ions. The trivalent ions form a passive film absorbed onto the material's surface, and are not very mobile. The hexavalent ions, however, are very mobile. When the coating is damaged, the hexavalent ions migrate to the damaged site, reduce to the trivalent ion, and reform the passive layer. [14] Hexavalent chromium ions are a very important component in chromate based coatings, but they have been found to be carcinogenic and toxic. [15, 16] Alternatives are being researched, including trivalent chromium passivation [17], cerium conversion coatings [18-20], titanium-based conversion coatings [21], sol-gel coatings [22], and molybdenum conversion coatings [23].

Cerium-based conversion coatings (CeCC) are a promising alternative to chromate conversion coatings for aluminum alloys. A CeCC is a thin film of a cerium compound, typically cerium oxide or cerium phosphate that provides corrosion protection and adhesion to organic coatings. The cerium-based coatings have been shown to be able to inhibit corrosion, although not as effectively as chromate-based conversion coatings. [24]

1.2 ALUMINUM SURFACE PREPARATION

Many surface treatments are used to prevent corrosion of aluminum and its alloys, but all of them require a clean aluminum substrate. Oils, grease, oxides, and impurities present on the aluminum will prevent effective surface treatment by forming a barrier, causing competing reactions, or producing another unintended harmful effect. Some surface treatments can tolerate unclean surfaces more readily than others, but surface preparation is always required. Many different surface preparations such as mechanical and chemical methods exist, and each has a unique effect on the substrate. Mechanical methods, such as abrasive blasting, remove the surface of the substrate and expose clean, underlying material. Chemical methods are used to dissolve surface contaminants and to etch away surface oxides. Other methods exist as well, such as ultrasonic processing. Often, a combination of these methods is used. Rinsing between preparation steps is very important; it stops the previous reaction and prevents dragging solutions from one tank into another and ruining the bath. [25]

Mechanical methods aim to reduce surface oxide and contamination by removing the substrate surface and exposing material under the surface. These methods include abrasive papers and media blasting. Abrasive blasting processes propel alumina, silica, or other hard abrasive media at high speeds towards the substrate using compressed air or mechanical action. The rapidly moving abrasive removes the surface by a cutting action, tearing into the surface a short distance and causing a roughened surface. This process does not uniformly attack the surface. The abrasive also impinges on the surface, requiring subsequent cleaning steps to remove the residual particles. Abrasive blasting, a simple process to operate, can achieve high material removal rates, leading to shorter process times. Typically no toxic or environmentally unfriendly substances are used; however safety precautions must be taken to avoid breathing the fine dusts generated. [26]

Many different chemical surface methods exist. These methods usually fall into one of several categories: solvent cleaning, alkaline cleaning, and etching. [27] Solvent cleaning is an easily applied method useful for removing organic substances from the substrate surface, while alkaline cleaners are effective at removing a wide variety of substances. Etching may be used to remove foreign substances, but is frequently used to remove surface oxides as the acidic or basic solutions attack the surface. These methods use a variety of chemicals, some of which are toxic, and care must be taken in the disposal of any chemical.

Solvent cleaning is a very simple procedure, usually performed near room temperature. [28] It is effective at removing oil, grease and other large contaminants and is usually used as a first cleaning operation or alone when surface preparation is not critical. Many different solvents are used, such as petroleum-based products, alcohols, and other organics. Most solvents are able to clean metals without damaging the surface; however, some solvents also have a very low flash point and require special handling to avoid excess evaporation or ignition. [29]

Alkaline cleaners are a more thorough cleaning process, and are used to remove a wide range of soils including oil, grease, dirt, and wax. [28] Alkaline solutions can be sprayed or used in an immersion tank and contain three major components: builders, additives, and surfactants. Builders are alkaline salts that are the major component of the solution. Additives, like chelating agents, are compounds that aid in the removal of specific contaminants. Surfactants are complex organic compounds often containing benzene or ammonium, and are added to ease solution wetting and lift contaminants from the surface. [30]

Pickling, acid dipping, and acid activation are types of acid etching. These processes all use acids that differ in the concentration or temperature of the solution. The procedure is adjusted so that the acid etch is strong enough to remove the contaminant, usually oxides, but not strong enough to damage the metal surface. Pickling is the strongest of the acid treatment categories and is usually used to remove large amounts of scale from heat treatments or forming, while acid dips are the weakest and are usually used to remove thin oxide films just prior to electroplating. Acid activation is an intermediate acid etch. [31]

1.3 ALUMINUM SURFACE PREPARATION AND DEPOSITION OF CERIUM CONVERSION COATINGS

Surface preparation of aluminum alloys prior to cerium conversion coating is critical for good corrosion protection. The first step is to remove the bulk of the grease and oils present on the surface, which is typically accomplished with an isopropyl alcohol wipe. Then, the surface is thoroughly cleaned by immersion in an alkaline commercial cleaning agent. As the final step in preparation, the surface is activated by immersion into either 1 wt. % sulfuric acid solution at 50°C for Al 2024 [32] or 2 wt. % sodium hydroxide solution at room temperature for Al 7075 [33]. The surface activation step damages the protective oxide on the aluminum, which promotes deposition of a CeCC on the underlying metal.

A CeCC can be deposited from a solution containing cerium chloride, gelatin, and hydrogen peroxide. The solution is adjusted to an acidic pH before use. Immersion and spraying methods of deposition have been developed. [24,34] The solution, once on the surface, begins to dissolve aluminum, generating electrons. The peroxide reduces to hydroxide ions, raising the pH of the solution, and the dissolved cerium begins to precipitate. The cerium deposits as a hydrated cerium oxide. After deposition, the cerium coated aluminum is immersed in a sodium phosphate solution, adjusted to an acidic pH of

4.5. This final step changes the deposited cerium oxide into a cerium phosphate, which has better corrosion resistance. [35]

This thesis investigates alternative methods for surface preparation and deposition of CeCCs on high strength aluminum alloys. Immersion and harsh chemicals may not be suitable for all situations; alternatives to the traditional pretreatment method were investigated, including wipe application of solution, ultrasonic processing in deionized water, and abrasive blasting with alumina. Al 7075-T6 test panels were prepared using each of these methods and evaluated using compositional depth profiling, electrochemical response, and corrosion performance. A CeCC was produced by spray deposition on all panels prepared using the different preparation methods.

Spray methods are useful for coating large areas quickly. However, an alternative deposition method is needed for small touch-ups or when specialized spray equipment is not available. A brush-based deposition method was investigated on Al 2024-T3. A CeCC was deposited using both the brush-based method and the spray-based method. These methods were compared using coating thickness, morphology, and crystalline phases in the coating.

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PAPER

I. Alternative surface preparation methods for cerium conversion coating of Al 7075-T6 substrates

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Abstract

Cerium-based conversion coatings require surface preparation of the substrate prior to deposition, typically by immersion in acidic or basic solutions. Alternative surface preparation methods for Al 7075-T6 were investigated, including a chemical wipe using a commercial alkaline solution and surface activating NaOH solution, ultrasonic processing in deionized water, and abrasive blasting using alumina. Each of these alternative methods produced an aluminum surface with different properties, but cerium-based conversion coatings could still be deposited in each case. Surfaces prepared using the alternative methods were compared to a previously developed immersion-based cleaning method using Auger electron spectroscopy depth profiling analysis, electrochemical response measured with potentiodynamic scans and impedance spectroscopy, and corrosion performance in neutral salt spray. The prepared panels were less corrosion resistant than as-received aluminum, but the cerium-based conversion coatings deposited on them were shown to improve the corrosion resistance compared to the prepared surface. Coatings deposited on chemically wiped surfaces are most similar to coatings on immersion cleaned surfaces.

1. Introduction

Aluminum alloys such as 7075-T6 are used in aircraft for their high strength and light weight. Heat-treatable, high strength alloys are produced by selecting an alloy composition above the room temperature solvus of the minority elements, but below the solubility limit at elevated temperature. These alloys can precipitate during heat treatment dispersed second-phase particles that contain the excess alloying elements. Second phase particles are the strengthening mechanism for the aluminum as they pin defect movement. [1] However, the alloying elements in heat-treatable aluminum alloys, such as copper and zinc, have a different electrochemical potential than the aluminum matrix. The electrochemical difference between the particle and the matrix causes a local potential. [2] As a result, these alloys are especially vulnerable to pitting corrosion in halide environments. In order to minimize corrosion, organic coatings are frequently used to protect the alloy; however, adhesion of organic coatings directly to aluminum is typically poor. To improve adhesion, chemical conversion coatings are used to convert the surface of the aluminum from an inert aluminum oxide to a surface that provides not only better adhesion to the organic coating but also provides additional corrosion protection. [3] Chromate-based conversion coatings and chromate-based corrosion inhibitors in the organic coating have been used for decades due to the self-healing ability of the chromate coatings. [4] Hexavalent chromium, the ion responsible for the self-healing ability, has been shown to be a carcinogen and an environmental hazard. [5, 6] Increasing regulation on chromate-containing products and processes has resulted in interest in alternative, chromium-free coatings. Among the many alternatives, rare-earth based conversion coatings, especially cerium, have been shown to be a possible replacement for chromates. [7, 8, 9, 10]

Surface preparation is critical to the deposition and performance of any conversion coating. This has been shown to be the case for cerium-based conversion coatings. [11] Previous research on cerium conversion coating of Al 7075-T6 has focused on processes using immersion into aggressive chemicals to prepare the surface of the substrate. [12] Use of these chemicals may be difficult or impractical in certain situations. In other cases, immersion processes may be impractical for very large sections or assembled pieces of an aircraft. Alternatives for these processes would be useful for field repairs or touch-up of existing aircraft, which are often performed without access to specialized equipment.

Previous work has focused on surface preparation by immersion of the alumimum alloy into a commercial alkaline cleaner and then a second dip into a sodium hydroxide solution. [13] In the present study, three alternative preparation methods were investigated with the goal of developing non-immersion or less chemically aggressive processes: a chemical wipe process, an ultrasonic preparation method, and an abrasive blasting method. The chemical wipe process avoids immersing the substrate into solutions by applying the alkaline cleaner and sodium hydroxide solution by surface application. Aggressive chemicals were not used for ultrasonic processing or abrasive blasting. Surface prepared panels and coatings deposited on prepared substrates are compared using electrochemical testing, corrosion testing, and surface chemistry.

2. Experimental

The substrates used were cold rolled aluminum 7075-T6 sheets cut into 3.8 cm by 7.6 cm panels. The panels were first degreased with an isopropyl alcohol (IPA) saturated laboratory wipe, followed by rinsing in tap water. Panels were then given one of four different surface treatments; immersion cleaning, chemical wiping, ultrasonic cleaning, or media blasting. Unprepared panels were also tested to investigate the as-received condition.

For comparison with previous studies [13], panels were prepared using a chemical immersion method. The panels were immersion cleaned for five minutes using a commercial alkaline solution (Turco 4215-NCLT, Turco Products) held at 55°C. This step is intended to thoroughly degrease the substrates. The panels were then removed and rinsed with deionized (DI) water. The panel surfaces were then activated by immersion into a room temperature solution containing 2 wt. % NaOH for 20 seconds. The panels were given a final DI water rinse.

A saturated sponge was used for chemical wipe cleaning. The sponge was first saturated with 55°C commercial alkaline solution (Turco 4215-NCLT, Turco Products). The panel surface was wiped for 10 seconds, and then the sponge was returned to the beaker of solution for 10 seconds to resaturate. The wipe and soak cycle was repeated for a total of 15 cycles. The panels were given a DI water rinse after the final cycle. To activate the surface, a sponge soaked in room temperature 2 wt. % NaOH was wiped across panel surfaces for 10 seconds, then the panels were allowed to sit for ten seconds before being given a final DI water rinse.

Ultrasonically processed panels were placed horizontally into a ultrasonic cleaning bath (Ultrasonik Model 28X, Ney Dental) with the power set to 75% and the heating off. DI water was used as the cleaning medium. The ultrasonic bath was run for five minutes, then the panels turned over, and run for another five minutes. The panels rested on the bottom of the container, so that turning the panels over allowed both sides to be exposured to the solution and provided time for the solution to cool. After 10 minutes in the ultrasonic bath, the panels were given a final DI water rinse.

Abrasive blasting was done using 60 grit alumina abrasive in a blasting cabinet (50 psi, Cyclone Blasting Systems) to prepare one side of Al 7075-T6 panels. The panels were then ultrasonically processed using the procedure described above for the ultrasonically processed panels (ten minutes total) to remove embedded blasting media from the surface. After ultrasonic preparation, these panels were given a final DI water rinse.

Spray deposition of cerium-based conversion coatings (CeCCs) was done on panels prepared using each condition. The CeCCs were deposited from a solution containing 10 g cerium chloride (99.9% $CeCl_3 \cdot 7H_20$, Alfa Aesar), 20 mL hydrogen peroxide solution (30% H_2O_2, Fisher Scientific), 0.6 g gelatin (RDH, Rousselot), and 220 g DI water. Prior to coating, the solution was adjusted to a pH of approximately 2.3 using dilute HCl. The solution was sprayed onto panels with an air powered spray gun (Husky detail spray gun, Husky Professional Tools) using compressed air at 35 psi. The panels were held at an angle of approximately 70 degrees to the horizontal during spraying. After spraying, the panels were allowed to drain for 35 seconds and then rinsed with DI water. Only one deposition cycle was done in order to compare different preparation methods.

Surface characterization was performed using Auger electron spectroscopy (AES), electrochemical testing, and corrosion testing in neutral salt spray. AES depth profiling was completed using a Physical Electronics Model 545. Electrochemical testing was performed using solution containing 0.35 wt. % sodium chloride (100% NaCl, Fisher Scientific) and 0.7 wt. % ammonium sulfate (100% $(NH_4)_2SO_4$, Fisher Scientific), a frequency response analyzer (SI 1255, Schlumberger) and a potentiostat (273A, EG&G).

Tests were performed using a scan rate of 1 mV/s, and representative data was selected from three data sets. Corrosion testing was performed in a cyclic corrosion test chamber (Q Fog CCT 1100, Q Panel) according to ASTM B117. Panels were tested for 18 hours to compare corrosion resistance and the resulting electrochemical response.

Data fitting for the impedance spectroscopy used the equivalent circuit shown in Figure 1. A parallel RC circuit was used to model aluminum corrosion, with an added resistor to account for the solution resistance. Inductance loops were observed on some coatings so an inductor and resistor were added.

3. Results and Discussion

For an initial reference point, IPA wiped aluminum panels were examined using electrochemical testing. Alcohol wipe cleaning was used as a minimal surface preparation; the natural surface was not altered while removing dust, oil, and grease. Potentiodynamic scans, Figure 2, performed on these panels showed a low corrosion current (0.1-0.7 $\mu A/cm^2$), while fitting of data from electrical impedance tests, Figure 3, showed large charge transfer resistance values (24-26 $k\Omega$-cm^2). Corrosion currents are proportional to the corrosion rate, while charge transfer resistance values are inversely proportional to the corrosion rate. These tests indicate that the native oxide on the aluminum is providing some protection under these conditions, which leads to the slow corrosion rate. These experiments were repeated three times, with some variability in the measured values indicating that the aluminum oxide and the corrosion resistance were not uniform.

After surface preparation, the aluminum surfaces were optically different from the unprepared surfaces and from each other. Immersion prepared and chemically wiped panels were both dark in color, but the immersion cleaned panels tended to be darker than the chemical wiped ones. Ultrasonically processed panels did not appear different than unprepared panels. Abrasively blasted panels had visibly rough surfaces that tended to be a brighter color than unprepared panels.

Electrochemically, treated surfaces were more active than unprepared panels. Potentiodynamic scans, Figure 4, showed that the activated surfaces had nearly the same corrosion potential as IPA wiped panels (~500 mV), except for blasted panels, which were more active (~660 mV). The abrasively blasted panels also had the highest corrosion current (7.0 to 7.3 $\mu A/cm^2$), while the chemically wiped panels had the lowest (1.1 to 1.7 $\mu A/cm^2$). Table 1 summarizes the fitted values from the potentiodynamic scans. Impedance scans, Figure 5, showed the blasted panels had the lowest charge transfer resistance (3.4 $k\Omega$-cm^2) and that the ultrasonically cleaned panels had the highest (10-12 $k\Omega$-cm^2). The tests found that all of the prepared panels had higher corrosion currents and lower charge transfer resistances than the IPA wiped panels; therefore, they had higher corrosion rates. Based on these results, the protective oxide layer was compromised by the surface preparation.

The treated aluminum panels were also chemically examined using AES depth profiling. The oxide layer was not completely removed; there was an oxide layer present on aluminum panels prepared using each method with thicknesses from 50 to 75 nm. Figure 6 contains the depth profiles collected from the activated surfaces. The 7075 alloy contains magnesium (2.5 wt %). The magnesium migrates to the surface during heat treatment where it forms a Mg-rich mixed oxide. [14] All of the prepared surfaces had a Mg-rich layer (50-75 nm thick) on the surface, with the exception of the abrasively blasted panel. The abrasive blasting removed the Mg-rich surface layer, leaving an aluminum oxide surface.

After the surfaces were prepared, a single spray of the cerium containing solution was applied. A coating formed on all of the prepared panels when sprayed with the cerium deposition solution, while no coating was deposited on the IPA wiped sruface. The immersion and chemically wiped panels developed a coating that was uniform and had a dark yellow color. Blasted and ultrasonically prepared panels were lightly colored, but both were uniform in appearance. AES depth profiles of the activated, coated surfaces were done to determine coating thicknesses (Figure 7). The thicknesses of the CeCCs were ~125 nm on the immersion activated surface, ~75 nm on the chemically wiped panel, and ~25 nm on the ultrasonically processed and blasted panels. Most of the panels retained a layer of oxide containing both magnesium and aluminum between the CeCC and the substrate. The 75 nm thick aluminum oxide present on the blasted panel appeared to have dissolved during the deposition. Comparing these results to the electrochemical results, the panels that corroded at a faster rate formed a thicker cerium-rich coating. The exception was the abrasively blasted panel; it was the most active panel, but also had one of the thinnest coatings. This discrepancy may be due to the absence of magnesium in the oxide layer of the blasted panel.

Electrochemical tests performed on the coated surfaces found an increase in the measured corrosion resistance after coating. Results varied with the surface preparation used. The potentiodynamic scans in Figure 8 showed large differences in the corrosion current, ranging from ~0.1 $\mu A/cm^2$ for the immersion prepared coatings, to ~5 $\mu A/cm^2$ for the abrasively blasted and coated panel. Table 1 compares the fitted values from the potentiodynamic scans. The CeCCs decreased the corrosion current on all of the panels; the immersion prepared and chemically wiped panels showed the largest decrease in corrosion current. Impedance tests found variation in charge transfer resistance values for panels with CeCCs, from about 5 $k\Omega\text{-}cm^2$ for the abrasively prepared coating to about 44 $k\Omega\text{-}cm^2$ for the immersion prepared coating (Figure 9). Table 2 contains the fitted values from the impedance tests. The charge transfer resistance values for panels with CeCCs were higher than the uncoated surfaces, but the immersion prepared and chemically wiped panels improved the most, consistent with the potentiodynamic scans. All of the coatings offered some protection compared to the prepared panels. These tests show that CeCCs deposited on immersion prepared surfaces were the most protective while the thin coatings on the abrasively blasted panels were only slightly more resistive than the prepared surface.

Salt spray testing was also performed to compare corrosion performance of panels with CeCCs. Figure 10 contains images of the uncoated, prepared panels after 18 hours of exposure. The salt spray tests on the uncoated panels show the same trend as the electrochemical tests on the uncoated panels. The abrasively blasted panel corroded the most; it had a continuous layer of corrosion product on the surface. The immersion prepared panel had many large pits with tails, while the chemically wiped panel had fewer pits and smaller tails. The ultrasonically prepared panel had the fewest pits and the least amount of tailing of the prepared panels. Panels with CeCCs were less corroded than the uncoated panels (Figure 11). The salt spray results were consistent with the electrochemical tests on the coated panels. The most corroded panel was the blasted panel, again with a continuous corrosion product layer. The CeCC on the immersion prepared and chemically wiped panels performed the best in salt spray, with few pits and little tailing. The immersion pretreatment had slightly fewer pits. The ultrasonically prepared panel was the least corroded of the uncoated panels but the coating on the ultrasonically prepared panel did not protect as well as the coatings on the immersion prepared and the chemically wiped panels.

4. Conclusion

Chemical wiping, ultrasonic processing, and abrasive blasting were compared to immersion as alternative preparation methods for cerium-based conversion coating on Al 7075-T6 panels. All of these methods were effective pretreatments for the deposition of CeCCs. The pretreatments that produced thicker cerium-based conversion coatings resulted in better corrosion protection. However, surface treatments that led to thicker coatings also made the uncoated panels more vulnerable to corrosion. Abrasive blasting was the exception; this method resulted in thin coatings but the uncoated surface was highly susceptible to corrosion. Based on the AES depth profiling of the uncoated panels, the other methods left a mixed magnesium and aluminum oxide layer, whereas the oxide layer of the abrasively blasted panel did not contain magnesium. The deposition of cerium-based conversion coatings on the abrasively blasted panels also appeared to dissolve the aluminum oxide layer. Overall, the chemical wipe method produced surfaces and coatings that were the most comparable to the immersion preparation method, but all methods tested were effective alternatives for pretreatment.

5. Acknowledgements

The support and guidance of Bruce Sartwell of the Strategic Environmental Research and Development Program (SERDP), Donna Ballard of AFRL/MLLB under SERDP Project

WP-1519, Contract W912HQ-06-C-0030, is gratefully acknowledged. Also thanks are extended to Jeff Wight (AES) and Surender Maddela (electrochemistry) from the Materials Research Center at Missouri S&T.

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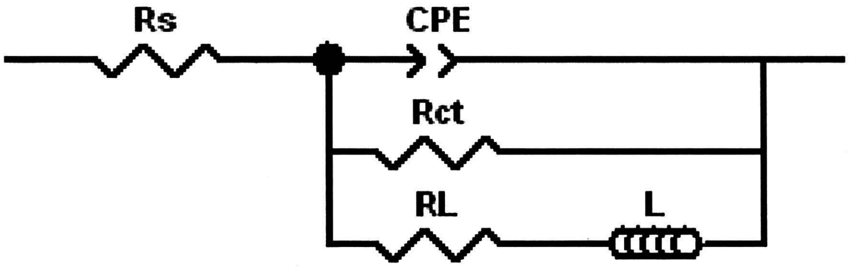

Figure 1 - Equivalent circuit used for fitting impedance spectroscopy results

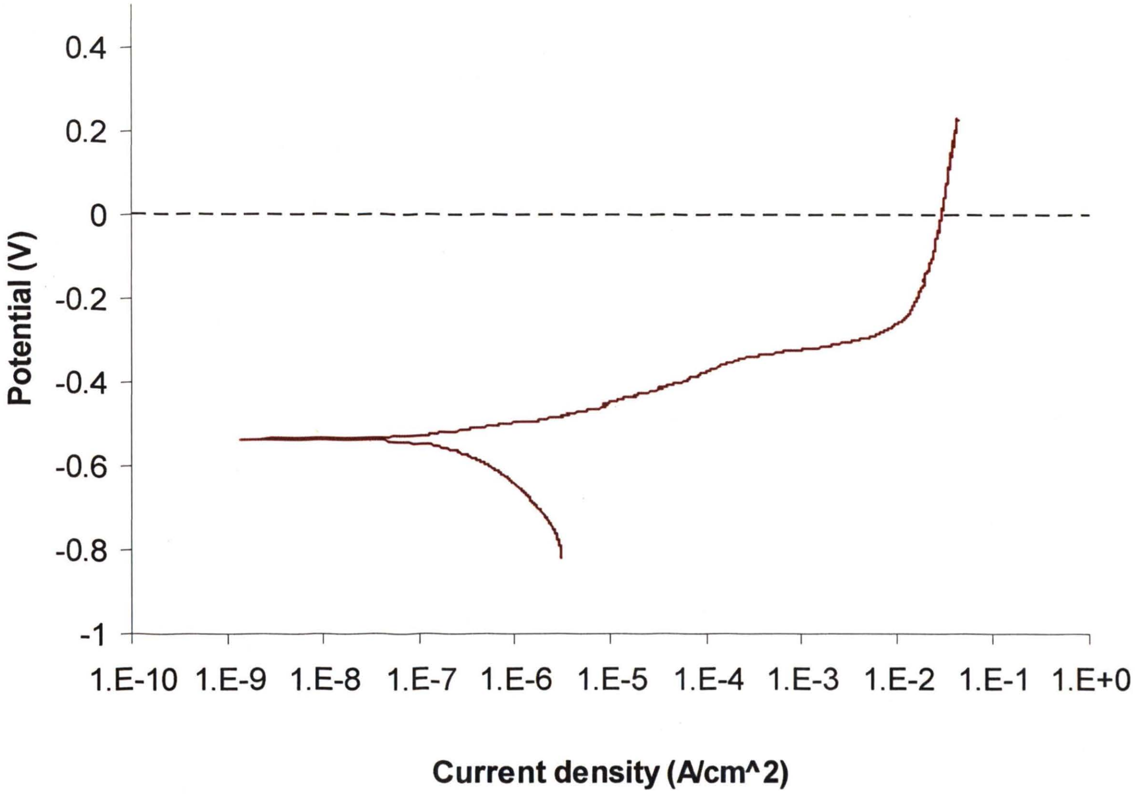

Figure 2 – Potentiodynamic scan on an isopropyl alcohol wiped aluminum 7075-T6 panel

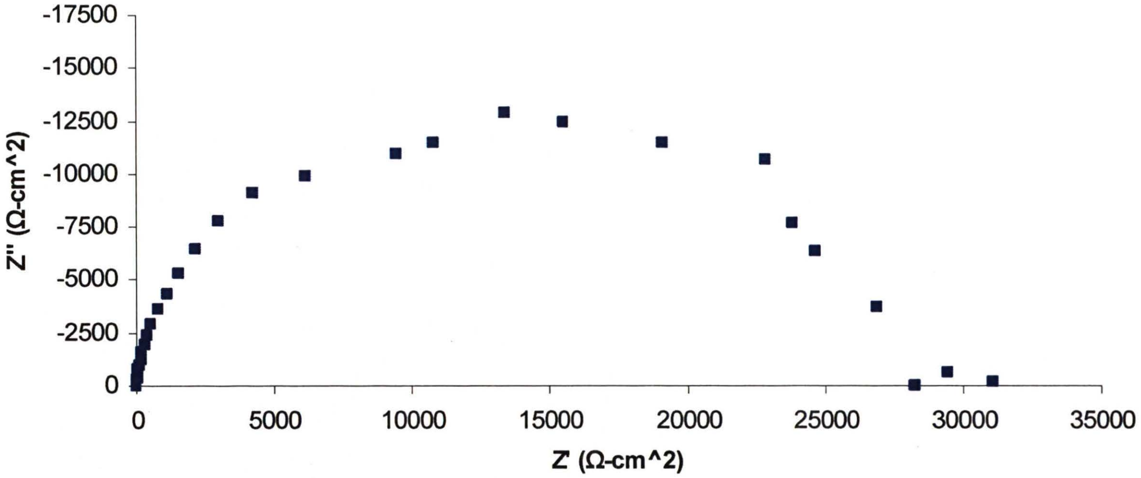

Figure 3 - Nyquist plot for an isopropyl alcohol wiped aluminum 7075-T6 panel

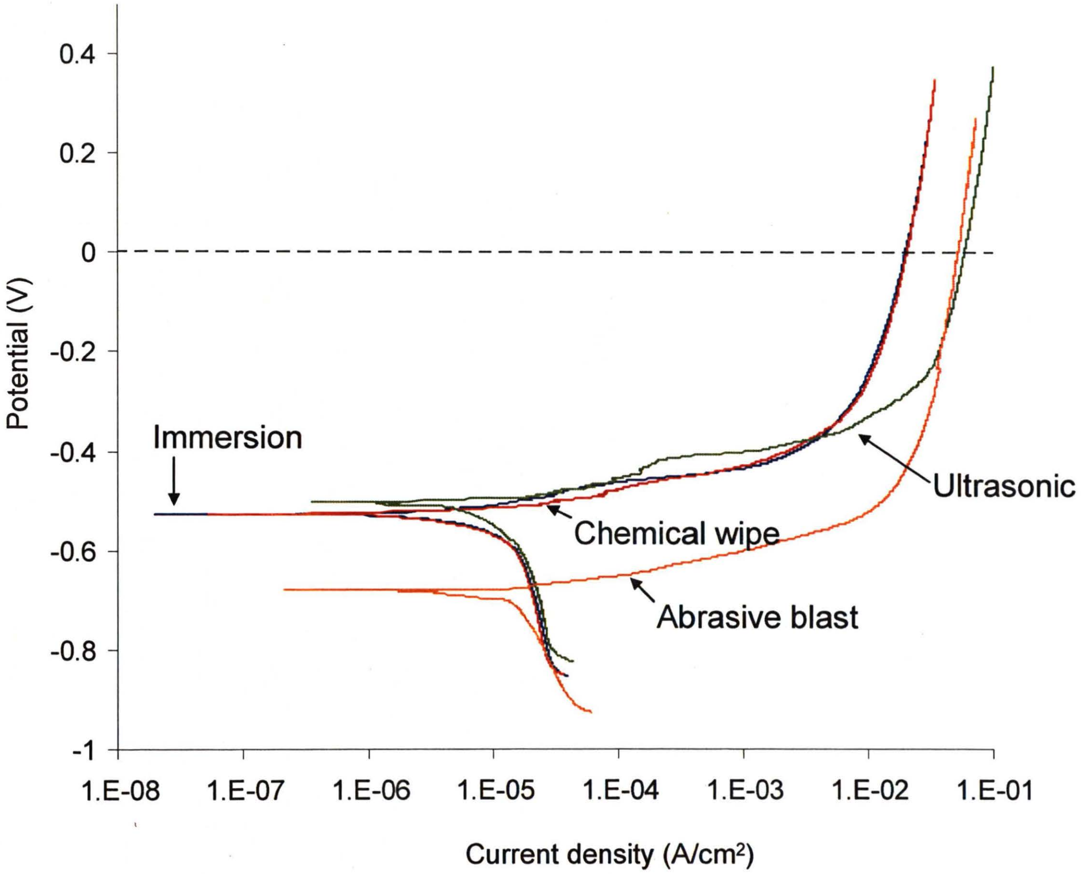

Figure 4 - Potentiodynamic scans performed on aluminum 7075-T6 panels prepared using different methods

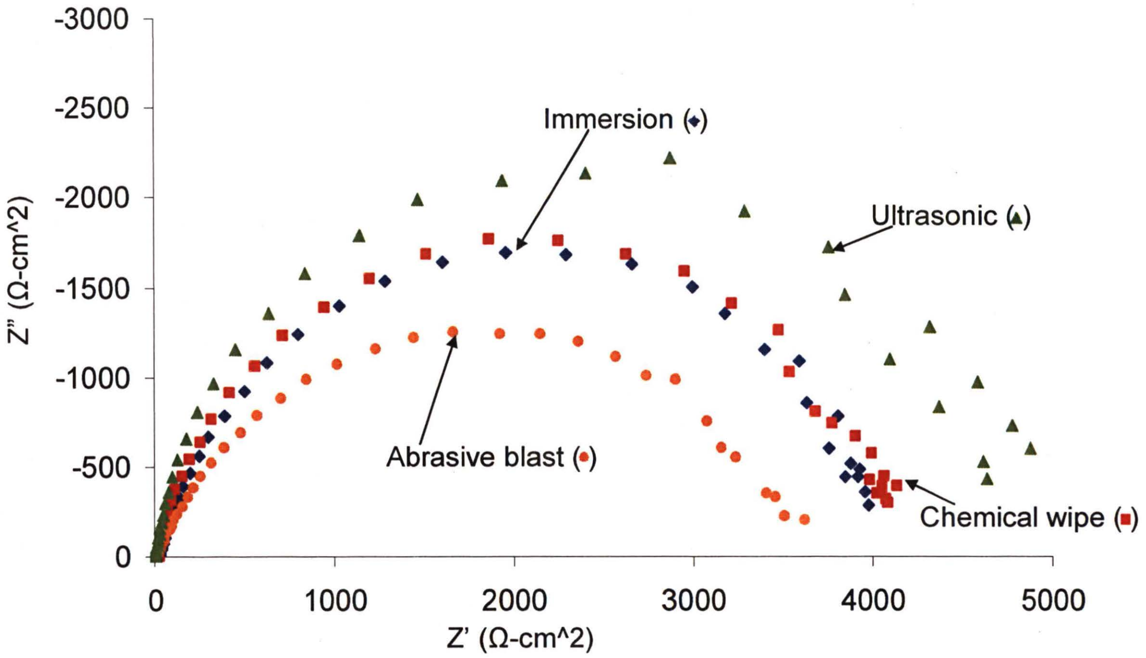

Figure 5 – Nyquist plots for aluminum 7075-T6 panels prepared using different methods

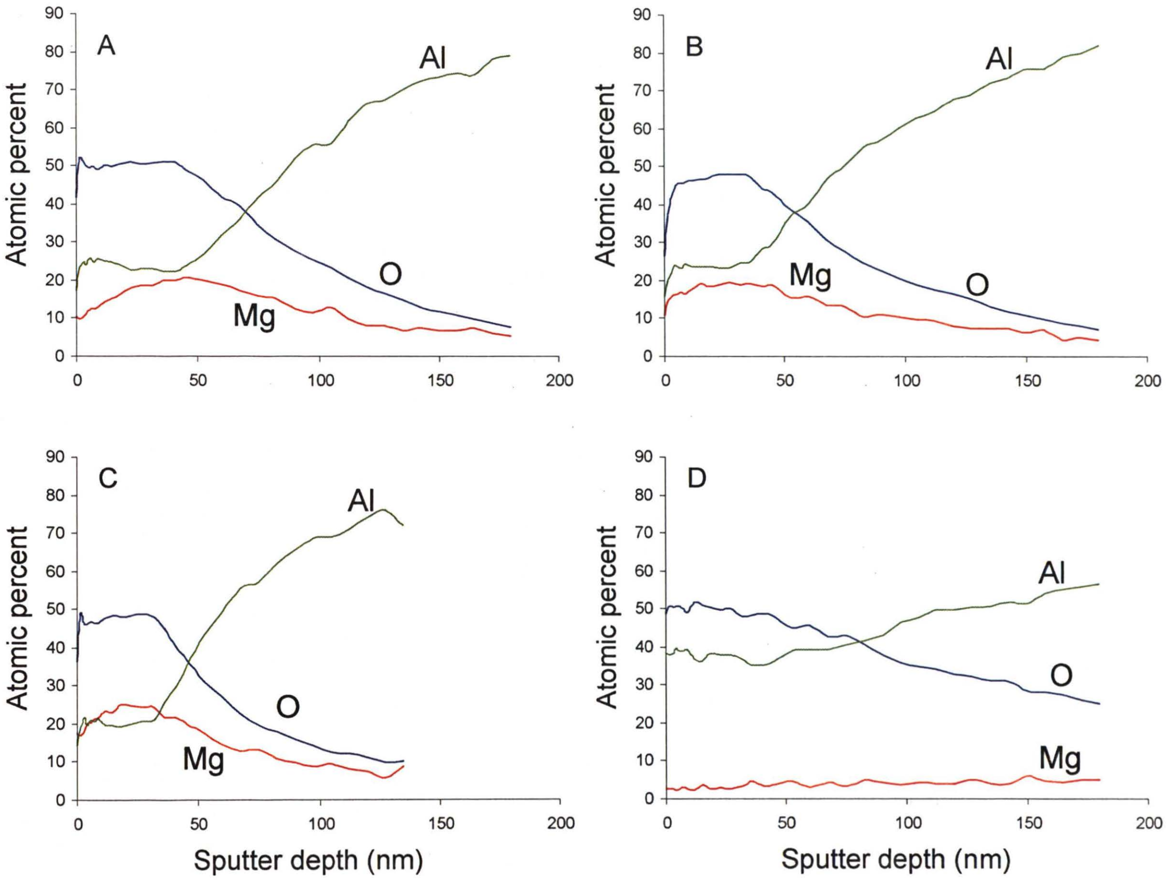

Figure 6 - AES depth profiles of prepared aluminum 7075-T6 panels
A) immersion procedure, B) ultrasonic processing, C) chemical wipe, and D) abrasive blasting

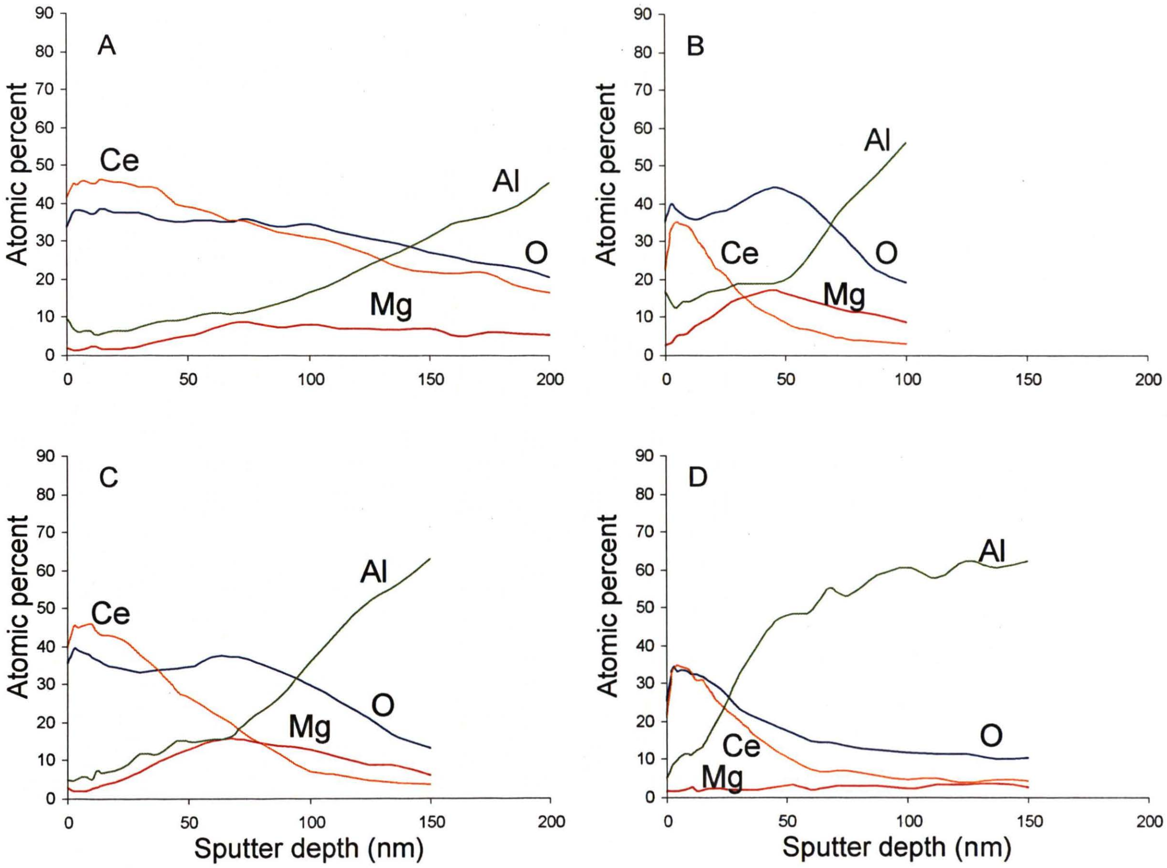

Figure 7 – AES depth profiles of coated aluminum 7075-T6 panels
A) immersion procedure, B) ultrasonic processing, C) chemical wipe, and D) abrasive blasting

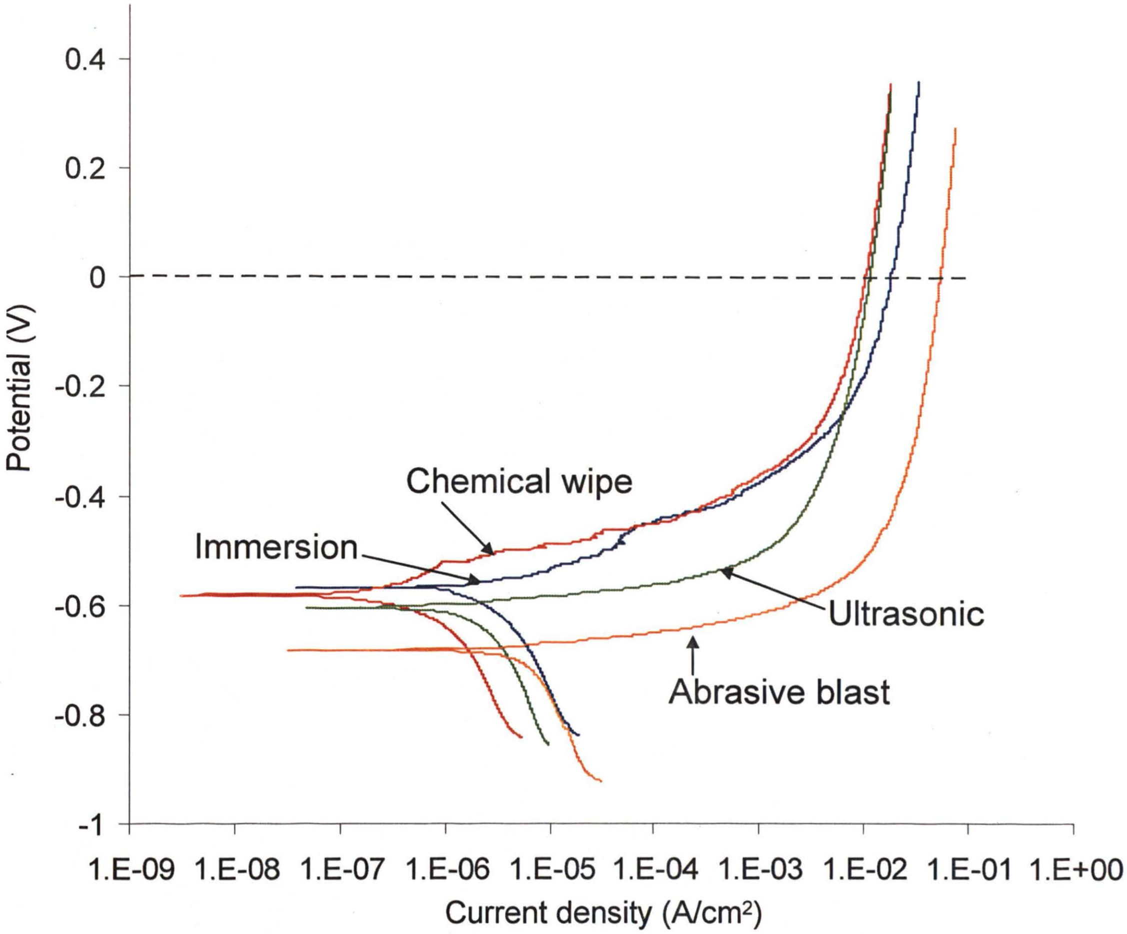

Figure 8 - Potentiodynamic scans performed on aluminum 7075-T6 panels with CeCCs deposited on panels prepared using each method

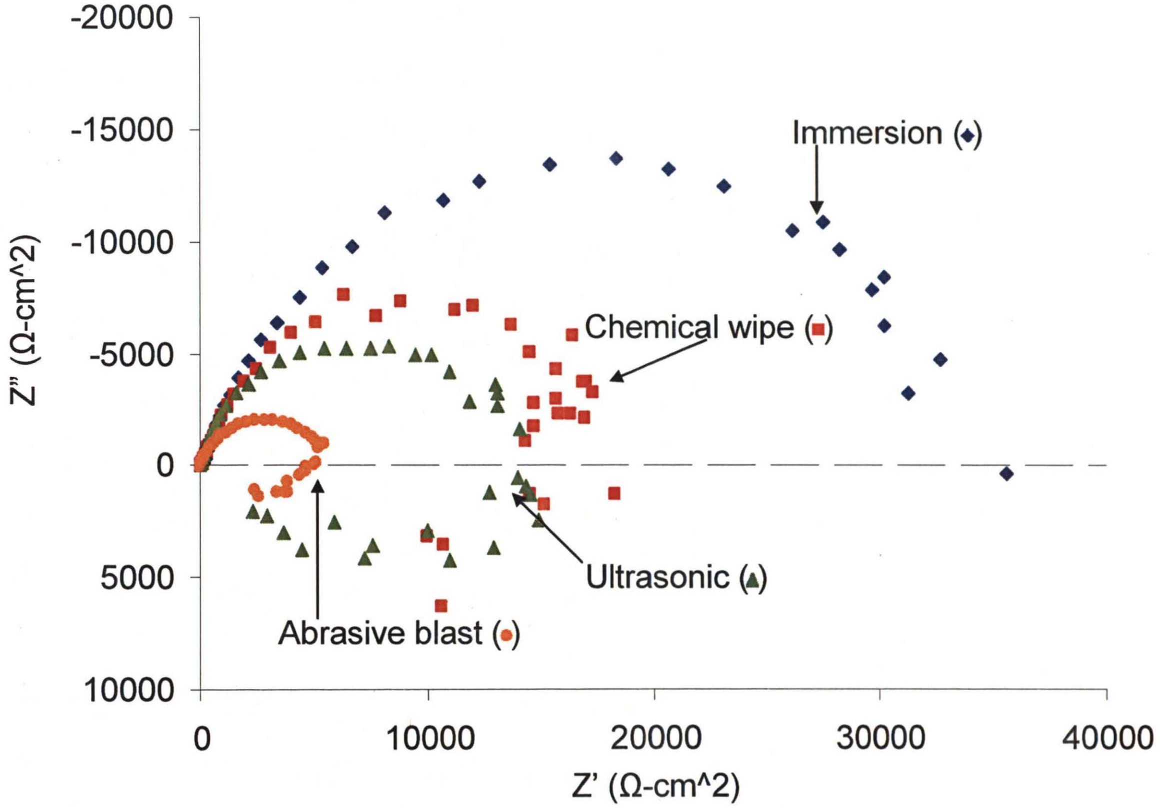

Figure 9 - Nyquist plots for aluminum 7075-T6 panels with CeCCs deposited on panels prepared using each method

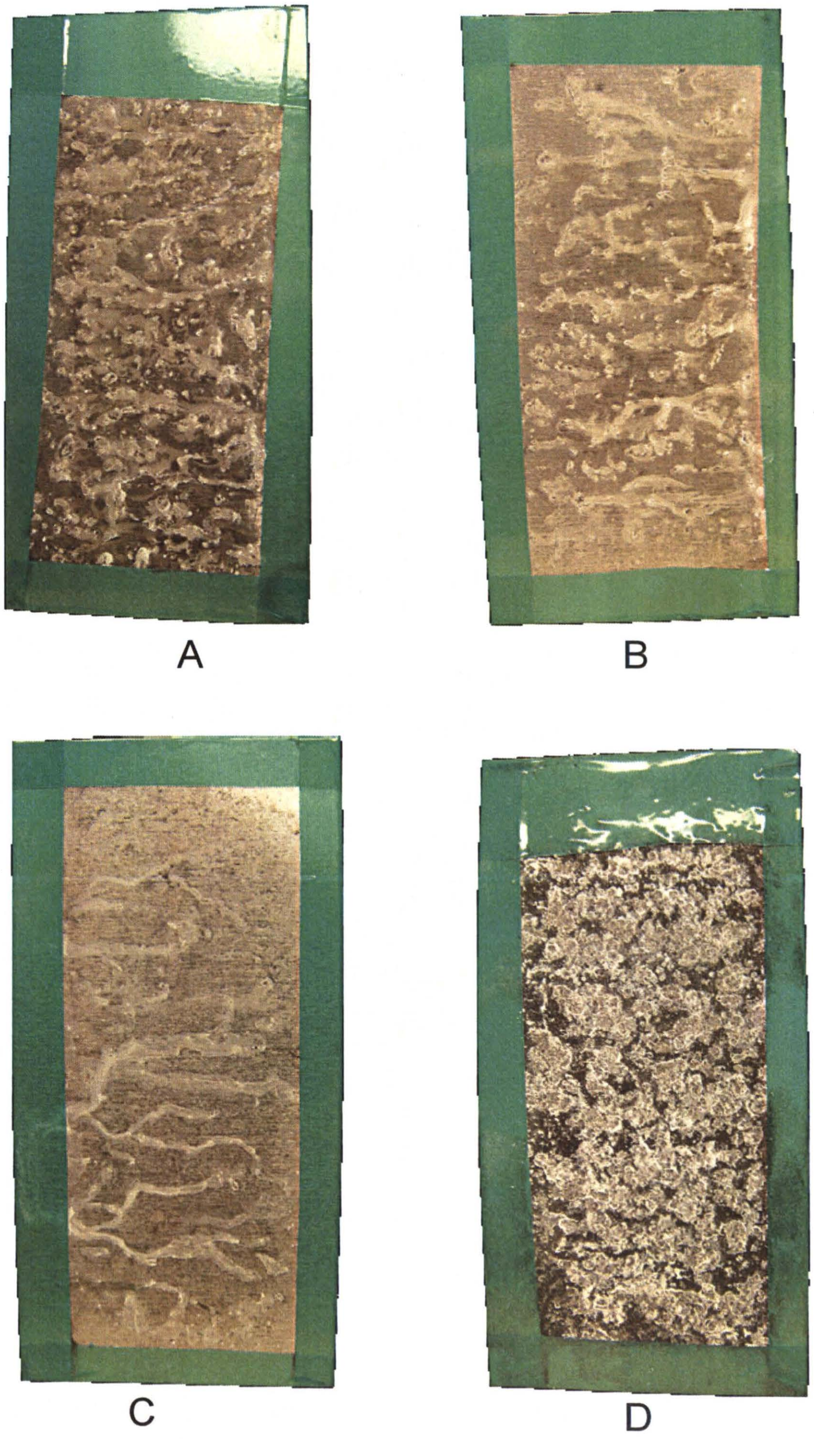

Figure 10 - Optical images of prepared aluminum 7075-T6 panels after exposure to salt fog for 18 hours A) chemical immersion, B) chemical wipe, C) ultrasonic processing, and D) abrasive blasting

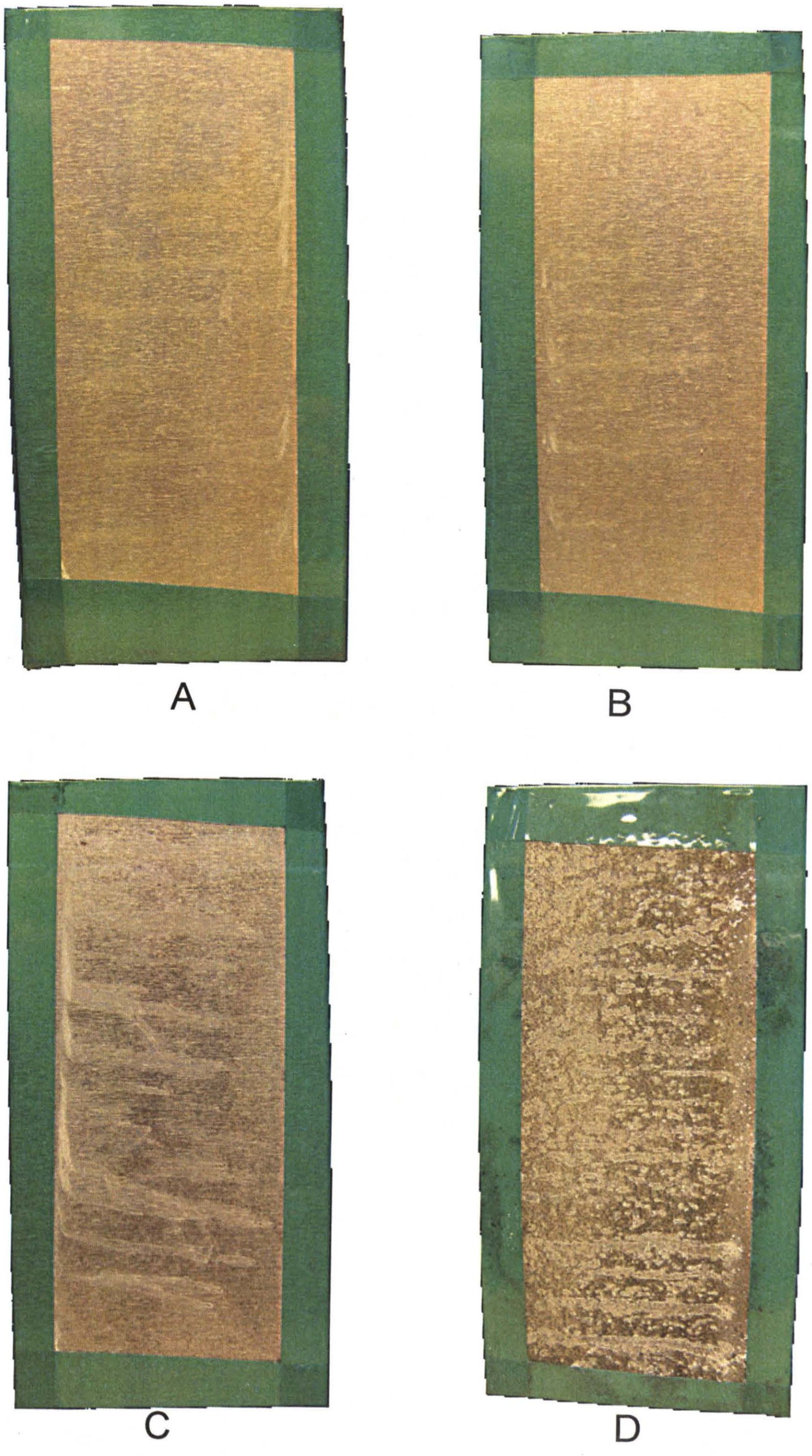

Figure 11 - Optical images of coated aluminum 7075-T6 panels after exposure to salt fog for 18 hours A) chemical immersion, B) chemical wipe, C) ultrasonic processing, and D) abrasive blasting

Table 1 – Potentiodynamic fitted values

Surface Preparation	B_{anodic} (mV/dec)		$B_{cathodic}$ (mV/dec)		I_C ($\mu A/cm^2$)		E_C (mV)	
	Uncoated	Coated	Uncoated	Coated	Uncoated	Coated	Uncoated	Coated
Alcohol wiped	32 - 69	X	-92 - -160	X	0.09 – 0.73	X	-530 - -540	X
Immersion prepared	23 - 39	132 - 180	-33 - -84	-95 - -140	3.23 - 3.24	0.13 - 0.39	-530 - -580	-600 - -620
Chemically wiped	20 - 26	49 - 84	-50	-45 - -87	1.09 - 1.74	0.08 - 0.21	-500 - -530	-500 - -580
Ultrasonically prepared	46 - 121	28 - 41	-35 - -76	-194 - -309	0.16 - 0.36	4.40 - 4.50	-500 - -550	-600
Abrasively blasted	22 - 28	24 - 28	-167 - -180	-129 - -351	7.00 - 7.30	3.30 - 5.80	-660	-680

Table 2 –Impedance fitted values

Surface Preparation	R_S $(\Omega\text{-cm}^2)$		C $(\mu F/cm^2)$		n		R_{CT} $(k\Omega\text{-cm}^2)$	
	Uncoated	Coated	Uncoated	Coated	Uncoated	Coated	Uncoated	Coated
Alcohol wiped	19 - 75	X	4.4 - 5.8	X	0.97 - 0.98	X	24 - 26	X
Immersion prepared	22	29 - 41	10 - 16	19.0	0.83 - 0.87	0.71 - 0.75	4.4 - 4.8	12 - 44
Chemically wiped	24 - 25	51 - 52	7.0	11.0	0.88 - 0.89	0.76 - 0.77	4.1 - 4.4	13 - 18
Ultrasonically prepared	22 – 23	28 -49	5 – 6	5 – 6	0.95 - 0.99	0.87 - 0.90	10 – 12	12 – 15
Abrasively blasted	20	22 -28	0.1	27 - 33	0.78	0.81 - 0.85	3.4 - 3.6	4 - 5

II. Deposition of cerium-based conversion coatings using a spontaneous brush application process

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Abstract

A spontaneous, brush-based method was investigated to deposit cerium-based conversion coatings on aluminum 2024-T3 as an alternative to spray or immersion deposition processes. Brush application was shown to be feasible, but produced coatings that were only ~200 nm thick after three deposition cycles compared to spray deposition that produced coatings ~400 nm after the same number of deposition cycles. The brush and spray applied coatings had a similar morphology, sub-micron cerium-rich nodules with a network of fine cracks. X-ray diffraction patterns found the brush deposited cerium coating contained cerium oxide, while the spray deposited coatings contained cerium oxide and cerium phosphate. Testing in ASTM B117 neutral salt spray showed that brush deposited coatings provided some corrosion protection but did not perform as well as spray deposited coatings.

1. Introduction

High strength aluminum alloys, such as Al 2024-T3, contain second phase intermetallic particles. The second phase particles precipitate during heat treatment and strengthen the alloy. Precipitation depletes alloying elements from the matrix surrounding the particles and concentrates the alloying elements into the second phase particles. The composition differences between the matrix and the intermetallic particles can lead to galvanic corrosion. [1] As a result, chromate conversion coatings are frequently used for corrosion protection for these alloys. [2] Because chromates are carcinogenic and environmentally hazardous [3, 4], alternative coatings are being researched. [5, 6, 7, 8] Cerium-based conversion coatings (CeCC) are a promising potential alternative.

Previous research has investigated spontaneous methods for immersion and spray deposition of CeCCs on Al 2024-T3. [9, 10] Immersion processes are useful when components can be separated and submerged into coating baths. Spray processes can be used to coat large surface areas quickly, parts that cannot be disassembled, and components that may be damaged by, or too large for, immersion. A brush application process would be useful for touch-up and repairs, which are often performed in locations without access to specialized coating facilities.

This study investigates a brush based deposition method for CeCCs on Al 2024-T3 as an alternative to spray and immersion deposition methods.

2. Experimental

The substrates were cold rolled aluminum 2024-T3 sheets cut into 3.8 cm by 7.6 cm panels. These panels were degreased with an isopropyl alcohol saturated laboratory wipe, followed by rinsing in tap water. The panels were then immersed into a 5 wt% solution of an alkaline cleaner (Turco 4215NC-LT) for 5 minutes at 55°C followed by rinsing with deionized (DI) water. The cleaned panel surfaces were activated by immersion in an aqueous solution containing 1 wt. % sulfuric acid held at 50°C for 10 minutes. Coatings were deposited from a cerium-based solution containing 10 g hydrated cerium chloride (99.9% $CeCl_3 \cdot 7H_20$, Alfa Aesar), 20 mL hydrogen peroxide solution (30% H_2O_2, Fisher Scientific), 220 mL DI water, and 0.8 g gelatin (RDH, Rousselot). The coating solution was adjusted to a pH of ~2.3 using dilute HCl. Panels were held at an angle of 70° to horizontal for deposition. Coatings were deposited using two inch wide natural bristle brushes. A layer of coating solution was spread on the panel surface using a brush that had been dipped in the coating solution. After producing a uniform layer over the entire panel surface (~10 seconds) the coated panels were allowed to drain for 35 seconds. The brush-drain cycle was repeated up to 7 times to form the desired coating.

For comparison, coatings were also deposited using an air powered spray gun (Husky detail spray gun, Husky Professional Tools). Panels were held at an angle of ~70° to horizontal and sprayed for approximately 5 seconds to produce a uniform layer of solution on the surface. The panels were then allowed to drain for 35 seconds. Panels were coated using one, three, or five spray-drain cycles.

After deposition, the panels were rinsed with DI water and post-treated by immersion in a solution containing 2.5 wt. % Na_3PO_4 hydrate (98.8% $Na_3PO_4 \cdot 12H_2O$, Fisher Scientific) adjusted to a pH of 4.5 using phosphoric acid. The solution was held at a temperature of 85°C, and panels were immersed for five minutes.

Corrosion performance of coated panels was evaluated using neutral salt spray in a cyclic corrosion test chamber (Q Fog CCT 1100, Q Panel) according to ASTM B117. Panels were exposed to the salt spray for one week (168 hours). Surface morphology was examined using scanning electron microscopy (SEM, Hitachi S-570) and crystalline phases were identified using X-ray diffraction (XRD, Philips X-Pert) analysis. The XRD analysis was repeated three times. Coating thickness was measured using Auger electron spectroscopy (AES, Physical Electronics Model 545) depth profiling analysis.

3. Results and Discussion

Cerium-based conversion coatings were applied using the brush deposition method and were first examined optically for color. The brush applied coatings initially produced light yellow surfaces with some darker areas. Increasing the number of brush-drain cycles produced darker, more evenly colored coatings. After the initial deposition, spray coatings were darker and had a more uniform appearance than the initial brush coatings. As with the brush process, spray deposited coatings became darker as the number of spray cycles increased.

Coating appearance can be influenced by a number of factors such as the phases present, thickness, and film cracking. AES depth profiles were collected to measure coating thickness. Depth profiles were taken from the darkest and lightest areas of the brush coatings. Darker areas were thicker than the light areas. Single brush cycle coatings varied from ~80 nm in light areas to ~160 nm in dark areas, while 5 cycle coatings varied from ~225 nm in light areas to ~325 nm in darker areas. For comparison, coatings deposited using a single spray cycle had a thickness of ~130 nm , while 5 spray cycle coatings were ~450 nm . Figure 1 compares the thickness values for the two methods as a function of coating cycles. The thicknesses of the coatings deposited using one spray cycle and one brush cycle were similar (~100 nm). However, the measured thickness per cycle for the two methods was different. Based on AES depth profiling, each coating deposited using the brush process was thinner than the coating deposited using an equal number of spray cycles. The brush deposition slows after five cycles, indicating that brush deposited coatings may not be able to produce a total thickness comparable to the 5 spray coating of ~450nm.

Coating morphology was investigated using SEM (Figure 2). No peeling or bare areas were observed in either coating method. The 5 brush cycle coating (Figure 2a) was cracked and had several craters and pinholes. The surface cracks varied in size; about 15 percent of the surface had large cracks while the remainder of the surface had smaller cracks (Figure 2b). The 5 spray cycle coatings had similar surface cracking with a small fraction (~10%) having large cracks and the remainder consisting of a network of small cracks (Figure 2c). Despite the presence of cracks, previous research has found that coatings with this surface morphology were able to provide significant corrosion protection in salt spray testing. [11]

The phases in post-treated coatings were identified using XRD analysis. Figure 3 shows the representative XRD spectra obtained from post-treated coatings deposited using brush (3, 5, and 7 cycles) and spray (3 and 5 cycles). The brush cycle coatings had a broad, low intensity peak near 29° that is consistent with the presence of nanocrystalline cerium oxide (CeO_2), in agreement with previous CeCC research. [12] In contrast, the coating deposited using spray cycles had a different diffraction pattern. Broad peaks were observed which are consistent with the formation of hydrated cerium phosphate during the post-treatment. The formation of hydrated cerium phosphate has been correlated to improved corrosion protection. [12] X-ray diffraction results indicate that the deposition method can influence the ability to form cerium phosphate, which should impact corrosion protection.

Coatings deposited using 5 brush cycles offered moderate protection in neutral salt spray testing. After one week in ASTM B117 salt spray, the surface of the brush coated panels had many pits (~10 per cm^2 detected with optical microscopy) with some tailing, indicating that these panels were corroding. For comparison, coatings deposited using 5 spray cycles provided better protection in the neutral salt spray with less pitting (~6 per cm^2) and no visible tailing. In salt spray testing, coatings deposited using 3 spray cycles performed similarly to coatings deposited using 5 brush cycles. Based on analogy to the improvement in performance seen when increasing the number of spray deposition cycles from three to five, increasing the thickness of the brush applied coating by increasing the number of deposition cycles may improve performance.

4. Conclusion

A brush application process for depositing CeCCs was developed. Coating thicknesses for brush application were lower than for spray application, producing coatings up to ~325 nm thick in five brush cycles whereas five spray cycle coatings were ~425 nm. SEM analysis of the surface showed the brush applied coatings had surface morphologies that were similar to spray applied coatings. XRD analysis indicated the formation of a hydrated cerium phosphate layer during post-deposition treatment was dependent on the deposition method; brush coatings did not form the phosphate phase whereas spray-deposited coatings did. All post-treated coatings provided some protection in ASTM B117 neutral salt spray. The coating deposited using five brush cycles had similar corrosion protection as coatings deposited using three spray cycles.

5. Acknowledgements

The support and guidance of Bruce Sartwell of the Strategic Environmental Research and Development Program (SERDP), Donna Ballard of AFRL/MLLB under SERDP Project WP-1519, Contract W912HQ-06-C-0030, is gratefully acknowledged. Also thanks are extended to Jeff Wight (AES), Clarissa Wisner (SEM), and Eric Bohannan (XRD) from the Materials Research Center at Missouri S&T.

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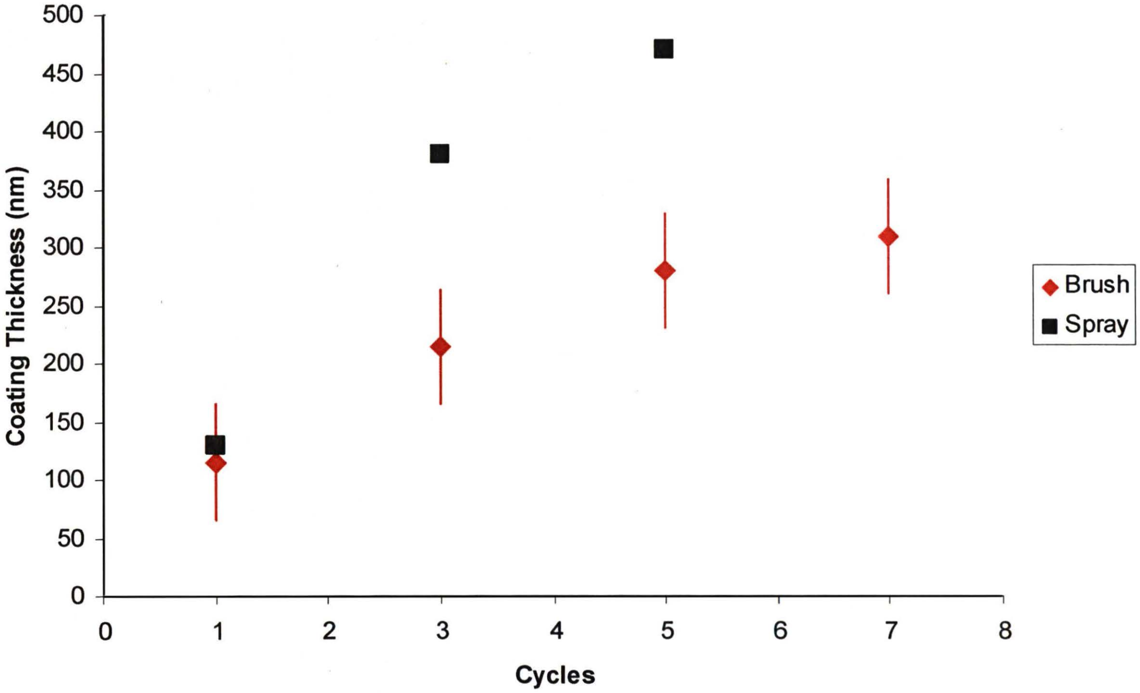


Figure 1 - Coating thickness as a function of the number of brush or spray deposition cycles

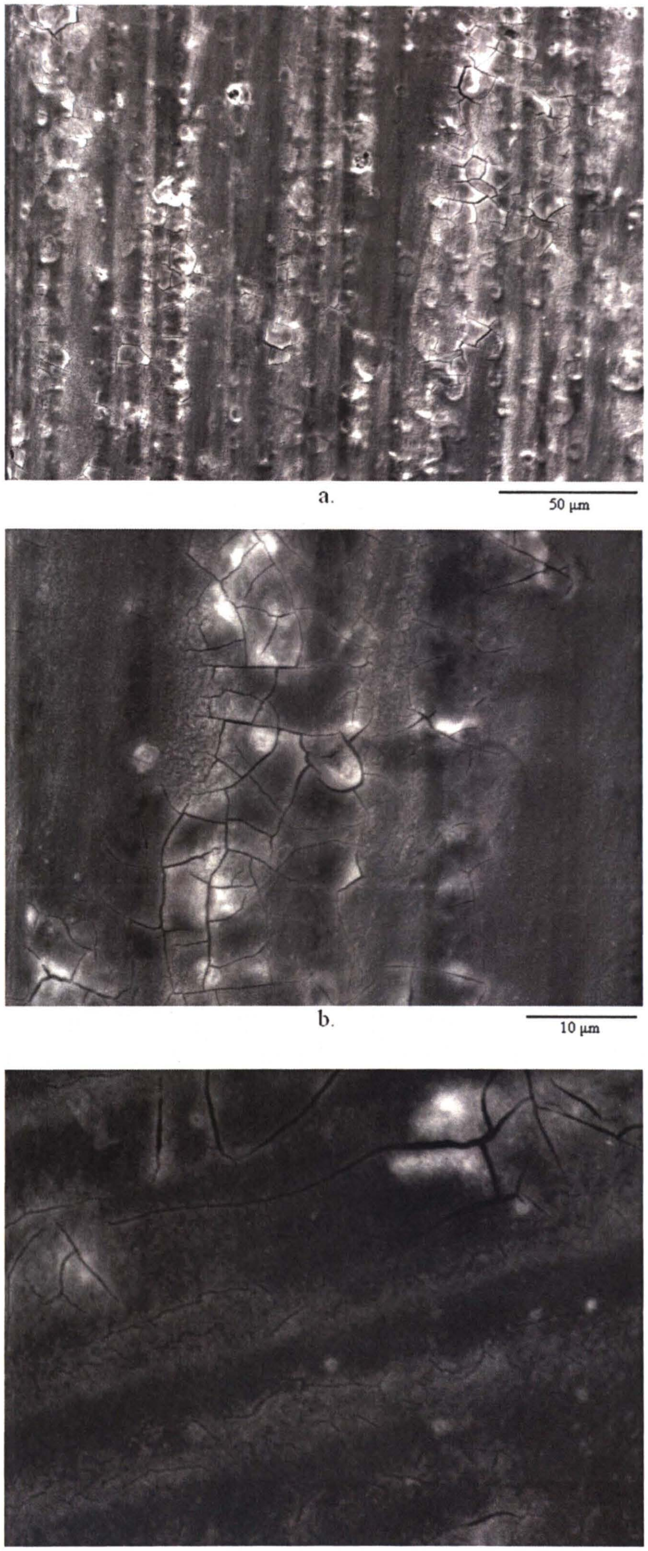


Figure 2 - SEM images of coatings that were brush or spray deposited a) Brush deposited, low magnification, b) Brush deposited, high magnification, c) a spray deposited, high magnification

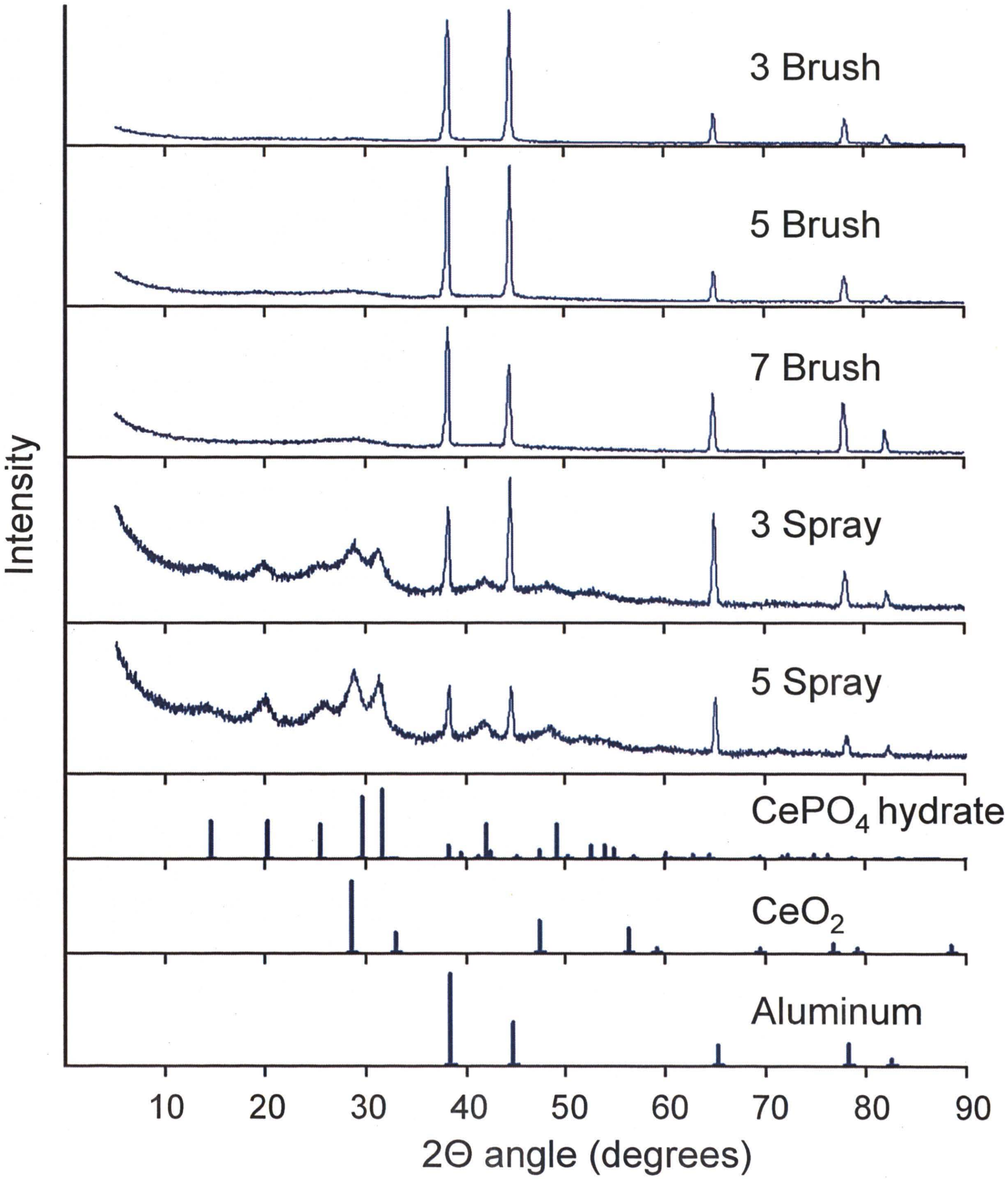


Figure 3 - XRD spectra for coatings deposited using three, five, and seven brush cycles, and three and five spray cycles

SECTION

3. CONCLUSIONS

Three different alternative surface preparation methods and an alternative deposition method were investigated for deposition of cerium-based conversion coatings on high strength aluminum alloys. The alternative surface preparation methods on Al 7075-T6 were compared to a previously developed immersion method of surface preparation based on coating thickness, surface chemistry, electrochemical responses, and corrosion performance. All surface preparation methods were effective pretreatments for cerium conversion coatings. The deposited coating thickness depended on the preparation method used; uncoated surfaces that were more inert had a thinner coating. Abrasively blasted panels were an exception. The blasted panel has a thick, but unprotective oxide layer that dissolved into the acidic deposition solution and caused a thin initial CeCC deposition. Conversion coatings improved the corrosion resistance of the surfaces over the prepared surfaces in all cases. The chemical wipe method produced the surface that was most electrochemically and chemically similar to the standard immersion method; however, the coating deposited was thinner than the immersion method. The chemical wipe coating also performed the most like the immersion coating in corrosion testing. All alternative methods tested were effective alternatives for pretreatment; the chemical wipe process produced coatings most similar to coatings on immersion prepared substrates.

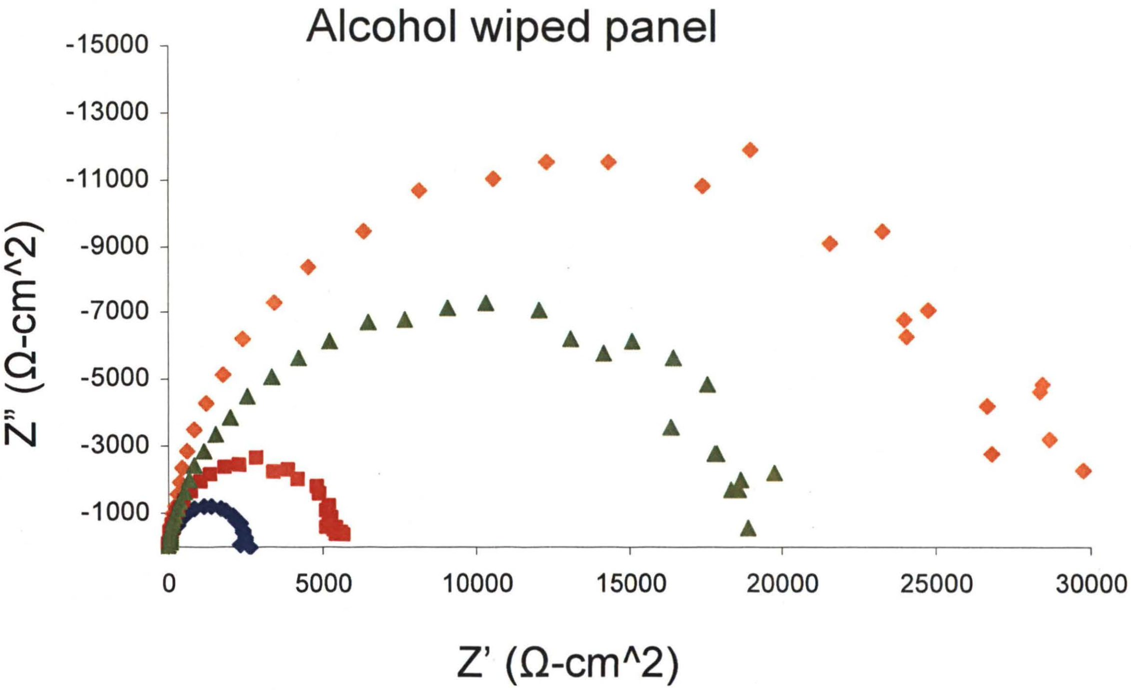
An alternative brush-based process for cerium-based conversion coating deposition on Al 2024-T3 aluminum was also developed and compared to the previously established spray-based deposition process. These processes were compared based on coating thickness, coating morphology, and crystalline phases present in the finished coating. The brush-based process deposited thinner coatings than the spray-based process; coating thickness after five brush cycles was comparable to coating thickness after three spray cycles. The morphology of the deposited coatings appeared similar in the SEM. Cerium phosphate, a phase that has been shown to increase corrosion protection, was not detected in the brush-deposited coatings; it was detected in spray-deposited coatings. Brush applied coatings are able to provide corrosion resistance without the need for spray processes.

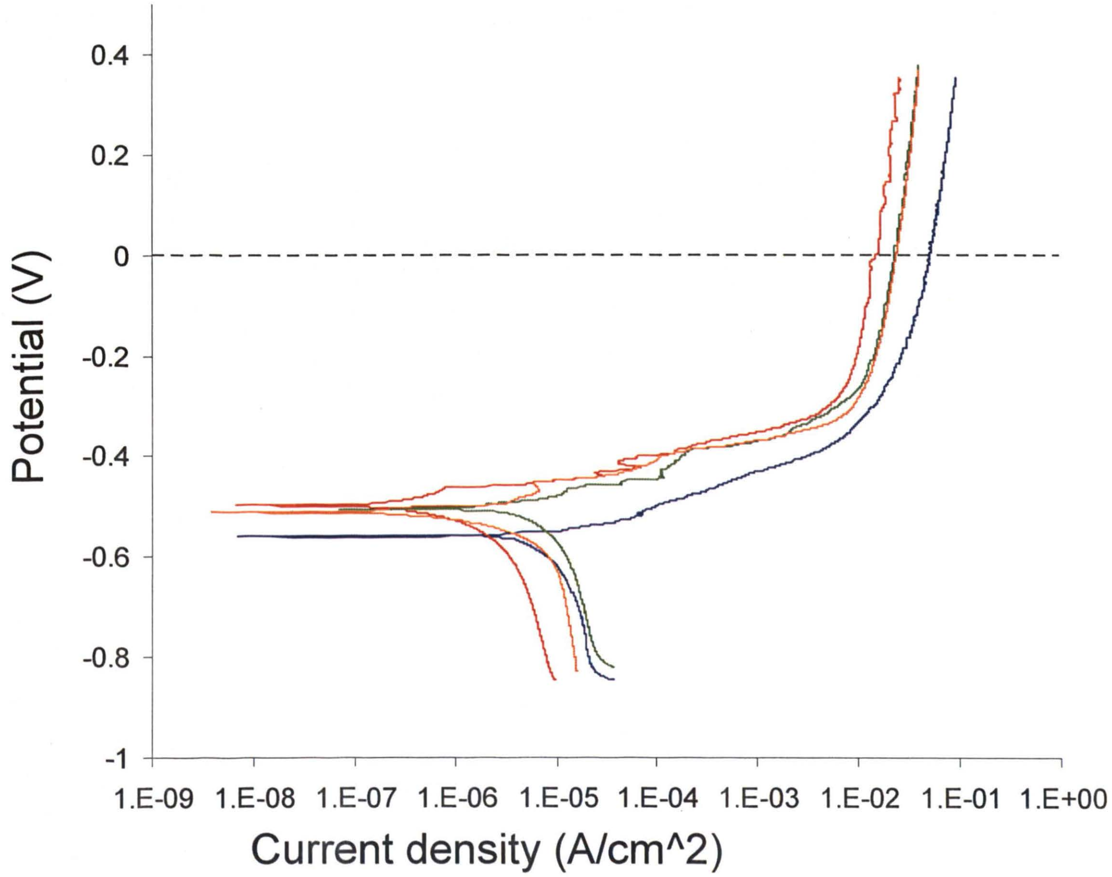
4. FUTURE WORK

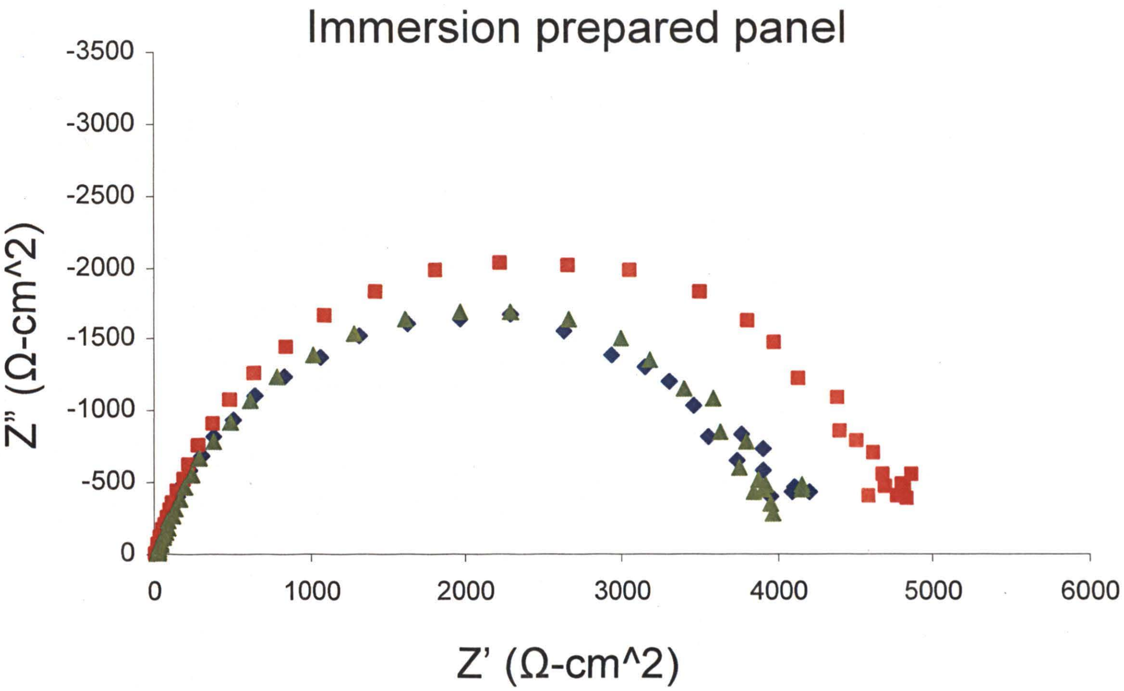
There are experiments that would expand and improve this study. The first experiment would be to determine the effect the ultrasonic process has on the substrate and protective oxide, the process does not change oxide thickness but noticeably changes electrochemical response and improves coating deposition. A second area of study would be the reason cerium phosphate is not found in brush applied coatings but is found in spray applied coatings processed under the same conditions.

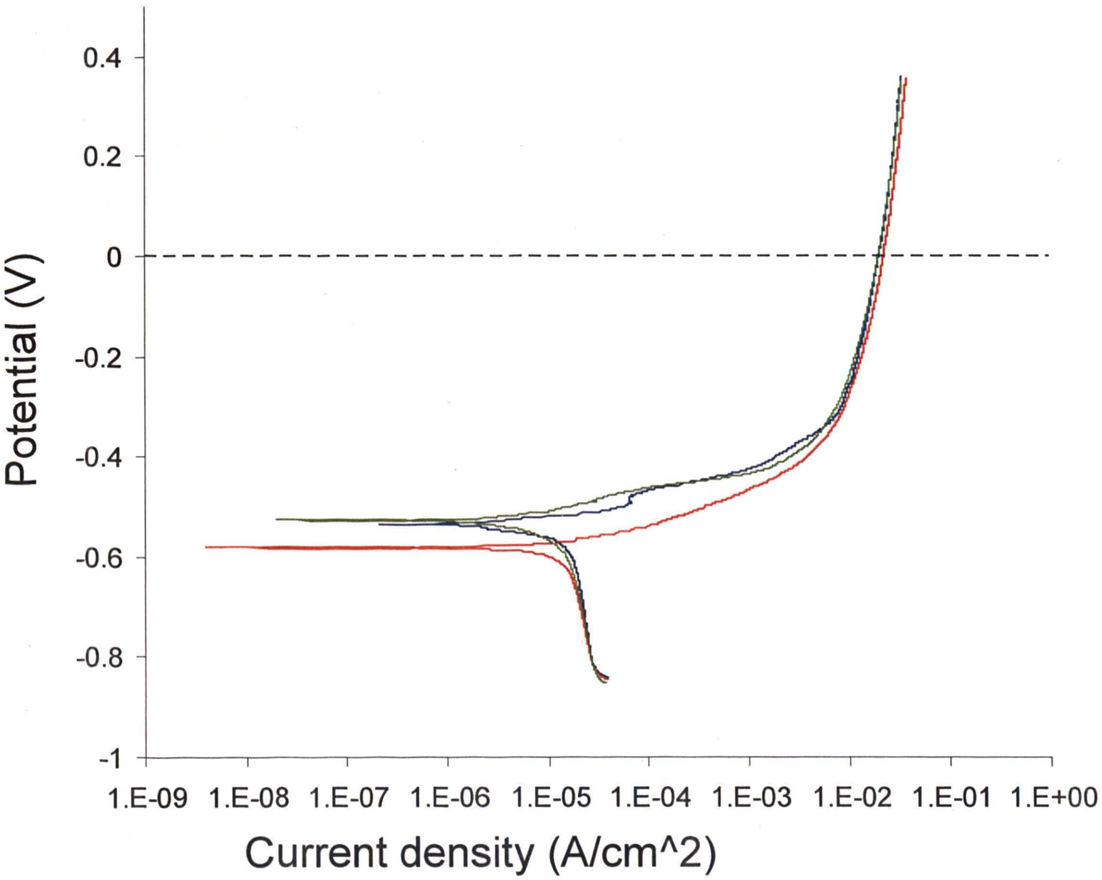
5. APPENDIX

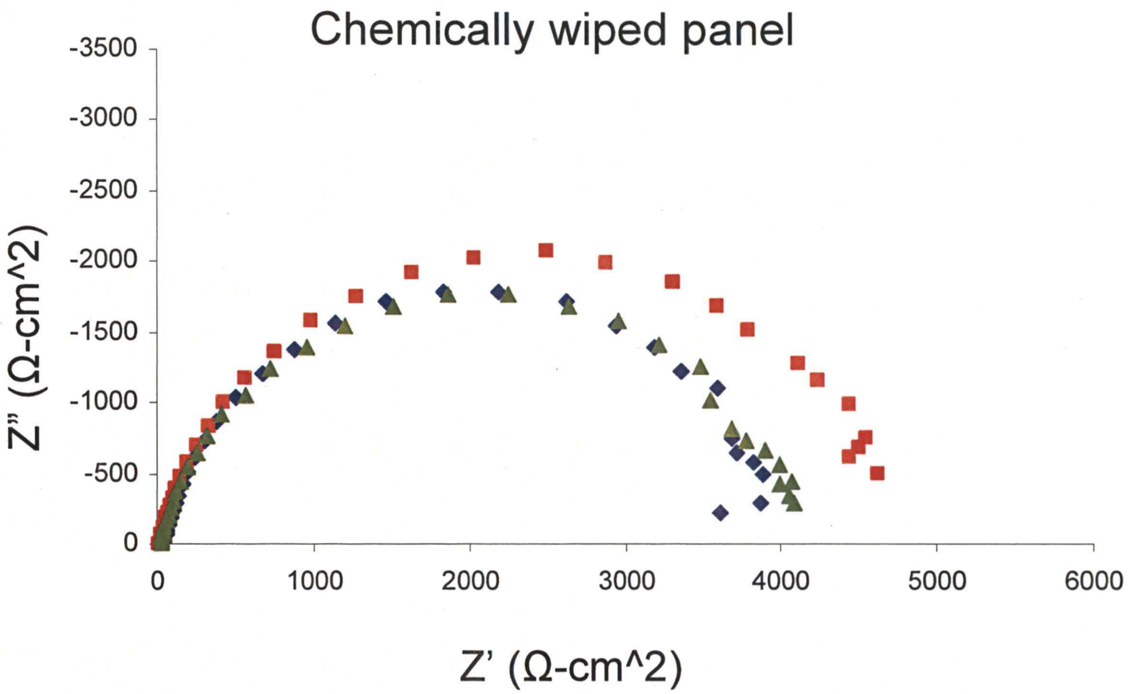
Al 7075 panels were degreased with isopropyl alcohol and then given one of four surface treatments: immersion treatment, chemical wipe, ultrasonic preparation, or abrasive blasting. Immersion treated panels were cleaned by immersing into a 55°C alkaline cleaning solution (Turco 4215 NC-LT) for five minutes and then surface activated by immersion into a room temperature 2 wt. % NaOH solution for 20 seconds. Chemically wiped panels were prepared by wiping solution onto the panel for approximately 10 seconds then the wipe was resaturated for 10 seconds. The alkaline cleaning solution was applied 15 times for a total time of five minutes, while the NaOH solution was applied for one cycle or 20 seconds. Ultrasonically prepared panels were placed into a water bath, which was run for five minutes. Only one side of the panel was exposed to the solution, so the panel was then turned over and the bath run for another five minutes, for a total process time of ten minutes. The abrasively blasted panels were blasted using alumina until one side of the panel had a uniform frosted appearance, and then the same ultrasonic process was used to remove embedded abrasive. Coatings were deposited from a solution containing 10 g hydrated cerium chloride, 20 mL hydrogen peroxide solution (30% H_2O_2), 220 mL DI water, and 0.8 g gelatin, which was spray applied using a air-powered spray gun. No post-treatment was used. Impedance spectroscopy and potentiodynamic tests were performed on alcohol wiped panels, prepared panels, and panels coated with one spray cycle. Three tests were performed on each condition except the alcohol wiped condition; four tests were used for the alcohol wiped condition.

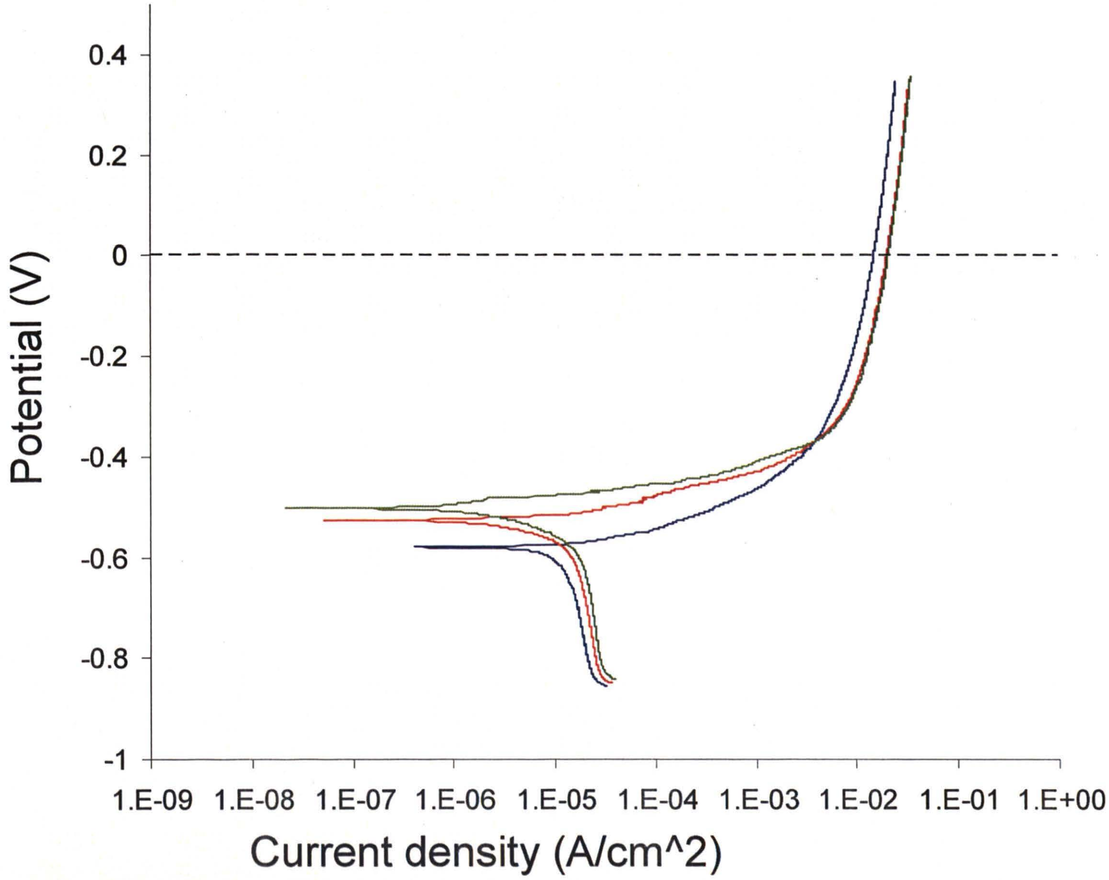

Alcohol wiped panel
-15000
-13000
-11000
-9000
-7000
-5000
-3000
-1000
Z" (Ω-cm^2)
0
5000
10000
15000
20000
25000
30000
Z' (Ω-cm^2)

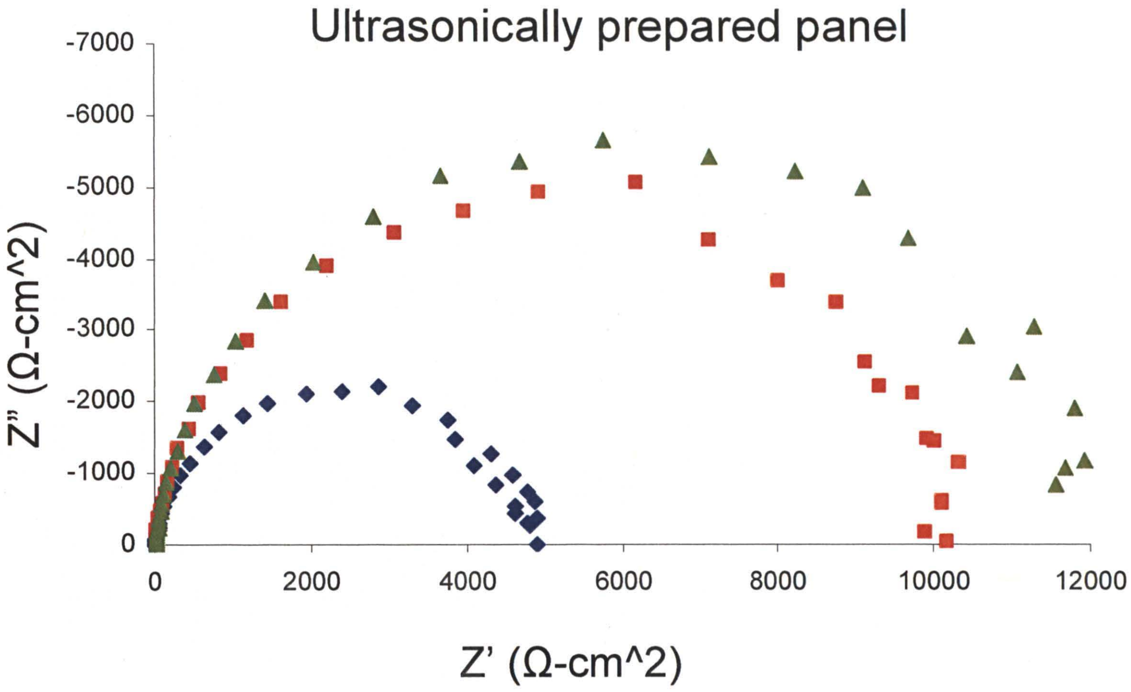

0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
Potential (V)
1.E-09
1.E-08
1.E-07
1.E-06
1.E-05
1.E-04
1.E-03
1.E-02
1.E-01
1.E+00
Current density (A/cm^2)

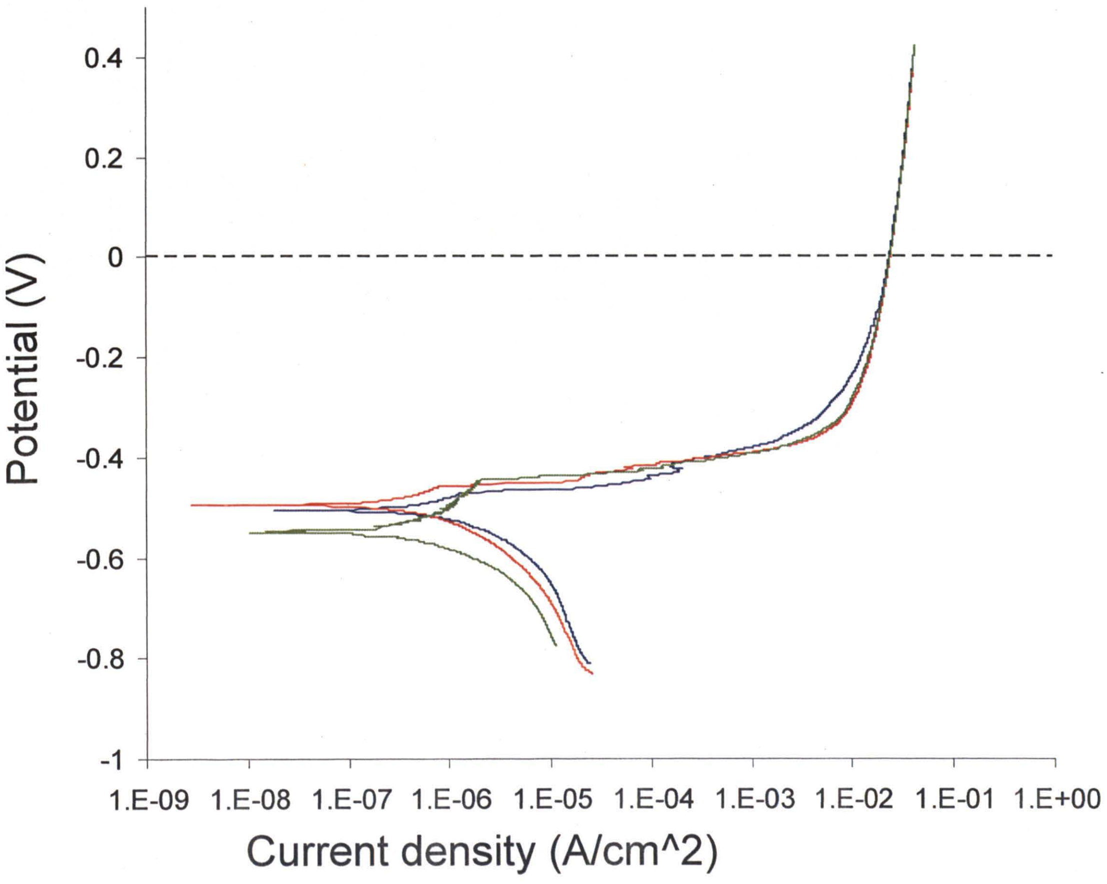

Immersion prepared panel
-3500
-3000
-2500
-2000
-1500
-1000
-500
0
Z" (Ω-cm^2)
0
1000
2000
3000
4000
5000
6000
Z' (Ω-cm^2)

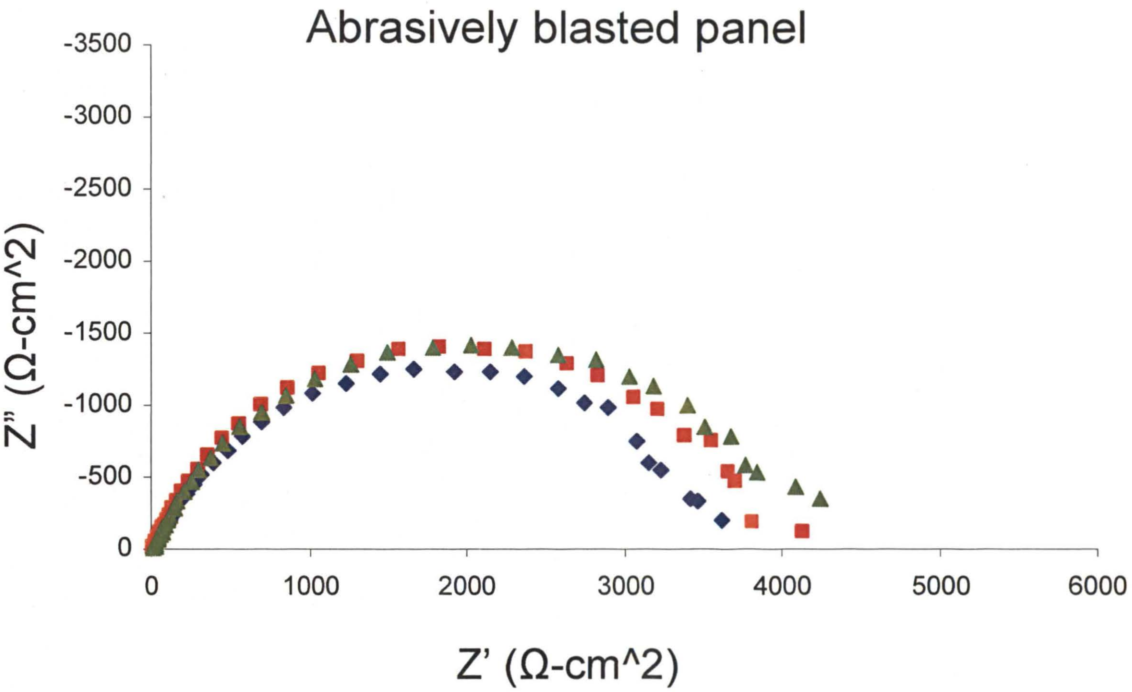

0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
Potential (V)
1.E-09
1.E-08
1.E-07
1.E-06
1.E-05
1.E-04
1.E-03
1.E-02
1.E-01
1.E+00
Current density (A/cm^2)

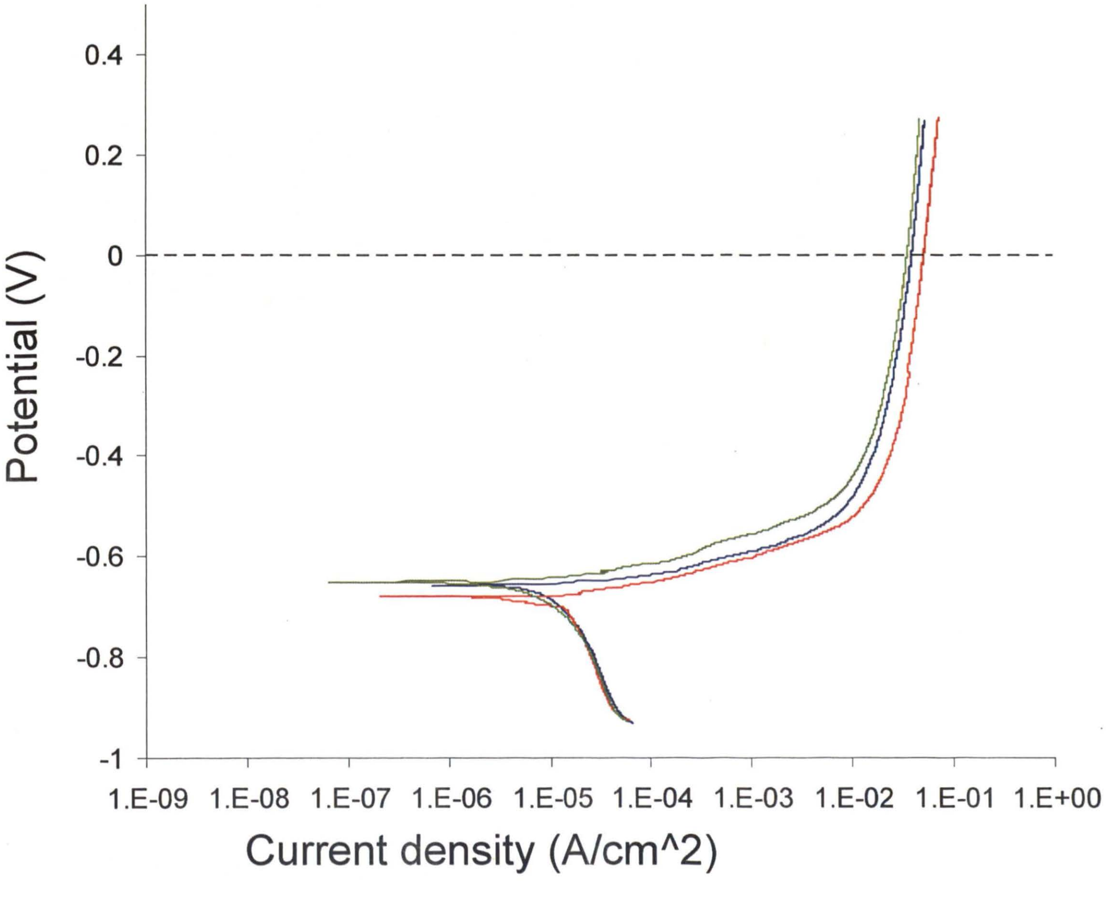

Chemically wiped panel
Z" (Ω-cm^2)
-3500
-3000
-2500
-2000
-1500
-1000
-500
0
0
1000
2000
3000
4000
5000
6000
Z' (Ω-cm^2)

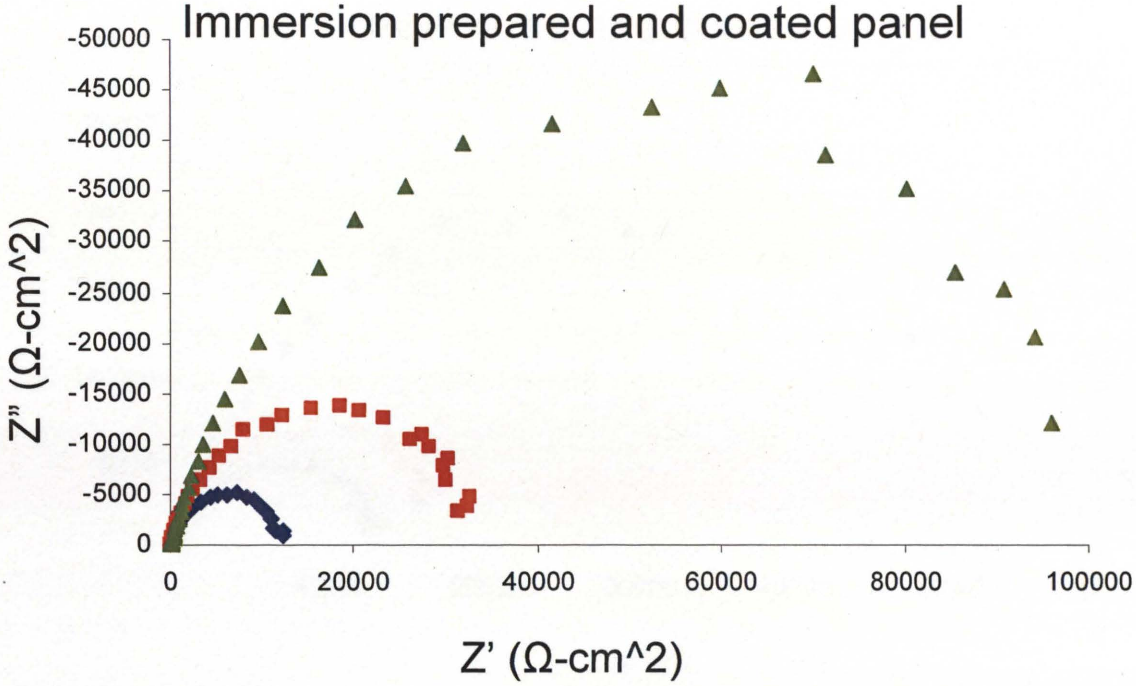

Potential (V)
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
1.E-09
1.E-08
1.E-07
1.E-06
1.E-05
1.E-04
1.E-03
1.E-02
1.E-01
1.E+00
Current density (A/cm^2)

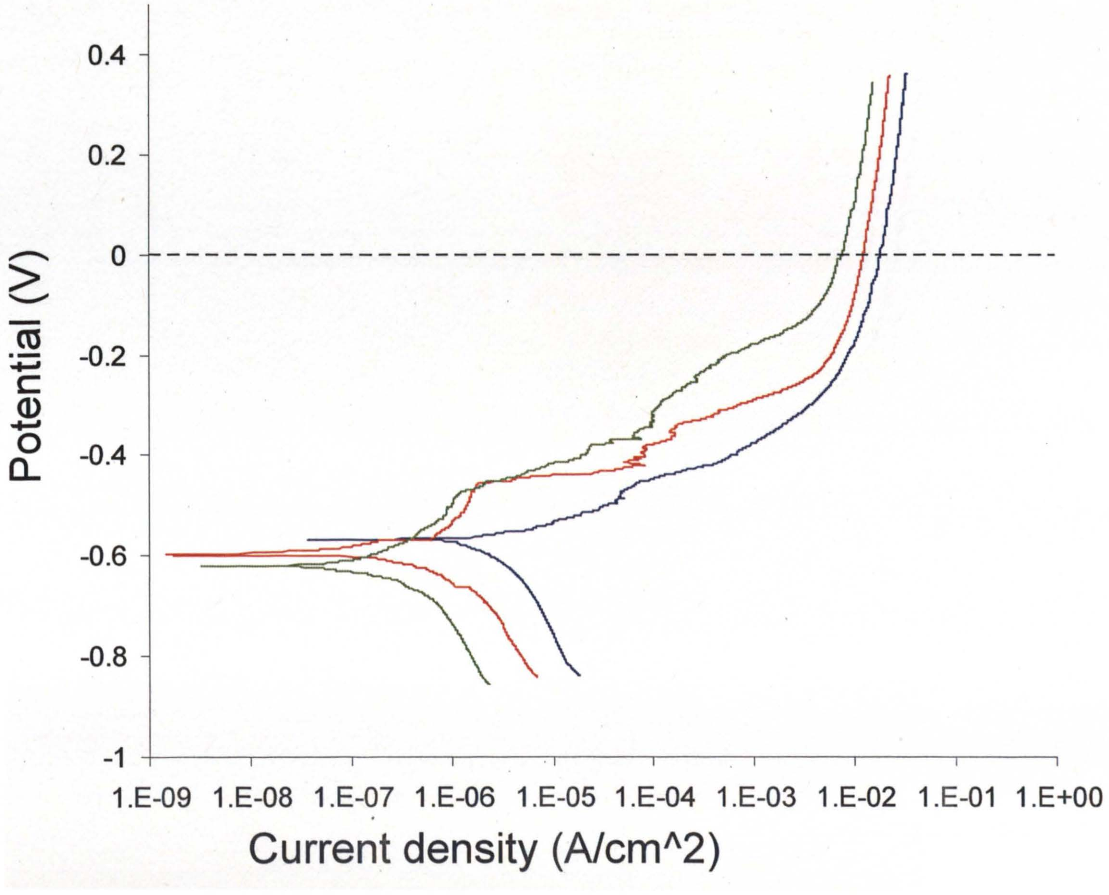

Ultrasonically prepared panel
Z" (Ω-cm^2)
-7000
-6000
-5000
-4000
-3000
-2000
-1000
0
0
2000
4000
6000
8000
10000
12000
Z' (Ω-cm^2)

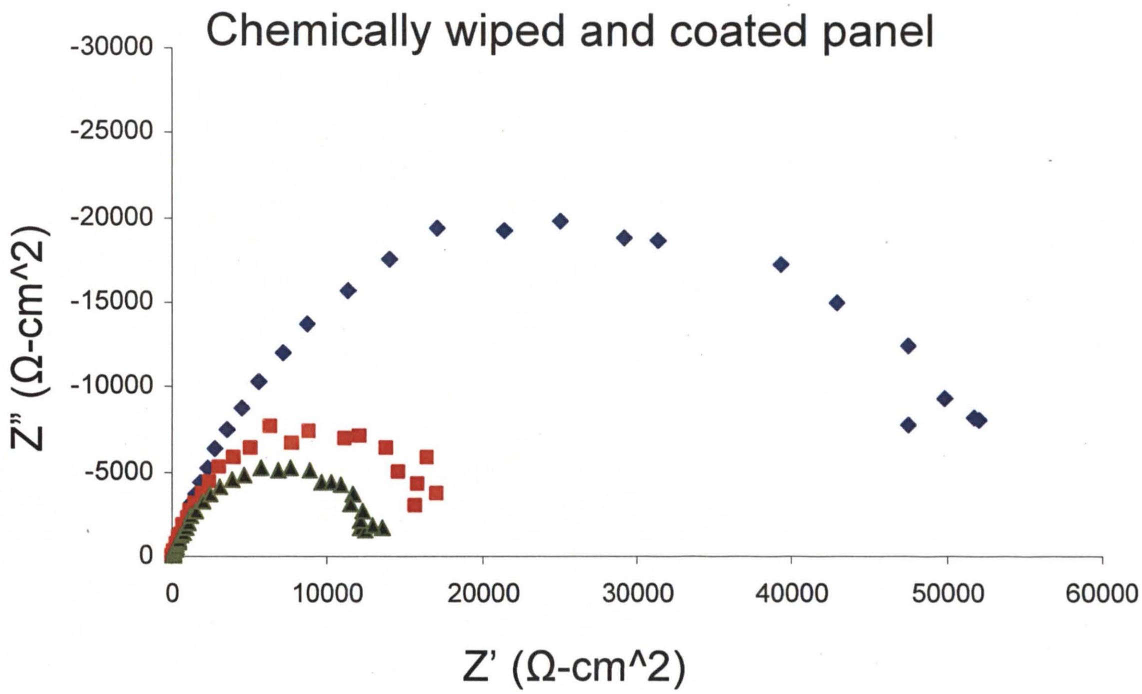

Potential (V)
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
1.E-09
1.E-08
1.E-07
1.E-06
1.E-05
1.E-04
1.E-03
1.E-02
1.E-01
1.E+00
Current density (A/cm^2)

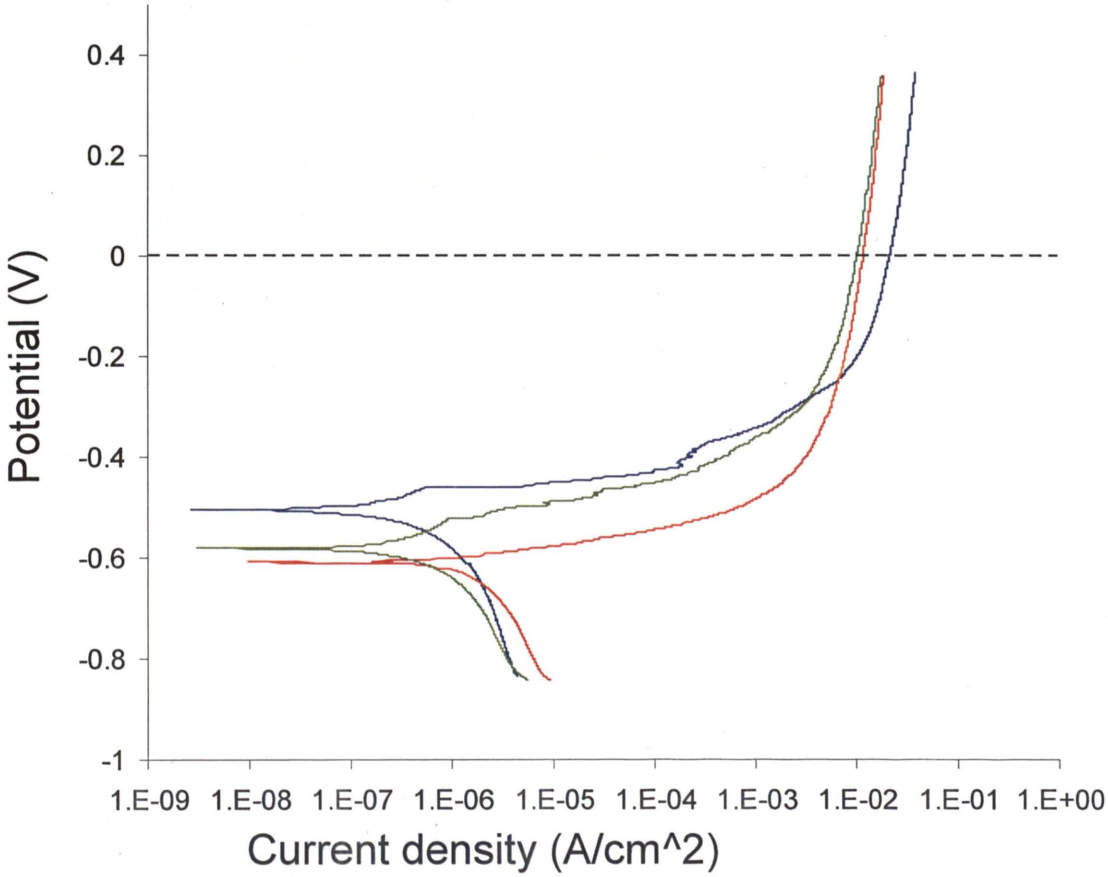

Abrasively blasted panel
-3500
-3000
-2500
-2000
-1500
-1000
-500
0
Z" (Ω-cm^2)
0
1000
2000
3000
4000
5000
6000
Z' (Ω-cm^2)

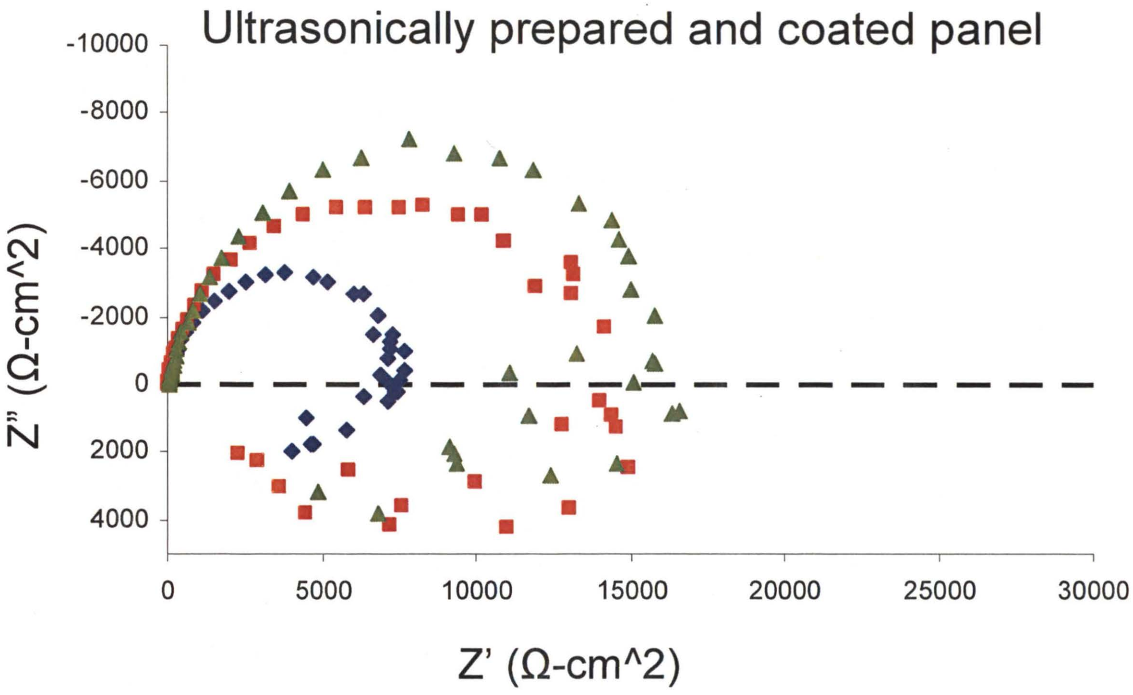

0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
Potential (V)
1.E-09
1.E-08
1.E-07
1.E-06
1.E-05
1.E-04
1.E-03
1.E-02
1.E-01
1.E+00
Current density (A/cm^2)

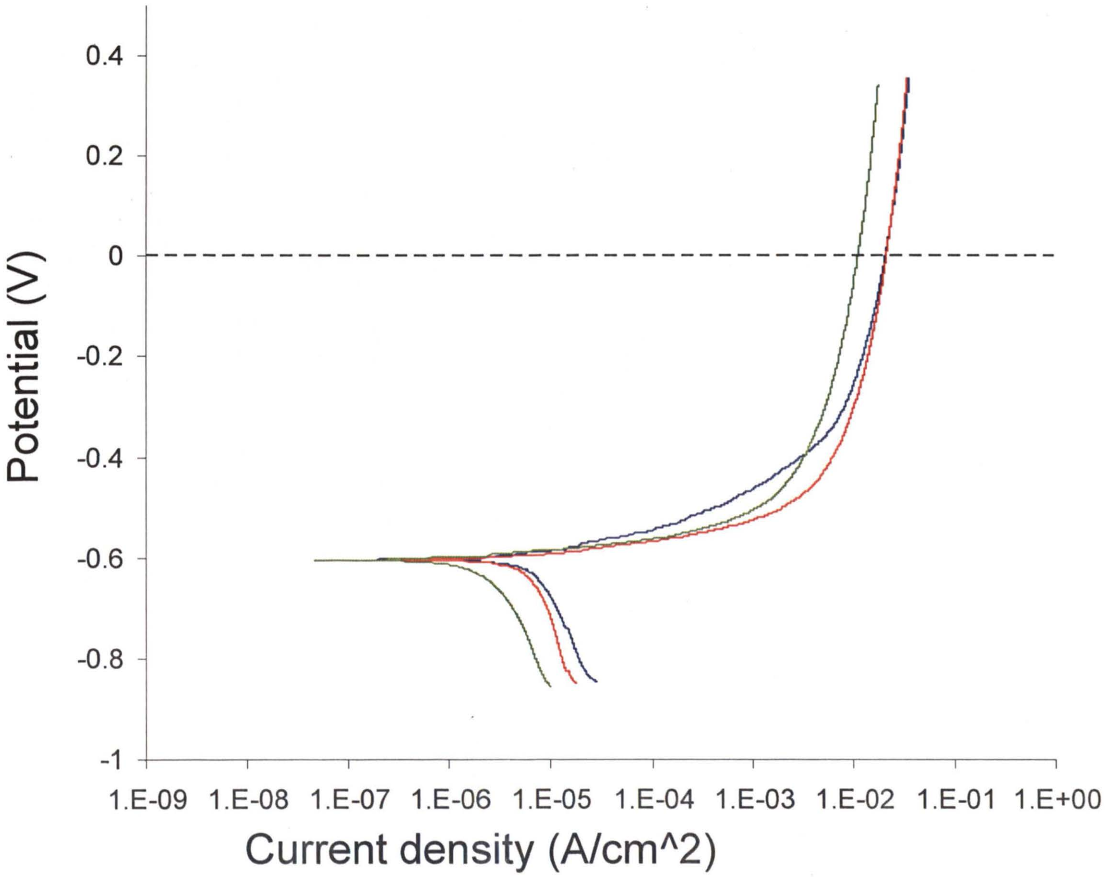

Immersion prepared and coated panel
-50000
-45000
-40000
-35000
-30000
-25000
-20000
-15000
-10000
-5000
0
Z" (Ω-cm^2)
0
20000
40000
60000
80000
100000
Z' (Ω-cm^2)

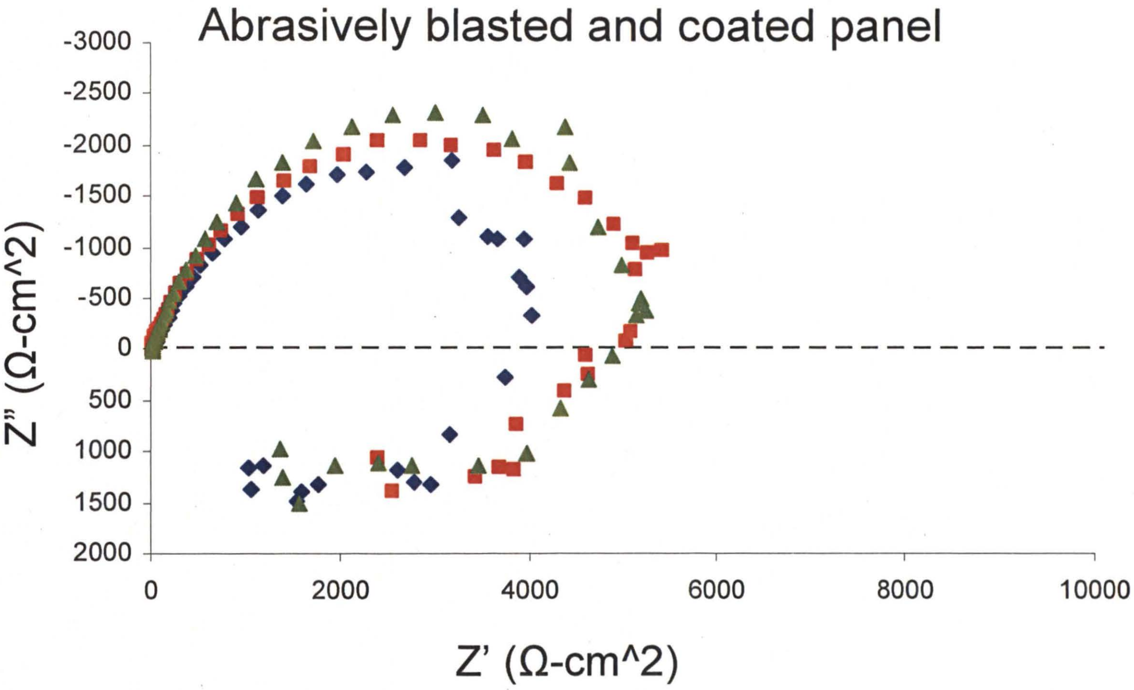

0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
Potential (V)
1.E-09
1.E-08
1.E-07
1.E-06
1.E-05
1.E-04
1.E-03
1.E-02
1.E-01
1.E+00
Current density (A/cm^2)

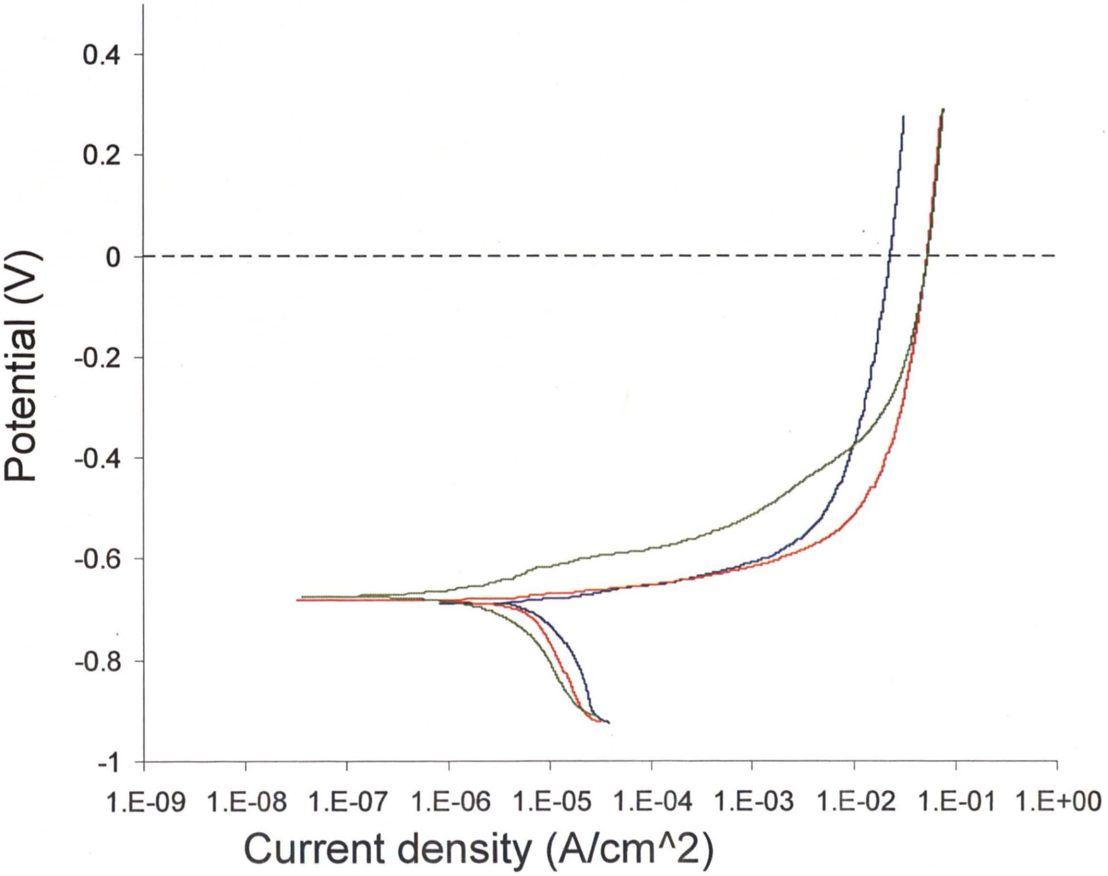

Chemically wiped and coated panel
-30000
-25000
-20000
-15000
-10000
-5000
0
Z" (Ω-cm^2)
0
10000
20000
30000
40000
50000
60000
Z' (Ω-cm^2)


0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
Potential (V)
1.E-09
1.E-08
1.E-07
1.E-06
1.E-05
1.E-04
1.E-03
1.E-02
1.E-01
1.E+00
Current density (A/cm^2)

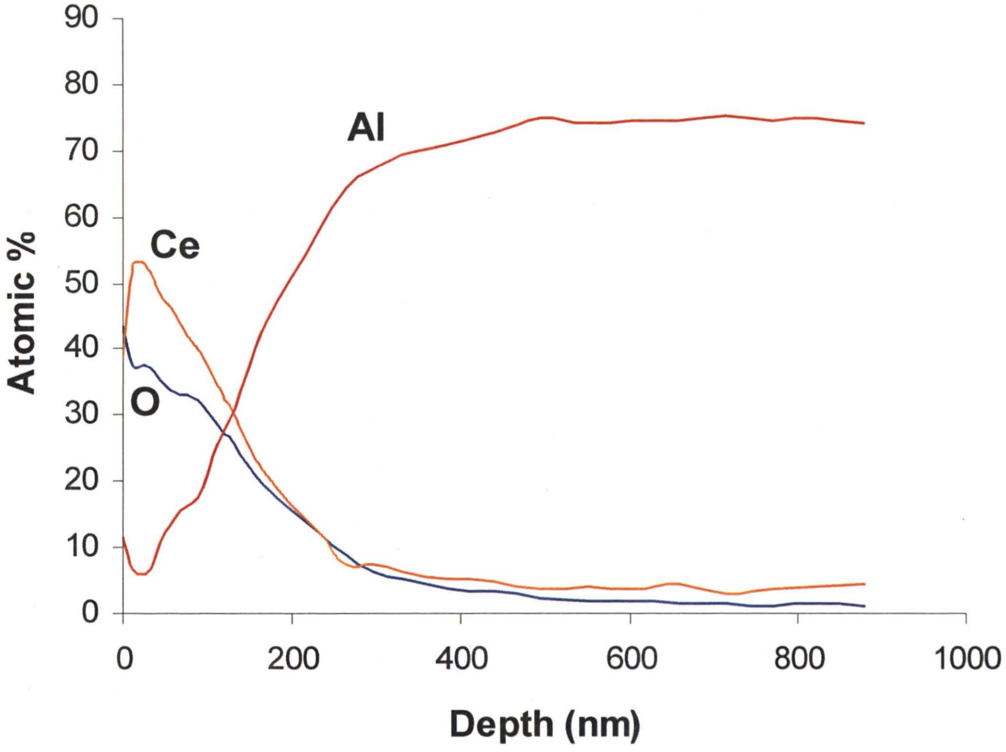

Ultrasonically prepared and coated panel
-10000
-8000
-6000
-4000
-2000
0
2000
4000
Z" (Ω-cm^2)
0
5000
10000
15000
20000
25000
30000
Z' (Ω-cm^2)


0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
Potential (V)
1.E-09
1.E-08
1.E-07
1.E-06
1.E-05
1.E-04
1.E-03
1.E-02
1.E-01
1.E+00
Current density (A/cm^2)

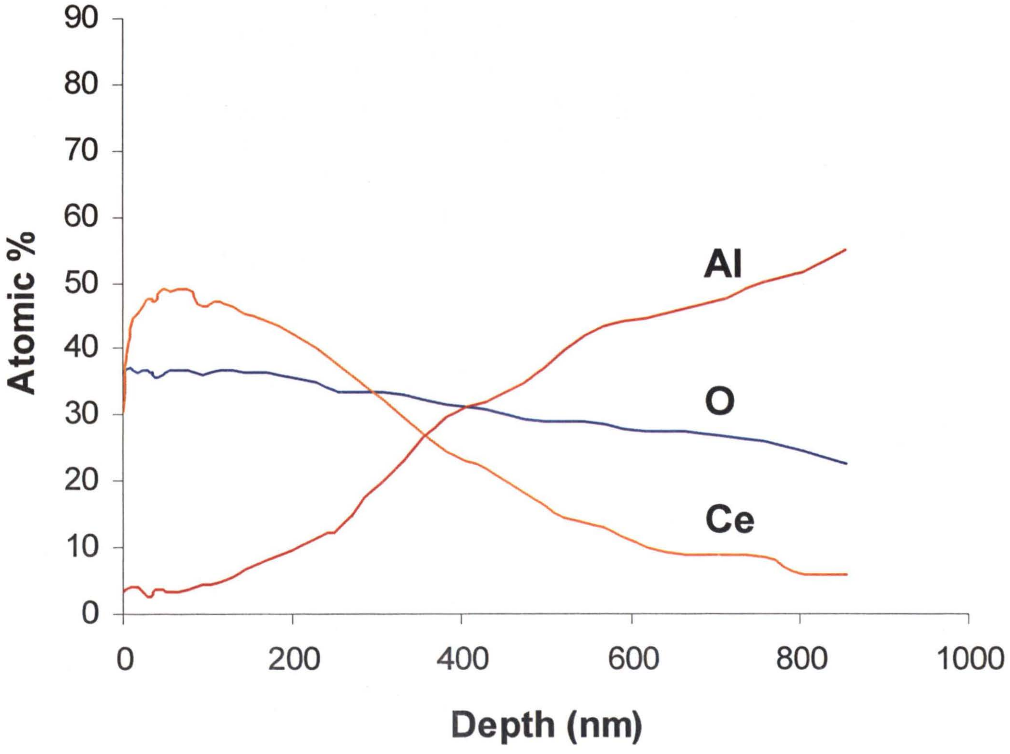

Abrasively blasted and coated panel
Z" (Ω-cm^2)
-3000
-2500
-2000
-1500
-1000
-500
0
500
1000
1500
2000
0
2000
4000
6000
8000
10000
Z' (Ω-cm^2)


Potential (V)
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
1.E-09
1.E-08
1.E-07
1.E-06
1.E-05
1.E-04
1.E-03
1.E-02
1.E-01
1.E+00
Current density (A/cm^2)

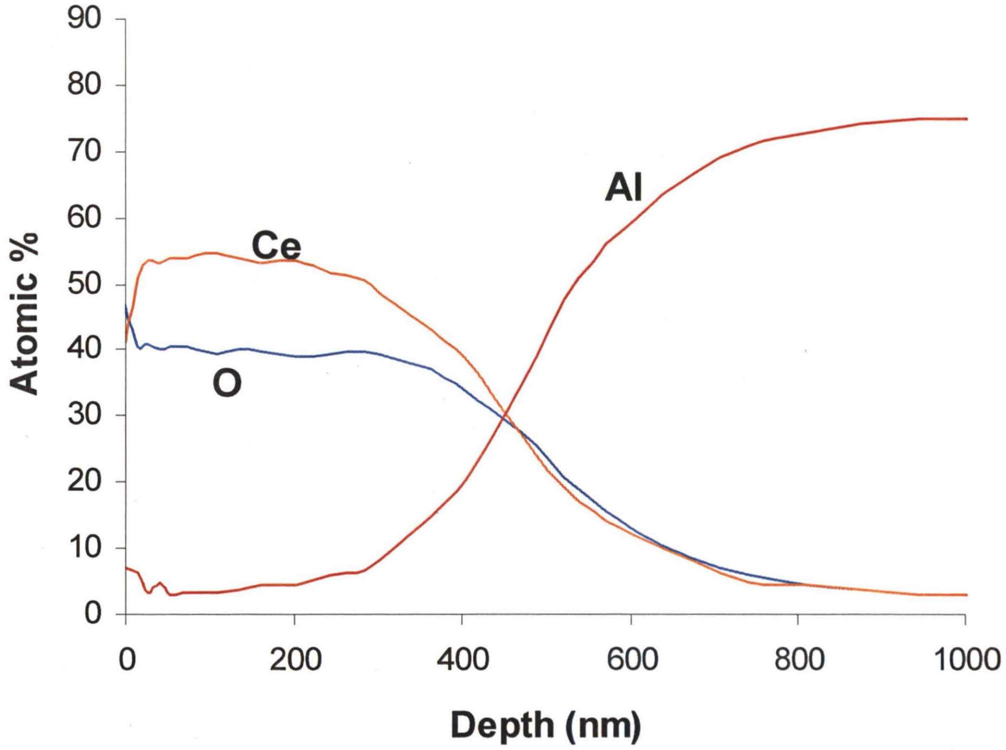
Al 2024 panels were degreased using an alcohol wipe, rinsed in tap water, immersed into a 5 wt. % solution of an alkaline cleaner (Turco 4215NC-LT) held at 55°C for five minutes, and surface activated by immersion into 1 wt. % sulfuric acid solution held at 50°C for 10 minutes. Coatings were deposited on the prepared panel from a solution containing 10 g hydrated cerium chloride, 20 mL hydrogen peroxide solution (30% H_2O_2), 220 mL DI water, and 0.8 g gelatin. The solution was adjusted to a pH of approximately 2.3 using HCl. The solution was applied by wiping a continuous layer on the panel surface using a natural bristle brush or spraying the solution using an air powered spray gun for about five seconds, the solution was allowed to drain approximately 30 seconds. The spray/drain cycle was repeated up to five times while the brush/drain cycle was repeated up to seven times. After deposition, the coated panels were post-treated by immersion into a 2.5 wt. % Na_3PO_4 hydrate solution, held at 85°C, for five minutes. The brush deposited coatings were not evenly colored. Depth profiles were taken of the lightest and darkest areas of the surface. The difference in color between the two areas decreased with additional deposition cycles, the seven brush cycle coating did not have lighter or darker areas.



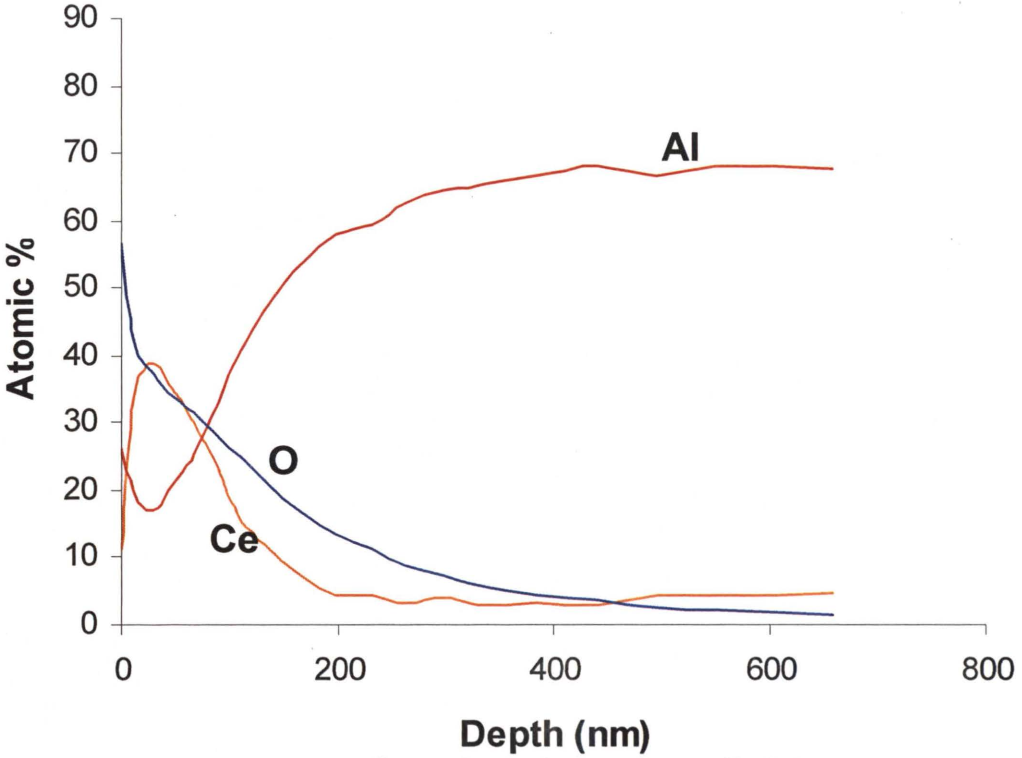
One spray cycle



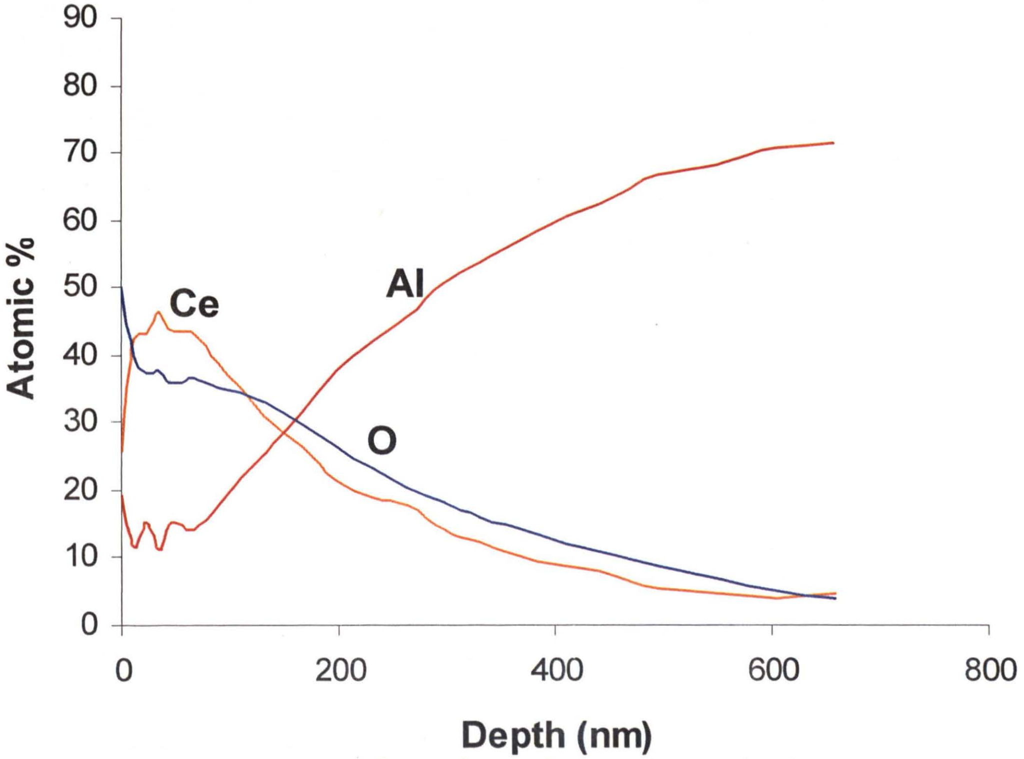
Three spray cycles



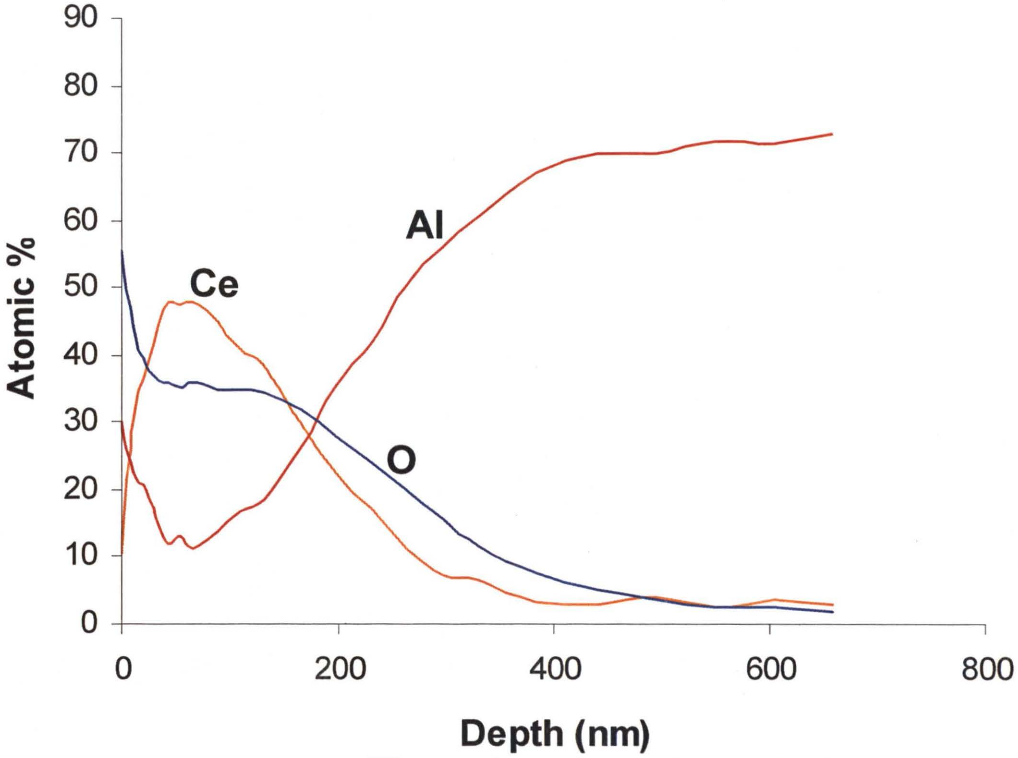
Five spray cycles



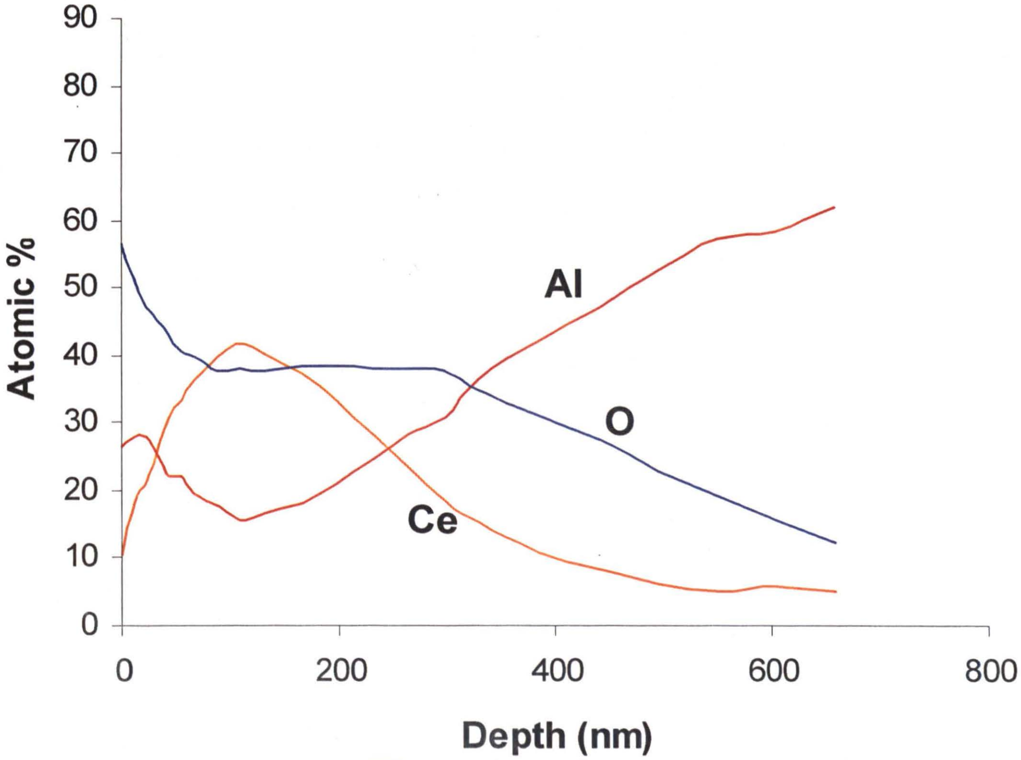
One brush cycle – light area



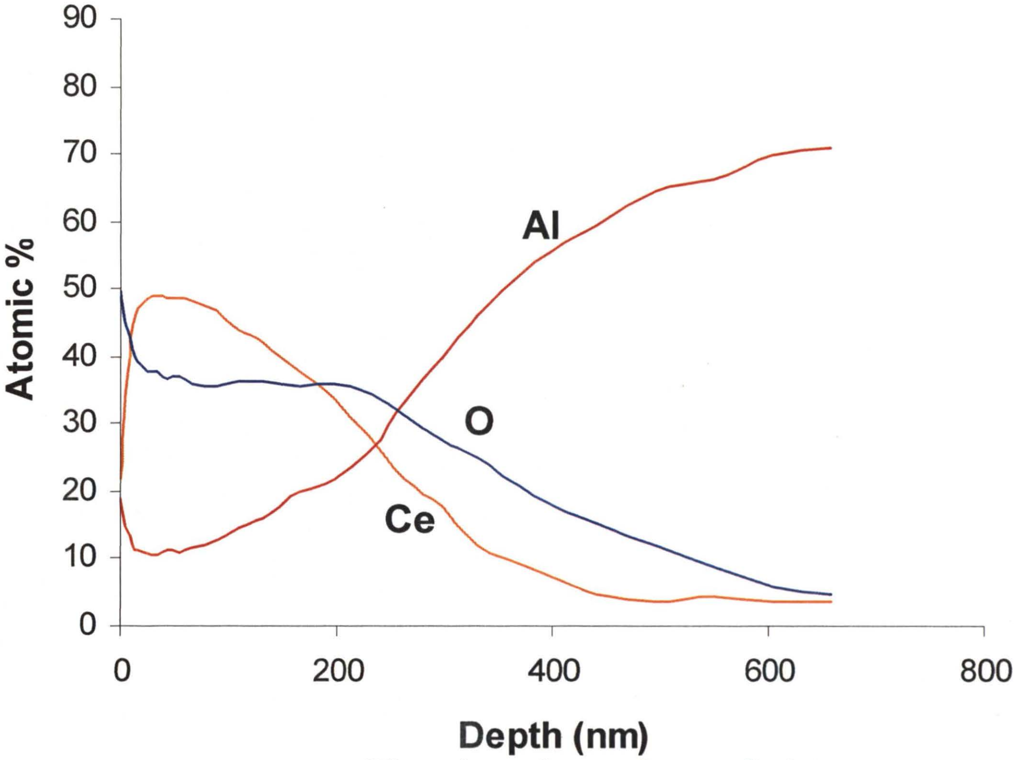
One brush cycle – dark area



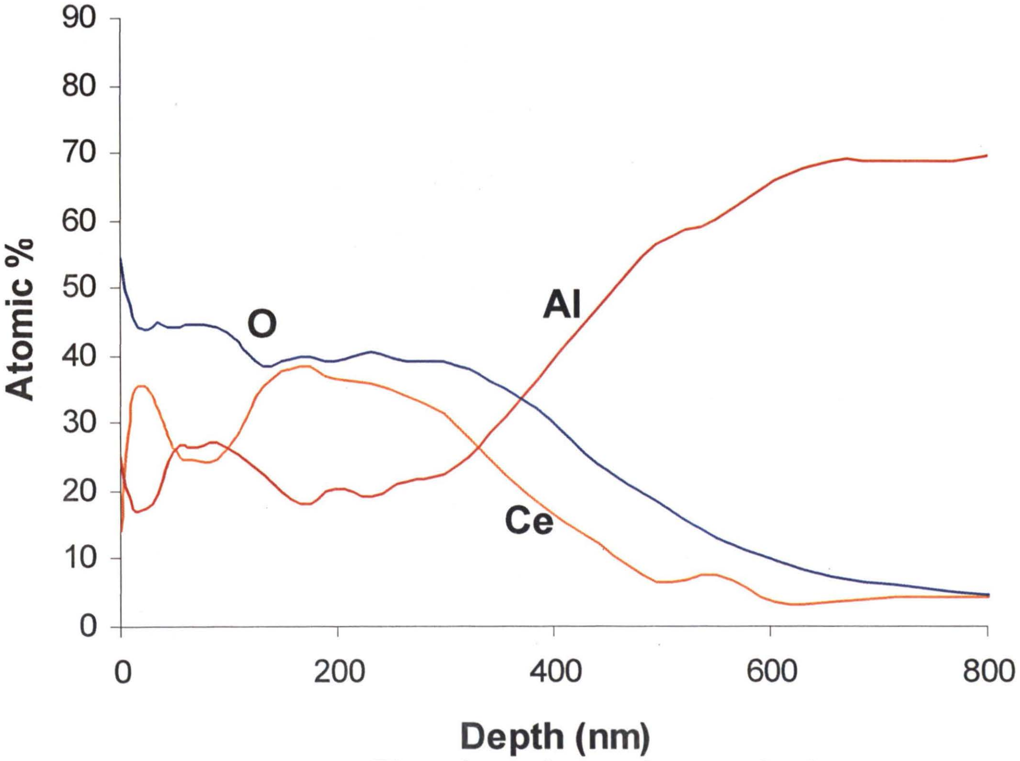
Three brush cycles – light area



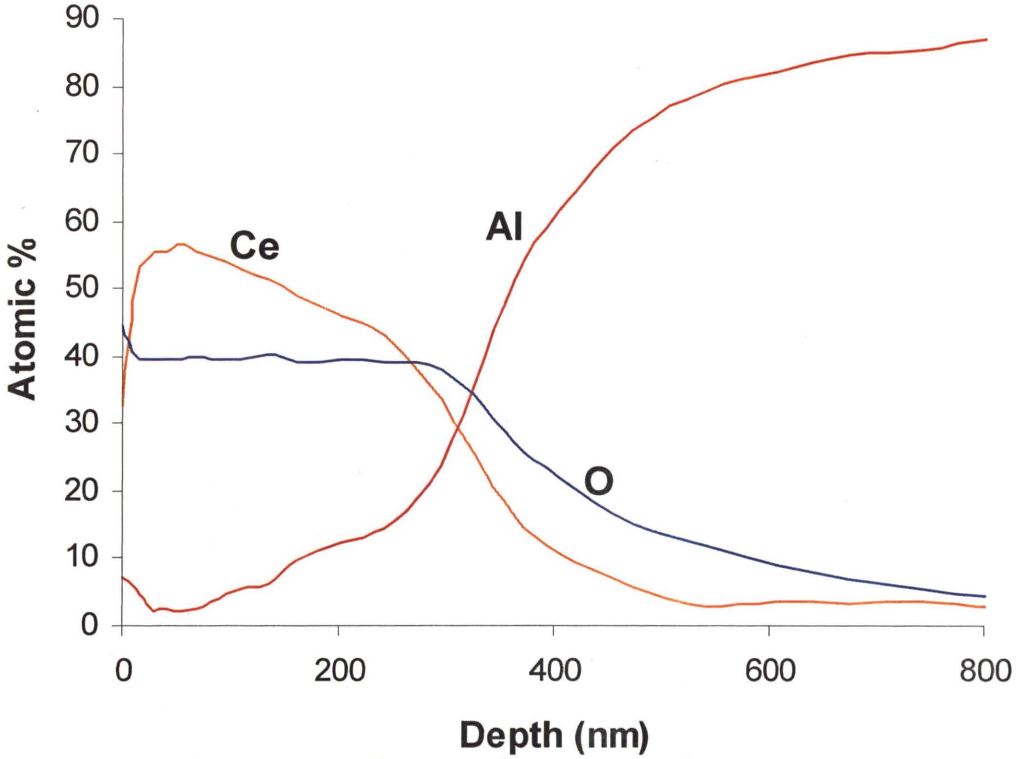
Three brush cycles – dark area



Five brush cycles – light area



Five brush cycles – dark area



Seven brush cycles

VITA

William Gammill was born in Oklahoma City, OK on November 29th, 1984. He moved to Raytown, MO, a suburb of Kansas City, MO before beginning school. He completed high school in Raytown. In the fall of 2003, William began undergraduate studies at the Missouri University of Science and Technology in Metallurgical Engineering. He was an undergraduate research assistant for Dr. David Van Aken. William graduated in December of 2007 with a BS in Metallurgical Engineering.

In January of 2008, William began his graduate studies at the Missouri University of Science and Technology. He was employed as a graduate research assistant under the direction of Dr. Matt O'Keefe while working on his Master's degree in Metallurgical Engineering, which was received May 2010.