

A close-up photograph of several interlocking metal gears that are heavily corroded with a thick, brown, flaky layer of rust. The gears are set against a dark, out-of-focus background.

Smart Corrosion Inhibition Strategies: Substrate, Coating, and Inhibitors

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Corrosion is a persistent problem for machinery and vehicles constructed out of metals, in particular those comprised of steel or aluminum alloys. The design of metal structures, as to the material and how it interfaces with the environment, plays a large role in the tendency to corrode since corrosion is a surface reaction. Surface composition and morphology, therefore, greatly affect the ability of metal to remain passive or to become corrosively active. Materials design should dictate what surface compositions or morphologies are desired, and supplement the mechanical architecture, to maximize corrosion resistance. For active metal alloys, the currently utilized bulk alloy specifications do not appear sufficient for ensuring a particular corrosion activity. Surface conversion of the metal to either a less active or an actively corrosion-preventing coating may or may not passivate the resulting surface. The application of a coating to a reactive metal surface is commonly utilized to retard or prevent corrosion of the surface, which can provide either passive or smart inhibition of corrosion processes. Smart systems attempt to utilize environmental or behavioral triggers to induce a response in the coating or substrate that changes surface composition to better inhibit corrosion. Design of active coating systems and their mechanisms are reviewed.

INTRODUCTION

Corrosion is an electrochemical reaction comprised of two separate processes, called the anode and the cathode, where oxidation and reduction of species occur, respectively. The dissolution process of a metal occurs at the anode resulting in the metal atoms being converted from unoxidized metal, of zero oxidation state, to a positive oxidation state. Each element has a certain number of protons and electrons; the number of protons minus the number of electrons present is called oxidation state. Valence state is similar to oxidation state except that a further stipulation of the energy levels of the electrons in the orbitals must be made. Oxidation is the increase in oxida-

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tion state of an atom caused by a loss of electrons. Corrosion is, therefore, the oxidation of elemental metal resulting in either dissolution of the elemental metal, i.e., a conversion into ions, or conversion of the metal into an oxide with a concurrent reduction in the oxidation state of another chemical species, such as oxygen.

At the cathode is a reaction that consumes the electrons liberated at the anode. Common species that consume electrons and their products upon consuming the electron(s) are: oxygen, which produces oxide anions in the absence of water or hydroxide in the presence of water; Brönsted acids, including water, which can produce hydrogen gas; or oxidized noble metals. Each of these materials possesses an energetic need to acquire electrons and the magnitude of this energetic need is also a measure of their ability to induce corrosion of a metal. Cathode species and the metal anode surface are chemical reagents, each possessing a chemical potential (energy) to consume or liberate electrons, respectively.

Like any chemical reaction, the corrosion reaction direction is governed by an equilibrium based on the relative potential energies of the products as compared to the reactants. Stability for a chemical state is conveyed by valence state and interaction with the surrounding environment, e.g., by the presence or absence of solvation. Very low potential energy products and high energy, unstable reactants support corrosion whereas the environment can affect the relative stability of the products and/or reactants and influence corrosion spontaneity. Noble metals are those metals that prefer, in most cases, to remain in an unoxidized, elemental state. The energy available for reaction is quantified via a materials electromotive force (emf or E) that is equated, as an electrical potential, to reaction-free energy by the equation $\Delta G = -nFE$, where ΔG is the free energy (J/mole), n is the number of electrons (or equivalents = eq) transferred per mole of reactant, and F is Faraday's constant (96,483 coulombs/eq = 96,483 (Joules/volt)/eq).

A standard reference potential against which all other elements are compared is the reduction of a hydrogen electrode, $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$, defined as occurring at 0.0 V. Noble materials are those possessing positive reduction potentials while active metals are those possessing a negative reduction potential. An oxidation potential is the negative of a reduction potential, their being for reactions in opposite directions. Examples of active metals include magnesium, aluminum, zinc, and iron, while those of noble metals include gold, platinum, metallic carbon, and the somewhat less noble silver and copper.

The potential for corrosion does not indicate the kinetic rate of the corrosion reaction. Rather than reac-

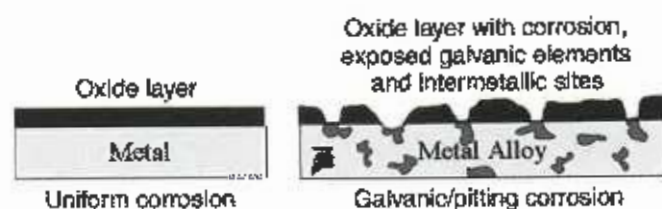
tion potential, transport at the metal surface is most often the enabling or limiting factor. As such, reactions at interfaces such as corrosion are inherently limited in this respect. Metal oxides and/or hydrated oxides, as reaction products of metal with oxygen and/or water, are mostly inert and insulating to additional effects of water, oxygen, and electric current. An oxide layer produced by corrosion thus acts as a protective coating for the reactive metal beneath to prevent extensive contact with water or air in the environment; hence, the reaction rate of the cathodic reaction is reduced by preventing the transfer of electrons from the metal.

It is the susceptibility of oxide layers to chemicals including moisture, impurities in the air dissolved in the moisture, or corrosion products that dissolve these barriers away, physical flaws within the oxide layers themselves, and external corrosion forces that can enable fast corrosion rates. Visual aids, such as the "Atlas of Electrochemical Equilibria in Aqueous Solutions,"¹ show potential to corrode as a function of an applied electrical potential and pH. Metals tend to show sensitivity toward being positively polarized via removal of electrons. Toward extremes in pH, dehydroxylation and ionization of the native oxides occurs at acidic and basic pH, respectively. The dehydroxylation produces metal ions and ionization produces oxoanions that are soluble, giving dissolution of the protective oxide layer and exposure of unoxidized metal beneath.

Corrosion is an odd chemical reaction in that the reactive equivalents are electrons. Given an electrical connection between the individual half cells, corrosion can occur. The cells can be considerably separated and can be visualized, e.g., by the scanning vibrating electrode technique (SVEIT).²⁻⁵ Localized corrosion cells are responsible, for example, for galvanic and crevice corrosion.⁶ They are also responsible for the corrosion behavior of alloys possessing multiple elements of nonhomogenous reduction potentials in a nonhomogenous distribution throughout the solid. When the different metals are electrically connected, corrosion currents will take the path of least resistance and the most easily oxidized metal will preferentially corrode. Since the more noble metals prefer to remain unoxidized, these metals will often present a clean, unhindered site for the cathodic reaction at the expense of more reactive metals. Such sacrificial corrosion may be utilized to protect metal structures,^{7,8} called galvanic protection, where a sacrificial metal supplies electrons to the cathode instead of the structural metal.

Since anode and cathode reactions are required to be balanced in their electron transfers, a strong driving force for one of the individual reactions can cause the other to occur. A strongly spontaneous or prevalent cathodic reaction can push a sluggish anode towards corrosion or a very sluggish cathodic reaction can be used

Figure 1—Schematic of the oxide layers of homogenous compared to nonhomogenous metal alloys showing how defects in the oxide film provide access of oxygen and water to the bare metal alloy surface.

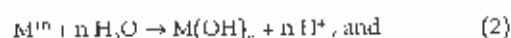


to hinder a very spontaneous anodic reaction. These statements form the basis of corrosion inhibition strategies. However, their reduction to practice is complicated by materials designs that permit localized corrosion through nonhomogenous surface compositions resulting in localized corrosion currents.

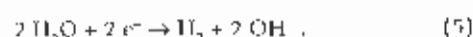
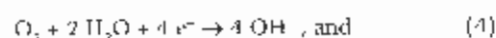
Alloy designs often sacrifice corrosion resistance for improved strength despite the fact that corrosion can catastrophically mitigate the improvements in strength such as with the onset of stress corrosion cracking.² For example, copper is often added to produce high-strength aluminum alloys but the corrosion sensitivity of aluminum alloy is directly proportionate to the copper concentration, whose intermetallic compounds act as sites for the cathodic reaction (Figure 1). Carbon in steel is a similarly active promoter of corrosion activity, being highly stable in its reduced form. Graphitic corrosion results in delloying of the iron from the steel, leaving noble carbon residue. Consumption of a more active element due to a localized, noble cathode is termed galvanic corrosion. With galvanic corrosion, material next to the cathodic domain is consumed most rapidly as there is higher electrical resistance for greater distances away from the cathode. Pitting and stress corrosion cracking can be initiated as a result of galvanic cells.

For some alloys, the sites for anodic and cathodic reactions are cyclic and turn on and off as corrosion products and the localized environment around the anodes and cathodes changes.

Environments around anodes tend to become increasingly acidic, increasing the rate of dissolution of nearby passive oxide coatings due to the common reactions:



where M is a corroding metal atom and n indicates the oxidation number of the corrosion product ion. Acidity is enhanced via production of metal hydroxides or acid protons or by consumption of hydroxide such as that produced at a nearby cathode. The localized environment around cathodes, on the other hand, becomes increasingly alkaline due to the reactions:



The common cathodic reactions found in the presence of oxygen and/or water, respectively, cause an increase in the local hydroxide ion concentration through reduction of oxygen and hydrogen ion, respectively. As the reactions progress, the active metals are consumed and replaced by different active metal sites. The progression of anode to cathode and cathode to

Table 1—Transport Rates of Oxygen, Carbon Dioxide, and Water Vapor Through Passive Barrier Films.^{1,2} Measurements Were Made at 100% Relative Humidity

Polymer	Permeation Rates [$cm^3/100\mu m (m^2 d atm)^{-1}$]		
	Oxygen (23°C)	Carbon dioxide (23°C)	Water Vapor (38°C)
Poly(vinyl alcohol) ^a	0.04	0.12	1900
Poly(vinylidene chloride)	0.4	1.2	0.79
Cellophane ^a	0.5	1.2	1400
Epoxy (bis-A/amine)	12	35	16
Nylon 6	20	35	70
Poly(ethylene terephthalate)	20–39	47–79	8–16
Poly(vinyl chloride)	31–59	79–157	8–12
Poly(vinyl fluoride)	59	118	7
Poly(methyl methacrylate)	67	157	47
Poly(vinyl acetate) ^a	220	450	420
Cellulose nitrate ^a	390	1180	315
High density polyethylene ^a	433	1180	2
Polyurethane ^a	530	1380	480
Polypropylene ^a	590	1770	2
Polytetrafluoroethylene ^a	866	2360	1
Polycarbonate ^a	890	2165	55
Polystyrene ^a	1640	4920	51
Low density polyethylene ^a	1890	5900	6
Polybutadiene ^a	15000	31000	67

(a) Oxygen and carbon dioxide permeabilities measured at 0% relative humidity.

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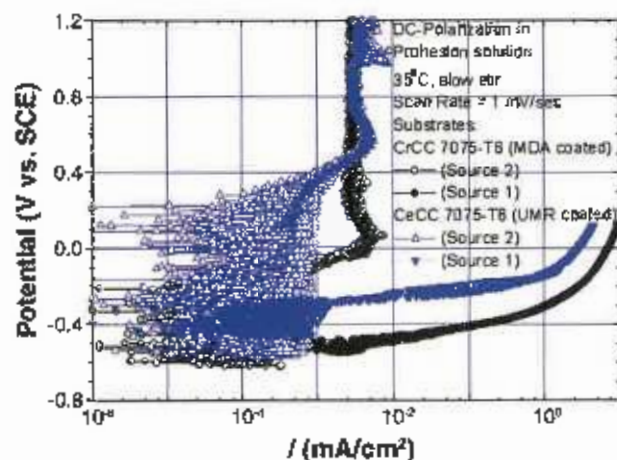
anode can be visualized by SVEI^{2,5} and electrochemical noise (EN).¹⁰⁻¹¹

All inhibitors are designed to provide, protect, and/or (re)form a protective layer, especially a surface oxide layer, that can serve as a primary inhibitor of metal corrosion. Prevention of corrosion processes by coatings is obtained through hindering the cathodic reaction, called cathodic inhibition, or by hindering the anodic reaction, called anodic inhibition. Cathodic inhibition involves preventing oxygen and/or water from contacting the metal surface and, thus preventing oxygen and/or water from acquiring the released electrons and their consequent reduction. Retention of a corrosion byproduct at the corrosion site also tends to reduce the spontaneity of the corrosion by perturbing the reaction equilibrium. Barrier films are a common method utilized to prevent corrosion, e.g., surface oxides or hydrophobic coatings. Barriers are not considered a "smart" means to combat corrosion but passive methods to reduce the transport of oxygen and/or water. The transport rates of oxygen, water, and carbon dioxide through various films are shown in Table 1.¹² Note, as general trends, that the apolar, hydrophobic materials such as polypropylene have low water transmission rates but high oxygen transport rates while polar, oxygen containing materials have high water transmission rates and relatively lower oxygen transport. The presence of water greatly increases the transport rate of oxygen through a barrier film. In this way, a smart system can begin its design through the control of oxygen and water transmission rates through choice of material composition and film thickness.

Anodic inhibitors are intended to inhibit the anodic reaction, i.e., the metal dissolution process, and may be classified as highly oxidizing and weakly oxidizing. The typical means that an anodic inhibitor utilizes is to accelerate corrosion within the anode to build up corrosion products at the anode surface and thereby hinder the activity of the anode. Another way anodic inhibitors help passivate the corrosion site is achieved by precipitation of corrosion products, which buffer the local acidity and perhaps allow alkalinity from a nearby cathode to further increase pH. An increase in local pH deactivates the anodic site by stabilizing the native oxide at the metal surface. Anodic inhibitors may also complex with the bare metal surface to stabilize the surface atoms and retard their ionization. Anodic inhibitors can themselves tend to be corrosive and hence are deemed "dangerous inhibitors"¹³ since too little inhibitor accelerates corrosion but does not produce sufficient corrosion rates to cause passivation. Too much of the inhibitor, on the other hand, can help dissolve the oxide layer and prevent passivation.

From this discussion, the basics of how a corrosion inhibition system is designed have been presented, as

Figure 2—DC polarization measurements of chromate (CrCC) and cerium (CeCC) coated AA7075-T6 alloy, which shows the corrosion current density (i) as a function of potential for each aluminum source lot.¹⁴ Measurement was performed in prohesion test solution at 35°C at a 1 mV/sec scan rate.³¹ (Copyright William Andrew Press.)



well as inhibitor design variables and pitfalls, and how corrosion inhibitor systems can be responsive to the corrosion environment. While corrosion is too complex a subject to treat in one monograph, insight into corrosion prevention may be obtained through examples and how corrosion performance was affected by materials limitations or a system design.

DISCUSSION

The substrate, either through composition or pretreatment, can drastically affect the tendency of the metal to corrode. Following are two studies that discuss how the

Figure 3 - Bode plot of electrochemical impedance (EIS) measurements for taped 1 cm² area of aluminum alloy (AA) 7075-T6 panels from different suppliers immersed in 35°C prohesion solution. The panels were acetone degreased only but showed significant differences in low frequency polarization resistance as a function of the alloy source.³⁴ (Copyright William Andrew Press.)

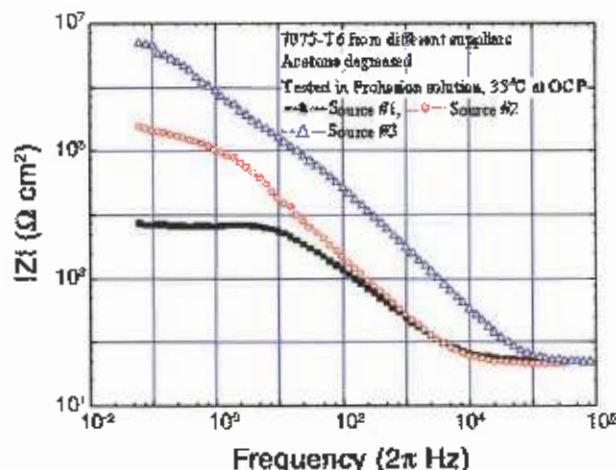
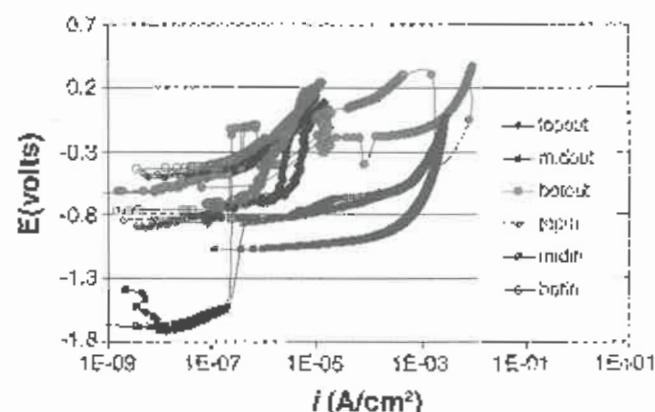


Figure 4—DC polarization of sulfuric-hydrofluoric acid-etched AA3xxx surfaces as a function of test location. Locations correspond to XPS test locations found in Table 2. Tests were conducted at 35°C in a pH 2 electrolyte.



surface composition has been observed to affect reactivity and paths for remediation of the metal surface to reduce corrosion sensitivity.

Substrate Composition

In examining the effect of inhibitors on the corrosion properties of aluminum aerospace alloys AA2024-T3 and AA7075-T6, the influence of the alloy lot and its composition were investigated. These alloys are often subjected to removal and reconstruction of their oxide layer to provide a uniform and chemically durable oxide layer, replacing the native oxide of the alloy. The obtained results were related to the initial corrosion sensitivity of the starting alloy and their ability to be passivated with an applied oxide. In this case, chromate and cerium-based conversion coatings were each applied to the AA7075-T6 alloys in question. The corrosion rates before and after surface conversion to a chromium or cerium oxide, respectively, were measured by a direct current (DC) polarization.

In Figure 2 are shown the DC polarization scans of conversion-coated AA7075-T6 panels where the aluminum alloys were obtained from two different source lots. A DC polarization method measures the corrosion current density, equivalent to corrosion rate per surface area, as a function of the applied electrical potential in volts. The Source 1 aluminum alloy, after conversion coating via either method, was observed to have a nearly linear trend of higher corrosion current as a function of an increasingly anodic potential. Anodic potentials, increasingly positive surface charge, accentuate the anodic reaction through removal of electrons from the surface. Source 1 alloy was found to therefore remain corrosion sensitive even after conversion coating with either chromate or cerium-based

methods. Source 2, on the other hand, passivated to a constant, lower corrosion rate indicated by the constant corrosion current i above +0.2 V versus standard calomel electrode (SCE) for the chromate conversion coating and +0.7 V for a cerate conversion coating. Note that the bare Source 1 alloy initially appeared (Figure 3) the least corrosion resistant, showing the lowest impedance via electrochemical impedance spectroscopy (EIS).

The alloys were examined for their lot composition and tested by X-ray energy dispersive spectroscopy (EDS) to confirm the lot composition information. No distinct differences in the lot compositions were found upon comparing the alloys of Source 1, 2, or 3. While composition of the alloy material has a distinct effect on the corrosion sensitivity, these differences are not necessarily observed in bulk compositional measurements. Instead, assessment of corrosion resistance for an alloy lot seems best made by electrochemical analysis. Remediation of the incoming lot, including the application of a conversion coating, may not be successful in attaining a corrosion-resistant surface. Inhibiting a corrosion-sensitive surface from corrosion is yet more difficult.

Figure 5—EIS (top) and DC polarization (bottom) analysis of alkaline-rinsed sulfuric-hydrofluoric acid-etched AA3xxx alloy. Tests were conducted at 35°C in the same pH 2 electrolyte utilized for the testing of Figure 4.

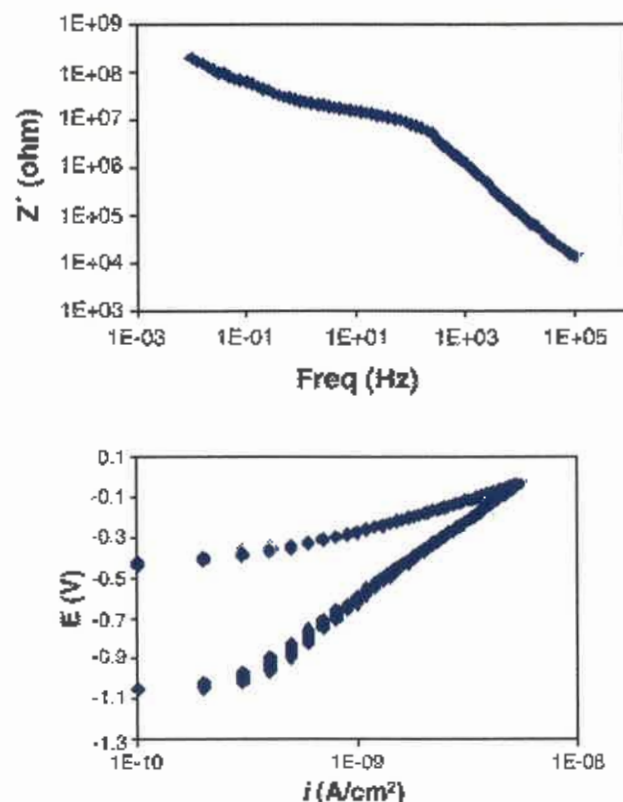


Table 2—X-ray Photoelectron Spectroscopy (XPS) Measured Concentrations of Elements at the Surfaces of Sulfuric-Hydrofluoric Acid Etch Pretreated AA3xxx Surfaces as Atomic Percent Concentration of the Respective Element

Average Composition →							
Atom Percent	C	O	Al	S	F	Si	N
Inside							
Top sidewall	33.30	37.33	28.60	0.51	0.77	0.00	0.00
Mid sidewall	29.97	39.33	28.74	0.60	0.93	0.17	0.00
Bot. sidewall	29.98	38.86	29.28	0.97	0.83	0.16	0.00
Bottom	43.26	32.77	22.52	0.72	0.43	0.08	0.23
Outside							
Top sidewall	31.23	35.63	30.13	0.74	0.93	0.18	0.53
Mid sidewall	29.76	37.36	30.44	0.71	1.25	0.09	0.96
Bot. sidewall	28.60	36.51	32.21	0.54	1.48	0.67	0.68
Bottom	34.25	35.68	28.07	0.59	0.81	0.25	0.37
Washed							
Acid wash	30.21	40.99	23.76	2.76	0.75	1.89	0.62
Neutral wash	30.71	34.56	28.99	1.15	1.07	2.61	0.93
Alkaline wash	34.76	41.62	22.73	0.42	0.00	0.46	0.00

Surface Pretreatment

An etching technology was being used to provide adhesion of a thin protective epoxy coating to an aluminum 3000 series alloy. The surface was steamed to degrease, hot-etched with a mixture of sulfuric and hydrofluoric acids and surfactant, rinsed, dried, and the organic coating applied and baked. The organic coating was found to have a near-DC polarization resistance of $\sim 1 \times 10^6 \Omega$ via EIS, demonstrating a highly resistant barrier to charge carrier transport. However, a coating defect would promote pinhole corrosion, requiring a recall of significant amounts of product, and it was desired that the pinhole corrosion be reduced.

Upon analysis of the alloy surface before and after the etch treatment, it was found that nearly a monolayer of sulfur and fluorine were residual on the metal surface after etching and after rinsing, even with hot or acidic water (Table 2). In general, the highest corrosion rates were observed with high residual concentrations of sulfur and fluorine on the alloy surface (Figure 1). There was difficulty taking measurements of the more reactive samples due to their tendency to vigorously pit corrode. An alkaline rinse of the etched surfaces was found effective at reducing the surface sulfur and fluorine concentrations (Table 2), which resulted in an increased EIS corrosion resistance and a decrease in corrosion rate as measured by DC polarization in the identical, acidic electrolyte (Figure 5). One should be smart about selecting a pretreatment process that controls surface composition to achieve both good adhesion and corrosion resistance. To do so, it is then advisable to understand what the pretreatment process changes in terms of chemical composition and reactivity.

Smart Inhibitors

The use of inhibitors in coatings can pose a series of challenges, including response of an inhibitor to changes in the environment around the inhibitor. Chromate is an example of an inhibitor that responds to its environment through the precipitation, complexation, and release of chromium oxides.¹⁶⁻¹⁸ A schematic of the chromate self-healing cycle is shown in Figure 6. Upon exposure to water or salt solution conditions, hexavalent chromium anion is released from complexation to mixed-valence chromium III/VI oxide via a Langmuirian-type isotherm relationship.¹⁸ Upon contacting a low pH environment, a reduced Cr^{VI} , i.e., Cr^{III} , oxoanion precipitates and can then adsorb additional Cr^{VI} oxoanions from solution.

Figure 6—Corrosion protection, transport, and feedback mechanism of chromate. The cycle is enabled by the reversal in electrochemical potential, complexation, and solubility of chromium oxide as a function of valence state and pH.²⁴ (Copyright: William Andrew Press.)

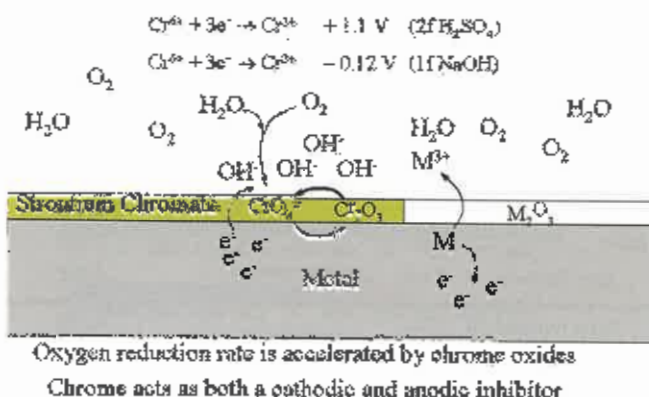
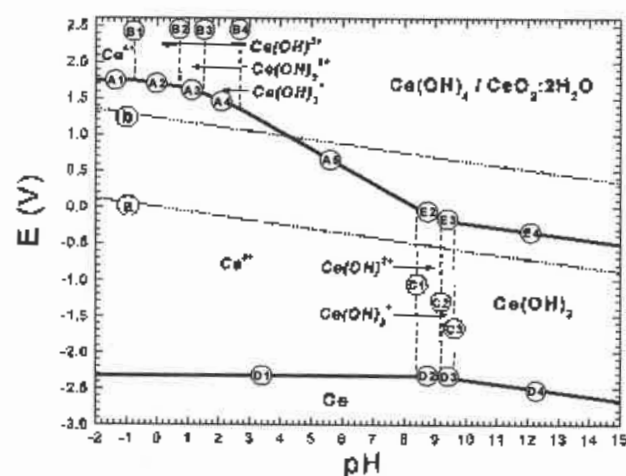
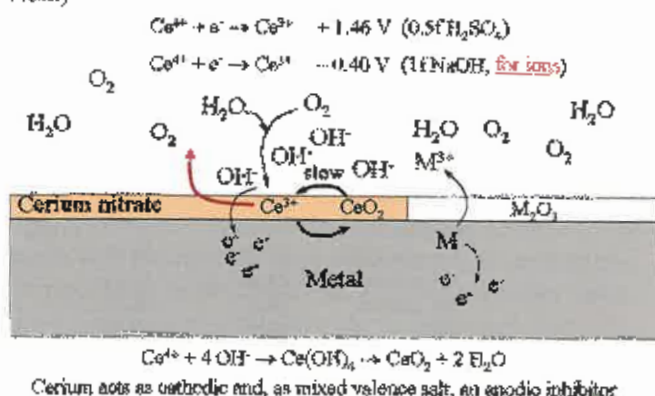


Figure 7—Revised electrochemical equilibria phase diagram for cerium in aqueous solution.²² (Reproduced with permission of The Electrochemical Society, Inc.)



As shown in Figure 6, conversion between Cr^{VI} and Cr^{III} can spontaneously occur due to change in the local pH, as suggested by the standard electromotive force (reduction) potentials in acidic compared to alkaline conditions, which would resupply the surface of a Cr^{III} hydrogel coating with fresh Cr^{VI} for an alkalinity-induced desorption. Contact of the Cr^{VI} with an acidic environment, i.e., an active anode, would induce a change in the oxidation potential of the Cr^{VI} to become oxidizing. In effect, the chromium is turned on by low pH to become a strong oxidant of aluminum as a typical anodic inhibitor,¹⁶ becoming insoluble as Cr^{III} at the anodic site.

Figure 8—The corrosion protection, transport feedback mechanism of cerium is analogous to Figure 6 for chromate. While the electrochemical potentials are quite similar, even advantageous, to the chromate cycle, note an apparent break in the conversion cycle due to the poor solubility of a cerium (IV) oxide. Nanomaterials may provide an alternative by improving the dissolution rate.³⁰ (Copyright William Andrew Press.)



Rare earth, or lanthanide, elements are characterized by: large atomic radii; a diversity of allowable electronic configurations; formation of multiple oxidation states, typically +3 and +4 with occasional +2 valence state¹; reactivity with water to form neutral oxides; formation of stable, insoluble oxides of mixed valence states¹²; complex coordination chemistry^{20,21}; instability of lower valence salts in alkaline conditions with a tendency to hydrolyze and precipitate as the hydrated oxide²²; and an extremely low reduction potential. An additional element that has been loosely grouped with the rare earths, though technically a d-transition ele-

Table 3—Waterborne Epoxy Polyamide Coating Formulation³⁹

Millbase	Weight (kg)	ρ (g/mL ³)	Volume (L)	% Solids	Solid wt (kg)	ρ Solid (g/mL ³)	Solid vol (L)
Polyamide	0.480	0.960	0.500	0.700	0.350	0.928	0.377
Texaphor 963	0.005	0.905	0.006	0.5/1	0.003	0.927	0.003
2-Butanol	0.090	0.807	0.112	0.000	0.000	1.000	0.000
TiO ₂ (R-960)	0.200	4.100	0.049	1.0	0.200	4.100	0.049
K-White 140W	0.200	2.500	0.080	1.0	0.200	2.500	0.080
Mistron 600	0.250	2.700	0.093	1.0	0.250	2.700	0.093
Total millbase	1.238		0.855		1.003		0.602
Letdown							
Nitroalkane epoxy resin solution: (50:50)	0.480	1.128	0.425	0.677	0.288	1.173	0.245
Water	1.930	1.000	1.930	0.000	0.000	1.000	0.000
Total letdown	2.410		2.355		0.288		0.245
Total formulation	3.648		3.210		1.291		0.848
PVC (dry film)		26.120					
PVC K-White (dry film)		9.439					

ment, is yttrium (Y), due to its large, negative reduction potential and similar chemical properties.

Essentially constant properties across the lanthanide series dictate consistent corrosion inhibiting mechanisms and properties over the rare earth elements. Of the lanthanide series, lanthanum, cerium, praseodymium, and ytterbium have been most often examined. Data for cerium are presented here, while the discussions regarding other rare earth elements that possess mixed valences are expected to behave in a similar fashion.

Mixed valence oxides result for rare earth oxides due to a mismatch of the atomic radii of the rare earth elements compared with oxygen and the typical oxide surface defect. Crystal lattice oxygen vacancies result and extra non-bonded electrons are present within cerium atoms of the crystal lattice, which are shared among neighboring cerium atoms. A localized, reduced valence of cerium is observed rather than a strict cerium IV. Therefore, lattice mismatch and crystal site vacancies result in locally reduced cerium formal valence throughout the crystal from +4 toward +3, where the average valence is between +3 and +4. The partial valence states give the potential for unusual redox properties, oxygen transport as observed in fuel cell technology, and hydration and ion complexation properties. Each of these contributes towards the cerium surface chemistry.

Cerium conversion coatings have generally been observed to function as barrier coatings, providing suppression of the cathodic half-reaction.^{13,26,30} Cerium salts have been examined as solution inhibitors of aluminum corrosion and have been found effective at cathodic reaction suppression but at effective concentrations greater than chromate.^{21,25,31} In addition, blends

Table 4—Codes Applied for Rating Corrosion of Organic Primer-Coated Panels Upon Exposure to Neutral Salt Spray

Rating	Scribe Line Description
1	Scribe line beginning to darken or shiny scribe
2	Scribe lines > 50% darkened
3	Scribe line dark
4	Several localized sites of white salt in scribe lines
5	Many localized sites of white salt in scribe lines
6	White salt filling scribe lines
7	Dark corrosion sites in scribe lines
8	Few blisters under primer along scribe line (<12)
9	Many blisters under primer along scribe line
10	Slight lift along scribe lines
11	Coating curling up along scribe
12	Pin point sites/pits of corrosion on organic coating surface (1/16" to 1/8" dia)
13	One or more blisters on surface away from scribe
14	Many blisters under primer away from scribe
15	Blisters over surface

Corrosion creepage beyond scribe

A.	No creepage
B.	0 to 1/64
C.	1/64 to 1/32
D.	1/32 to 1/16
E.	1/16 to 1/8
F.	1/8 to 3/16
G.	3/16 to 1/4
H.	1/4 to 3/8

of rare earth compounds have been found to give synergistic protection when the nitrate salts were applied as a surface treatment.³²

Figure 9—The SVET measurement of surface corrosion activity for a drilled cerium conversion coated AA/075-T6 panel after (a) 15 min and (b) 17 hr exposure to 5mM aqueous NaCl. In SVET analyses of a cerium conversion coating surface in the absence of co-inhibitors, the two cathodic (green) regions were inhibited and passivated at prolonged exposure while the anodic (red/white) region remained active. Also note the localized cathode adjacent to the active anode.³² (Copyright William Andrew Press.)

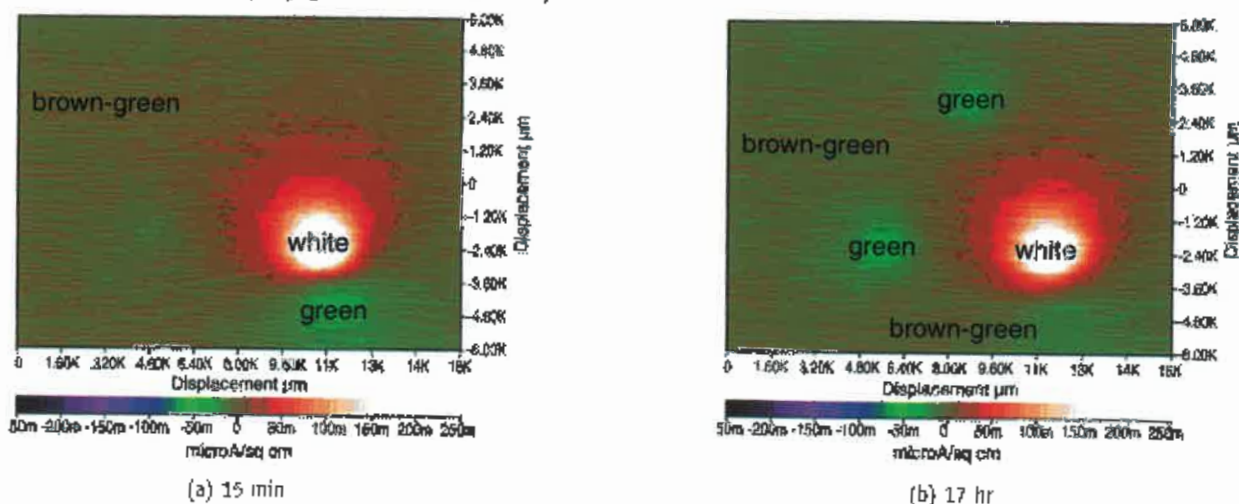


Table 5—Corrosion Rating for Epoxy Polyamide Coatings as a Function of Coating Formulation Conditions. Results Reported are for Air Saturated 5 wt% Salt Soak, Which Was Found to Correlate to Salt Spray in a Ratio of 2 hr Salt Soak Per Hour Salt Spray

Inhibitor Coatings pH	Time (hr)	Waterborne Epoxy Polyamide	
		7075-T6 Alloy CeCC	2024-T3 Alloy CeCC
Cerium oxide pH~12	500	5A	5A
Cerium oxide (Acetic acid) pH= 7.7	500	4A	4A
Cerium oxide 0.2 wt% KMnO ₄ pH~12	500	4A	4A
Cerium oxide 0.2 wt% KMnO ₄ (Acetic acid) pH= 7.7	500	3A	4A
No rare earth metal 0.2 wt% KMnO ₄ pH~12	500	6A	6A
No rare earth metal 0.2 wt% KMnO ₄ pH=7.7	500	6A	6A
Cerium nitrate pH~12	500	5A	5A
Cerium nitrate 0.2wt% KMnO ₄ pH~12	500	5A	5A
Cerium nitrate 0.2 wt% KMnO ₄ (Acetic acid) pH~7.7	500	5A	5A
Talc control pH~12	500	6A	6A
Cerium, 0.2wt% KMnO ₄ pH ~7	1500	3A	2A

A significant finding of this work was the predictive correlation between a convenient, short 3-day soak EIS test and 3-week salt fog performance for conversion coatings. Conversion coatings on a substrate that retain a final impedance higher than $10^5 \Omega\text{-cm}^2$ results (preferably over $10^6 \Omega\text{-cm}^2$) are most likely to pass MIL-C-5541 neutral salt fog testing.^{27,33} The procedure has been quite useful for screening chemistries as likely to pass a 336-hour neutral salt spray MIL-C-5541 specification.

Similar to chromate treatments,^{16,17} rare earth elements do form durable aluminum alloy surface conversions but do not appear to passivate anodic corrosion reactions.^{28,29,34} The chemistry of a rare earth conversion coating may be elucidated based on the electrochemistry and solubility of the species involved in corrosion inhibition (Figure 7). Cerium (III/IV) redox

potentials as a function of pH are similar to the chromium (III/VI) ion couple. However, cerium is insoluble in its higher oxidation state as the ceric/cerous mixed oxide but soluble in its lower valence salt state, such as cerous nitrate, in contrast to chromium that can be soluble in the Cr^{VI} oxidation state and insoluble as a Cr^{III} oxide.

Soluble cerium species can be synthesized at the acidic anode and insoluble ceric oxide at the alkaline cathode, whose schematic is shown in Figure 8, inversely analogous to that shown for chromate. While the oxide can inhibit oxygen reduction reactions as a barrier, as an insoluble coating it cannot be readily transported to an active anode. The stable rare earth oxide is not as strong an oxidant as the chromate anion and cannot effectively accelerate aluminum oxidation, i.e., quickly oxidize the aluminum surface to produce a passive layer. Even if ceric species near the anode can be transported in low concentration to the anode, upon reduction and in the presence of chloride they may become soluble cerous species to be washed away from the anode by adventitious water and cannot precipitate as an insoluble salt to further

passivate the corrosion site. Lack of transport for the cerium oxides is good for durable barrier properties but a detriment to a smart inhibitor response.

SVET measurements of cerium conversion coating corrosion activity in artificial, drilled pits show a similar early distribution of anodes and cathodes as drilled chromate conversion coatings. However, usually only cathodic regions were affected by the cerium conversion coating (Figure 9) while anodic regions continued their activity unabated. The anode develops a more localized cathode to support continued corrosion activity at rates greater than those observed for chromate coatings but significantly inhibited more than the bare alloy. These combined data and others^{24,25,28,29,35-37} support the inhibition mechanisms presented here.

Thus, limitations inherent in the solubility of rare earth species seem to prevent full use of otherwise su-

perb electrochemical properties. However, more recently, inhibitors that have been found to alter their solubility based on pH influence have been utilized to produce extended salt fog exposures with shiny or passive scribes. An analogous inhibition mechanism for cerium comparable to that of chromate has been proposed,³¹ though there remain technical issues to be overcome.

For instance, cerous salts are hydrolytically sensitive toward alkalinity. While useful in preventing corrosion of aluminum alloys, alkaline sensitivity makes the cerous salts only marginally compatible with common coatings systems, such as epoxies, that have significant alkalinity.³⁸ The alkalinity of an epoxy polyamide system (Table 3) was neutralized by adjusting the pH of the amine portion of the system with acetic acid prior to mixing with the rare earth inhibitor dispersed into the epoxy portion. The cerous inhibitor was then dispersed into the epoxy portion of the system. In this procedure cerium was found to retain a cerous state despite the presence of amine, and produced a storage stable coating. Phosphate pigments, as a co-inhibitor, must be similarly avoided to prevent precipitation of the active cerium inhibitor as an inactive cerium phosphate.

The corrosion rating system that was applied to coated test panels is shown in Table 4. Performance ratings that demonstrate the effect of coating parameters on the corrosion resistance of AA2024-T3 and AA7075-T6 alloys are shown in Table 5. Passive scribes have been obtained, retaining shiny appearance without scribe creepage after up to 750 hr of neutral salt spray for AA7075-T6 and up to 1200 hr for AA2024-T3. Lack of coating pH control, an anodic corrosion co-inhibitor, or solubility of the cerium inhibitor compound in the coating formulation permitted aluminum alloy corrosion similar to that coated with an uninhibited epoxy polyamide film (also containing control coating). Control coatings lacking cerium showed no detectable changes in performance regardless of pH adjustment or presence of the co-inhibitor. Testing is underway to expand smart use of the cerium inhibitors.

SUMMARY

Corrosion inhibition is a complex process where all components must work together as a team to prevent the corrosion reaction at the anode and/or cathode. Combination of incompatible agents, which can induce poor product stability, premature precipitation of inhibiting components, and poor corrosion performance must be prevented through coating design. A corrosion inhibition system design begins with selection of the metal alloy for a desired corrosion and physical strength performance. The pretreatment chemistry

alone will not induce corrosive elements at the surface of the alloy to enhance corrosion sensitivity. Selection of a smart inhibitor system, e.g., with pH stimuli-responsive agents, controls the release of the agents to provide longevity and localized, efficient performance. The smart features of an inhibitor system are influenced by, and can be deterred by, other aspects of the coatings design, e.g., coating formulation pH.

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