Corrosion-resistant metallic coatings

We describe recent computational and experimental studies on the corrosion properties of metallic coatings that can be tailored (tuned) to deliver up to three corrosion-inhibiting functions to an underlying substrate. Attributes are tuned by a selection of alloy compositions and nanostructures, ideally in alloy systems that offer flexibility of choice to optimize the corrosion-resisting properties. An amorphous Al-based coating is tuned for corrosion protection by on-demand release of ionic inhibitors to protect defects in the coating, by formation of an optimized barrier to local corrosion in Cl− containing environments, as well as by sacrificial cathodic prevention. Further progress in this field could lead to the design of the next generation of adaptive or tunable coatings that inhibit corrosion of underlying substrates.

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The epidermis–dermis–subcutaneous system is able both to resist and repair damage and also regrow over a defect that exposes underlying tissue. These are admirable qualities in biological systems because these processes are repetitive, autonomous, and can be triggered by damage without external intervention1. In corrosion of metallic materials, dip, spray, chemically or electrodeposited organic-based, metallic, and ceramic coatings are often used to protect a substrate from corrosive damage2.

Natural passive films, artificially grown oxide layers (i.e. anodized and sealed), and conversion coatings3–5 can also protect underlying metals and alloys. Successful native passive films can form a protective layer over many metals if the ingredients for passivation (i.e. alloying elements) are present in high enough concentration in the underlying alloy. The oxide quickly and automatically reforms to repair defects in many environments. Conversion coatings and anodized layers rely on the formation of a chemically engineered layer based both on
the oxidation of elements in the metal as well as on incorporation of selected species in a pretreatment bath to reinforce the natural oxide. Controlled additions of specific molecules to the conversion coating bath are required and these can seldom be applied in the field.

**Corrosion protection by passive films and coatings**

Passive films, conversion coatings, and metallic and organic coatings confer corrosion protection via a variety of mechanisms, including formation of barriers to the penetration of corrosants; high ionic resistivity in surface layers to minimize electrochemical reactions under the coating at the metal–coating interface; active corrosion inhibition where an inhibitor is stored, released, and delivered to a defect; and sacrificial cathodic protection. Chromate systems possess this active corrosion inhibition property but are being phased out due to their high toxicity and carcinogenicity. Oxides may also exhibit ion-selective permeability, as well as a desirable potential and/or pH of zero charge to limit detrimental anion (Cl–) adsorption and ingress. Enhanced adhesion, control of the liquid chemistry at the metal–coating interface and superhydrophobic properties may also operate in many exciting new systems.

**Active corrosion inhibition**

Traditionally, metallic coatings serve only one or two functions. For example, Zn has excellent corrosion resistance and functions as a sacrificial anode. Zn galvanizing provides sacrificial cathodic protection and acts as a barrier but does not usually supply inhibitor ions. The release of Zn ions during the sacrificial protection of galvanized steels only provides a small additional benefit compared to galvanic protection provided by the potential driving force. Metallic coatings used to protect Al alloys consist of a thin layer of nearly pure Al mechanically bonded to standard precipitation age-hardened Al alloys. The coating sacrificially cathodically protects the Al alloy substrate (a beneficial form of galvanic corrosion) but does not provide active corrosion inhibition. Galvanic throwing power is limited because the roll-bonded cladding has a limited electrochemical driving force for protection. The open circuit potential (OCP) of Alclad alloys is only ~80–100 mV below that of the structural substrate, such as AA 2024–T3, and their pitting potentials (E_pit) are actually below that of underlying structural Al alloys. The consequential virtual non-polarizability enables cathodic protection of the aerospace alloy but also ensures a high self-corrosion rate and considerable anodic inefficiency.

**Long-range corrosion protection of coating defects**

In the case of a coating containing active corrosion inhibitors or passivators that are stored, released, and transported, defects such as a scratch in the coating may be protected over long distances (i.e. possess a chemical throwing power) due to concentration (e.g. chemical potential) gradient-driven random transport from inhibitor-rich regions to unprotected sites. Sacrificial cathodic protection (i.e. galvanic throwing power) may also operate over long distances. The distance over which protection can be afforded is a function of the electrochemical properties of both the sacrificial anode and the unprotected site as well as the geometry and ionic conductivity of the ionic phase (often a thin electrolyte exposed to the atmosphere) over the coating. The electric field in the ionic solution established by the potential driving force difference between the anodic and cathodic half cell potentials facilitates long-range cathodic polarization. Such long-range functionality is superior to that of biological systems where an internal circulatory system is required to repair damaged sites. Similarly, self-healing of mechanical damage in man-made materials requires locally distributed microcapsules, or encased composites containing gels or monomeric polymers and catalysts spaced at a short distance from defects. The monomer cannot be easily supplied over long distances to repair damage sites.

**One vision for new coatings with multiple, tunable functions**

Unfortunately, existing corrosion protecting metallic coatings cannot provide active corrosion inhibitors to protect defects via transport of the inhibitor through the liquid corrosive phase. Moreover, corrosion properties are rarely tunable. For instance, the behavior of metallic claddings is often fixed by rather inflexible limits on compositions and microstructures. Therefore, there are few user-adjustable parameters available to tune cathodic protection to mitigate certain localized corrosion processes triggered above certain potential thresholds (e.g. pitting, stress corrosion, exfoliation at high potentials, or H embrittlement at very negative potentials). In addition, cathodic protection, active chemical inhibition, as well as the presence of a local corrosion barrier, are desired simultaneously. The addition of inhibitors is a particular challenge for metallic materials. While sacrificial and barrier attributes can be adjusted somewhat by changing composition or structure, inhibitors can rarely be added to a solid. Moreover, inhibitors, stored in the solid state, must be released as a liquid-soluble molecular or ionic species to enable transport through the liquid corrosive phase to a defect. In contrast, sparingly soluble inhibiting pigments can readily be added to organic coatings and released by chemical dissolution. An added challenge for both organic and metallic coatings is the desire to trigger inhibitor release on-demand so that the stored inhibitor is used only when it is needed.

We will now discuss some recent computational and experimental studies where several corrosion-protecting functions are achieved simultaneously in a single metallic coating. The desired properties include active corrosion inhibitor supplied on demand to enable corrosion inhibition and/or autonomous repair. Sacrificial anode-based cathodic protection and barrier properties can also be tailored to...
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 protect various substrates in a range of environments. Moreover, the electric field created by the galvanic couple between the coating and the substrate can be manipulated to augment transport of inhibitors over large distances. To demonstrate this possibility we discuss a specific nanoengineered, spray-applied, amorphous metallic alloy (Fig. 1) that illustrates some of the mitigation strategies and functions desired and achievable using a nanoengineered metallic coating such as a corrosion-inhibiting system. The challenges and issues involved in achieving these functions are highlighted.

Materials and fabrication of tunable amorphous metallic coatings

The challenges of tailoring the properties of metallic coatings compared to polymer-based coatings are numerous. In the case of polymers, a micrometer- or nanometer-scale composite can be created by mixing in the liquid state, and thus with great flexibility, a monomer, resin, filler, solvent, etc., and a phase encapsulating the inhibitor (e.g. strontium chromate pigment) in a slurry that is then reacted in various ways and solidified in a rigid state below the polymer glass transition temperature, \( T_g \). In contrast, metallic coatings are often applied at high temperatures and involve delivering a liquid metal via either a hot dip or spray process. Such heating may adversely alter the microstructure of the underlying alloy. Physical and chemical vapor deposition, pulsed thermal spray (PTS), cold spray (CS), and mechanical cladding are alternative methods to avoid excessive temperatures. Numerous nonequilibrium alloying techniques may also be employed to add beneficial alloying elements in significant enough concentrations to have a major impact on properties. Corrosion barrier properties can be improved by several routes. Minimizing structural defects such as intermetallic and metalloid phases and optimization of certain compositions in solid solution both usually significantly improve corrosion ‘barrier’ properties. Therefore, methods to produce supersaturated solid solutions which lack intermetallic and metalloid phases are highly desired. By using metallic glasses, metallic elements may be added or mixed in a soluble liquid solution with improved, although not unlimited, flexibility, and then solidified and trapped below \( T_g \) to achieve chemically homogeneous solid solutions. Moreover, active corrosion inhibitors might be supplied if some of the added alloying elements can function in this capacity. Amongst the possible replacements for Cr(VI)\(^{23–27}\), transition metal (TM) and rare-earth (RE) metal ions (\( \text{Co}^{2+}, \text{MoO}_4^{2–}\) and \( \text{Ce}^{3+}\)) are possible choices to inhibit localized corrosion of Al alloys\(^{23–25}\) and steels\(^{26–27}\). These elements also can be alloyed to form Al-based metallic glasses. RE metal ions may serve as inhibitors if they can be incorporated and released by a chemical or electrochemical process. Alloying a crystalline metal with these elements is traditionally difficult because of their limited
solubility in the solid state. This problem can be overcome by using a glassy alloy that dissolves these alloying elements in solid solution. Indeed, certain Al–TM and Al–refractory metal alloys can exhibit enhanced local corrosion barrier and sacrificial anode-based cathodic protection qualities. The Al–RE–TM alloy series is of particular interest because of its good glass-forming abilities, high strength, low density, and superior corrosion properties.

In fact, a new amorphous Al–Co–Ce alloy system was recently synthesized as an environmentally compliant metal coating with multiple corrosion protection functionalities. The notion of a multifunctional metallic coating need not be restricted to Al–TM–RE and there are likely to be many alloys that can be designed following these general strategies. The goal was to simultaneously provide a corrosion barrier, sacrificial anode-based cathodic protection, or prevention as well as active corrosion protection (e.g. contain and deliver a supply of inhibiting cations that can be released to suppress corrosion) to minimize corrosion at coating defects that expose the underlying structural alloy.

Cathodic protection abilities may also be optimized by lowering the OCP of the coating relative to the underlying substrate. For instance, the OCP of the Al–Co–Ce alloy can be lowered as much as 750 mV below that of AA 2024-T3 depending on the alloy composition and solution pH. Amorphous Al alloys also have the ability to store beneficial alloying elements in solid solution. For instance, the selected transition and RE metals (e.g. Ni, Fe, Co, Ce, Y, Gd) added as alloying elements improve amorphicity in concentrations up to about 15 at.%.

The amorphous alloy can be formed over a wide range of Co and Ce compositions, as seen in Fig. 2. The alloy’s amorphous state is very stable.

High-velocity oxygen-fuel spray (HVOF), CS and PTS methods are possible deposition methods to apply such coatings. PTS utilizes high heating and large quenching rates, which allows for either amorphous or crystalline powder feedstock material (Fig. 3) to develop an amorphous or nanocrystalline coating on a substrate material.

The structure of the feedstock material tends to dictate the resulting structure of the coating. The coating powder and deposited layer are shown in Fig. 4a–d. The feedstock powder is often supplied as a controlled particle size distribution ranging from 0.5 to 20 µm, although larger powder sizes can be attempted (Fig. 4a). PTS is distinguished by rapid particle acceleration and heating, a minimal residence time within a high enthalpy environment, and rapid particle quenching upon interaction with the target substrate. The quenching rate for particles less than 20 µm in size can be as high as 10^6 K/s. Also notable is that naturally aging precipitation age-hardened aerospace alloys, such as the AA 2024-T3 substrates, do not exceed 60 ºC during the coating process. Reduced substrate thermal loading enables short stand-off coating capability that, from an application standpoint, is desirable because it allows for localized repairs of the coating where a physical defect exists exposing the underlying structural alloy and gives the capability for coating complex geometries. The pulsed spray process raster over the surface of the substrate in such a way that the resulting spray-applied coating is actually a built-up series of layers. PTS and HVOF coatings have the advantage of accepting the feedstock powder for these alloys in either crystalline or amorphous forms, as the feedstock particles can melt mid-process as long as powders are small.
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High-density samples with favorable corrosion properties can be achieved. The CS process utilizes the plastic deformation of the sprayed, solid, feedstock particles on impact with the substrate to achieve a uniform coating. The spray event occurs below the melting point of the spray materials, so less microstructural change and less oxidation should occur. Numerous metallic coatings have also been deposited by these methods.

Al–Co–Ce alloy coatings have been produced by both HVOF and PTS with thicknesses ranging from 75 to 600 µm often with good adhesion and low porosity. In some studies these have been compared to melt-spun ribbon (MSR) alloys produced by the traditional method of streaming the molten alloy on to a spinning copper wheel to enable rapid quench rates.

Tunable barrier properties in multifunctional amorphous Al–TM–RE coatings

Coatings which act as barriers to corrosion are commonly used and date back to the use of noble decorative and corrosion-resistant metallic coatings. However, as in the case of sacrificial cathodic protection, barrier properties are often fixed by rather inflexible alloy compositions and structures. Porosity in coatings is often minimized by increasing coating thickness.

The advanced processing methods discussed above enable new coating compositions which break out of old constraints on alloy testing. For example, the addition of rare earths (RE) and transition metals (TM) to aluminum can result in amorphous metallic coatings with tunable barrier properties.
composition. In one study of an Al–Co–Ce alloy, three parameters were obtained from E–I plots (tests performed in NaCl) (Fig. 5) to characterize corrosion properties over a flexible range of compositions. These were the OCP, the pitting potential, \( E_{\text{pit}} \), and the repassivation potential, \( E_{\text{rp}} \). \( E_{\text{pit}} \) and \( E_{\text{rp}} \) are indicators of the pitting resistance, while OCP helps forecast the galvanic corrosion behavior of an alloy (e.g. potential driving force for sacrificial cathodic protection when coupled to a substrate). Various regression models suitable for use with alloys where the composition is constrained to 100% were explored and two examples are shown in Figs. 6 and 74. Plots include possible substrate structural materials (AA 2024-T3, Aermet 100® steel, etc.). The influence of Co on the OCP is based on Co’s effect on the cathodic kinetics of Al–Co–Ce alloys. By increasing the reaction rate for both the O reduction reaction (ORR) and the H evolution reaction (HER), additions of Co in solid solution results in a higher OCP. The decrease in OCP associated with the addition of Ce is most likely due to the suppression of the ORR by Ce. The positive influence of Co on \( E_{\text{rp}} \) is due to the decreased hydrolysis product of this cation72, probably resulting in a less aggressive pit environment and reduced anodic dissolution rates of a Al–Co solid solution. A complex trend with Co was seen. A parabolic shape also described the effect of Al and Ce on \( E_{\text{rp}} \). These three elemental behaviors, when considered together, describe a complex balance where Co and Ce reduce the aggressiveness of the pit solution: Co lowers the dissolution rate while Al aids oxide formation in an aggressive acidic solution. Therefore, optimization of alloying elements produces the highest \( E_{\text{rp}} \) values, with a complex dependency of \( E_{\text{rp}} \) on alloy content. To optimize the composition so as to provide a barrier with the highest resistance to localized corrosion, Co amounts should be relatively high (6-8 at.%), and Ce contents moderately low (3-5 at.%) in this particular alloy.

**Tunable sacrificial anode-based cathodic protection in Al–TM–RE coatings**

Sacrificial anode-based cathodic protection when two or more metals are galvanically coupled is a potent electrochemical protection method12. A coating that can polarize an exposed substrate material just a few hundred millivolts below its OCP can lower its corrosion rate by a factor of 100 or more. It is often more useful to polarize many structural materials that corrode by local corrosion mechanisms such as pitting or intergranular corrosion above some critical threshold potential (i.e. \( E_{\text{pit}} \)) to levels below this threshold potential. This is accomplished by engineering a galvanic couple potential below \( E_{\text{pit}} \) or \( E_{\text{rp}} \). This is called cathodic prevention. Unfortunately, the governing properties needed to optimize cathodic protection or prevention (material-dependent OCP, and electrochemical current–potential characteristics) have previously only been optimized through trial and error. Moreover, parameters such as OCP are often rather inflexible due to the limited choices of alloy composition and structure available.
Extreme cathodic potentials are not desired because ‘overprotection’ can lead to adverse side effects such as H embrittlement, alkaline attack, and paint blistering. Therefore, tunable cathodic protection is a highly desired capability.

The flexibility in OCP achieved by selecting particular compositions of the Al–Co–Ce alloy system (Fig. 7) is extremely beneficial, as it enables application of varying degrees of cathodic protection. By choosing an Al–Co–Ce composition with relatively low Co (3–5 at.% and low Ce levels (3–5 at.%) a sacrificial anode material can be produced with a moderately low OCP value, to avoid cathodic overprotection. An example is Al0.9Co5Ce5. The unique combination of OCP values more negative than pure Aermet 100® or AA 2024-T3 along with an enhancement of barrier properties in the coating makes this amorphous Al–Co–Ce alloy particularly well suited to serve as a protective coating material. The enhanced resistance to localized corrosion offered by this alloy results in greater Faradic efficiency for the sacrificial material, extending the theoretical lifetime of protection compared to the Al–Zn and Al–Mg alloys used as Al alloy cladding materials.

The sacrificial anode-based cathodic protection attributes sought have been recently investigated by computational methods focusing on galvanic couples between a metallic coating and exposed substrate under atmospheric conditions. Fig. 8a shows how atmospheric exposure (a thin electrolyte layer) of a structural Al alloy covered by a metallic coating with a scratch at the center of the sample Fig. 1) was modeled. A metric of the cathodic throwing power of the sacrificially anodic Al–Co–Ce alloy was taken as the galvanic couple potential distribution along the horizontal axis of Fig. 8a and its proximity relative to the OCP of the Al–Co–Ce coating and the AA 2024-T3. A figure of merit used is $\Delta E$, given as $(E_{\text{pit, AA2024}} - E_{\text{couple}})$, where $E_{\text{couple}}$ is the interfacial galvanic couple potential at the centerline of the scratch, $C_l$ (Fig. 8b). Effective cathodic prevention design maximizes $\Delta E$. The maximum $\Delta E$ that can be achieved during galvanic coupling is termed $\Delta E_{\text{max}}$ and is defined by $E_{\text{pit,AA2024}} - E_{\text{OCP, AlCoCe}}$.

Fig. 8 shows the extent of polarization given by the parameter $\Delta E$ obtained for a variety of situations as a function of scratch width at a fixed sample length. The parameter $\Delta E$ is shown as the ordinate for each case, with the value of $\Delta E$ at $S = 0$ being the theoretical $\Delta E_{\text{max}}$ (i.e. $E_{\text{pit, AA2024}} - E_{\text{OCP, AlCoCe}}$). The theoretical limit is approached for small scratches. A greater extent of protection can be achieved when the Cl– concentration is low. The potential distribution model predicts that substantial sacrificial cathodic protection of an AA 2024-T3 scratch could be achieved with a nanoengineered alloy coating. The extent of the sacrificial cathodic protection provided by the Al–Co–Ce alloys is a function of pH, Cl– concentration, the cathodic kinetics on the AA 2024-T3, and the Co content of the metallic coating. The metallic coating provides the best protection (i.e. largest cathodic polarization of the scratch) when it is tailored to contain a low Co content, and is exposed to either high or low pH solutions of low Cl– concentration. Finally, the combination of chemical and electrochemical protection predicted by computational modeling has been verified via experiments involving defects machined into PTS Al–Co–Ce alloys over AA 2024-T3. Corrosion protection is indeed

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**Fig. 8** (a) Schematic of the geometry associated with the galvanic coupling modeled between an Al–Co–Ce alloy coating (left) and AA 2024-T3 substrate (right) exposed as a scratch in a thin electrolyte (e.g. corrosive solution) of thickness $\delta$. Symmetry considerations allow solution of half of the scratch ($S$) exposing AA 2024-T3 by applying a zero flux boundary conditions. The half-scratch length, $S$, was varied from 500 to 5000 $\mu$m in width while the total length of the coating–scratch system was held constant at 1 cm. The $j = 0$ boundary condition reflects the physical situation at the right end of a specimen. This system was used to conduct finite element modeling of the galvanic protection provided by the Al–Co–Ce coating to the AA 2024-T3 scratch. (b) In this plot the galvanic couple potential distribution along the horizontal axis of Fig. 8a and its proximity relative to the OCP of the Al–Co–Ce coating and the AA 2024-T3 $E_{\text{pit}}$. A figure of merit used is $\Delta E$, given as $(E_{\text{pit, AA2024}} - E_{\text{couple}})$, where $E_{\text{couple}}$ is the interfacial galvanic couple potential at the centerline of the scratch, $C_l$ (Fig. 8b). Effective cathodic prevention design maximizes $\Delta E$. The maximum $\Delta E$ that can be achieved during galvanic coupling is termed $\Delta E_{\text{max}}$ and is defined by $E_{\text{pit,AA2024}} - E_{\text{OCP, AlCoCe}}$. The theoretical limit is approached for small scratches. A greater extent of protection can be achieved when the Cl– concentration is low. The potential distribution model predicts that substantial sacrificial cathodic protection of an AA 2024-T3 scratch could be achieved with a nanoengineered alloy coating. The extent of the sacrificial cathodic protection provided by the Al–Co–Ce alloys is a function of pH, Cl– concentration, the cathodic kinetics on the AA 2024-T3, and the Co content of the metallic coating. The metallic coating provides the best protection (i.e. largest cathodic polarization of the scratch) when it is tailored to contain a low Co content, and is exposed to either high or low pH solutions of low Cl– concentration. Finally, the combination of chemical and electrochemical protection predicted by computational modeling has been verified via experiments involving defects machined into PTS Al–Co–Ce alloys over AA 2024-T3. Corrosion protection is indeed
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provided in experiments when the PTS coating is electrically coupled to the AA 2024-T3 substrate.

On-demand active-corrosion inhibition based on tunable Al–TM–RE alloy coatings

Controlled-release technologies are often used to supply chemicals at given rates76,77. Release often occurs upon contact with solution. However, slow release only when needed is often desired. Conducting electroactive polymers are one means to provide controlled drug delivery77. In corrosion protection, triggered or on-demand release of inhibitor ions is also very important. Conductive polymers have recently been utilized as reservoirs for corrosion inhibitors whose triggered release occurs by galvanic reduction or ion exchange76–82. Amorphous Al–Co–Ce alloys enable pH-controlled release of corrosion-inhibiting ions from a metallic coating. The pH change that triggers release is a consequence of the chemistry changes brought about by corrosion itself43. Therefore, on-demand release occurs as a result of exposure to corrosive species when corrosion initiates, for instance, pH. ‘Turning off’ inhibitor release also occurs when the pH returns to near-neutral and changes the local pH of the solution over the coating. For a metal coating to behave like a pigmented paint that can supply active corrosion inhibitors, several attributes are desired83. The coating must store enough inhibitor to supply the critical inhibitor concentration once released. The aqueous solution formed over the metal surface must accumulate enough inhibitor to achieve the critical inhibitor concentration, $C_{\text{crit}}$, needed to stop corrosion in reasonable time periods. This necessitates a high inhibitor capacity in the alloy and a finite release rate. The $C_{\text{crit}}$ must be lower than the saturation concentration of the inhibitor ion in the solution. The $C_{\text{crit}}$ in a given electrolyte volume must be low enough so that the alloy can readily release enough ions to achieve it without completely depleting the inhibitor capacity83.

Al–Co–Ce alloys releasing Ce $^{3+}$ meet these requirements. The inhibitor is stored in the alloy and in its air-formed oxide layer in valence states that are useful for corrosion inhibition. Inhibitors are released by pH-dependent chemical dissolution of the oxide or direct oxidation of the metal23–25 (Fig. 10). Ce and Co oxides are highly soluble at low pH, insoluble under neutral, and partially soluble under alkaline conditions (Fig. 11) 13,84. Thus, a pH change can be exploited to trigger Co$^{2+}$ and Ce$^{3+}$ release. A pH change occurs during corrosion

![Fig. 9 Cathodic polarization obtained with AlcladTM compared to the Al–Co–Ce metallic coating expressed as the potential difference, $\Delta E$, between Epit and the galvanic couple potential at the center of the scratch (x = 1 cm; at C-line of Fig. 8a) attained for different scratch widths at a fixed half sample length of 1 cm. The theoretical $\Delta E_{\text{max}}$ for AlcladTM and the other coatings are shown on the ordinate at $S = 0$. The potential difference between the Epit of AA2024-T3 and the galvanic couple potential at x = 1 cm are shown in the plot for each half-scratch width. Boundary conditions for the AlcladTM used: $i_{\text{pass}}=0.002$ A/m$^2$, $E_{\text{EpitAlclad}}$ 45 mV below $E_{\text{Epit2024}}$. The conditions include 0.05 M Cl$^{-}$ and a pH of 3, with idl = 0.4 A/m$^2$ for the various alloys compositions. The results indicate that the Al–Co–Ce coating protects better than AlcladTM as indicated by the larger $\Delta E$. This suggests that the Al–Co–Ce coating can protect bigger scratches by cathodic prevention. Moreover, a low Co content (i.e. 0–1 > 3–5% Co > 7–9% Co ) in the Al–Co–Ce alloy helps to protect AA2024-T3 to a greater extent. (Reproduced with permission from © 2007 J. Electrochem. Soc.)

![Fig. 10 Schematic illustration of Al–Co–Ce coating (dark grey) on AA2024-T3 with a defect exposing the AA2024-T3 substrate. The less noble coating has been tuned to possess an OCP more negative (–) than the underlying structural alloy. Consequently, cationic inhibitors released from the dissolving coating can be transported to the defect by both migration as well as diffusion, while anionic species are transported in the opposite direction. A coating could also be engineered to enable anionic transport by migration to the scratch as long as the polarity was reversed. This could be accomplished by tailoring the coating composition and structure to create a coating with a potential greater than that of the scratch. The behavior shown has been confirmed for both MSR and spray-applied coatings.]
which releases metal cations that hydrolyze to produce H\textsuperscript{+} at anodic sites. High cathodic reactions at cathodic sites often increase the pH. Therefore, when a metal is scratched and a galvanic couple forms between the coating and newly exposed substrate, the pH will drop over the anodic coating and rise at the cathodic scratch site. pH-dependent release rates were found for Al–Co–Ce–(Mo) alloys\textsuperscript{41} (Fig. 11). The inhibitor ions released diffuse and then migrate towards the damage site, reach C\textsubscript{crit} and suppress corrosion (Fig. 10). When corrosion of the structural alloy stops, the pH of the environment returns to neutral and Ce\textsuperscript{3+} is subsequently released at much lower rate.

Computational studies\textsuperscript{42,45,73–75}, have also been used to study inhibitor release from such metallic substrates. Studies of inhibitor release, transport, and achievement of C\textsubscript{crit} were conducted with and without migration through the electrolyte phase. Migration-based transport of Ce\textsuperscript{3+} to the scratch occurs due to the potential difference established between the OCPs of AA 2024-T3 and the Al–Co–Ce metallic coating. The time needed to reach C\textsubscript{crit} over the scratch was determined, accounting for both transport processes as well as the effect of temporal and position varying local release rates. Fig. 12 shows how the released Ce\textsuperscript{3+} profile develops with time and position in one example. Migration aids Ce transport (for OCP\textsubscript{AlCoCe} < OCP\textsubscript{AA2024}), explaining the uphill transport of Ce\textsuperscript{3+}. The C\textsubscript{crit,Ce} is reached at the coating–scratch interface at various times for different scratch lengths. Accumulation was limited by ionic transport.

In summary, corrosion inhibition of a AA 2024-T351 scratch can be achieved with ions released from a metallic coating. Experimental exposure of AA 2024-T3 in a corrosive solution near an electrically isolated Al\textsubscript{67}Co\textsubscript{8.7}Ce\textsubscript{4.3} MSR alloy confirmed computational modeling. The Ce\textsuperscript{3+} supplied significantly decreased the maximum corrosion pit sizes.

**Summary**

A multifunctional amorphous alloy has been described that possesses three corrosion protection abilities when deployed as a coating over structural alloys. The coating (i) functions as a local corrosion barrier, (ii) serves as a sacrificial anode, and (iii) supplies soluble ions used as corrosion inhibitors by engineering metallurgical and electrochemical properties. The alloy system described is just one example of many exciting new possibilities in metallic coatings enabled by the progress in amorphous and nanocrystalline alloy development, as well as novel synthesis and coating deposition methods. In the case presented, excellent inherent resistance to corrosion is achieved through structural amorphicity and choice of composition to optimize corrosion functions. For instance, tunable electrochemical and chemical throwing powers to achieve long-range protection of substrate defects can be achieved. These concepts are generic and other alloys can in principle be developed to optimize these functions. Such alloys can also be manipulated to enable transport of inhibiting cations by both migration and diffusion. Inhibitor release can be triggered on-demand.

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REFERENCES

60. Kendig, M., and Hon, M., Corrosion (2004) 60, 1024