Designing green, self-healing coatings for metal protection

Anthony E. Hughes*, Ivan S. Cole, Tim H. Muster and Russel J. Varley

Commonwealth Scientific and Industrial Research Organisation (CSIRO), Australia

Metals are used extensively in modern society in a range of applications from infrastructure to aircraft to consumer products. The protection of metals, primarily from corrosion, has been an active area of materials science for many years. However, over the last 20 years, changing regulations governing both environmental issues and human health have driven even greater activity in this field. Addressing these regulatory changes presents some of the most exciting challenges in materials science. This review looks at current metal protection schemes, exploring the development of 'green' inhibitors and 'self-healing' paint films that have inbuilt capacity to maintain functionality. Inorganic and organic materials science has undergone rapid development in recent decades and this review looks at how some of those developments, particularly in encapsulation and polymer healing, can be applied to the design of new protective paint systems.

In 1973, the book, 'The Limits to Growth', highlighted chromium—used in tanning, metal production and finishing and corrosion protection—as one of the elements that human civilization would run short of by 2025 [1]. The intervening 37 years, however, have seen chromium use in many applications plummet due mainly to regulatory changes, driving the search for replacements, 'green alternatives', that comply with both health and environmental legislation. Chromate is an oxidizing oxyanion of chromium with superb corrosion prevention properties for a wide range of metals, but this property is also the reason why it is toxic and carcinogenic. In coatings, chromate has largely been eliminated except for some high-performance applications such as in the aerospace industry. Another environmental driver for change in the paints industry is reduction of the use of volatile organic compounds such as solvents [2]. Thus, solvent-based coatings have also been targeted, resulting in enormous effort to find water-based alternatives.

Aside from the environmental drivers, there is also a need for vastly improved protection of our assets. Recent studies have shown that corrosion costs 2–5% of the gross domestic product for industrialized countries [3]. While there are relatively few catastrophic failures related to corrosion [4], the burden of these costs results in operational limitations in a wide range of activities. For example, the large maintenance costs for the United States Air Force are now impacting the budget for the purchase of new aircraft [3].

The challenges for developing new coatings draw from many areas of materials science. Metallurgy and electrochemistry are required in order to understand the alloy microstructure and corrosion processes, and surface, inorganic and polymer chemistries are needed for the design of the coating system and physics for the transport properties within the coating system. The confluence of these different streams of science is the nexus for self-healing materials having the inbuilt capacity to repair themselves. It should be noted that the term 'self-healing' is used in its broadest sense here: self-repairing and mendable are also used in this field and are, perhaps, more appropriate given the use of external triggers [5].

The focus of this review is on the new generation of coatings for high-performance applications such as in the aerospace industry, although much of what is included in this review has applications outside the aerospace industry and some examples will be mentioned in passing.
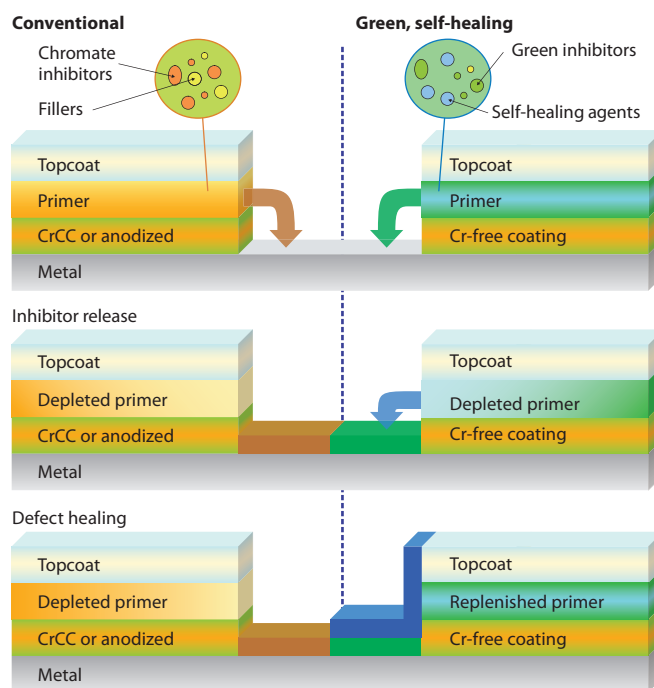

Figure 1. Schematic illustration of post-damage healing in conventional (left) and green (right) self-repairing films. The structure of a green self-healing system could be similar to a conventional coating except for the incorporation of green inhibitors and additional self-healing agents. On exposure of a defect to a moist external environment, water diffusion into the primer (the trigger) would result in the release of inhibitor into the defect resulting in corrosion repair. In the self-healing system, the functionality of the coating would additionally be restored through the release of self-healing agents after initial repair to develop a barrier coating in the defect.

Figure 1 depicts a typical mutilayered protective coating system used in aerospace. First, a chromate conversion coating (CrCC) or an anodized coating is developed on the surface through a multi-step process. Chromate conversion is a process that 'converts' the natural

*Corresponding author. Email: tony.hughes@csiro.au

Division of Materials Science and Engineering, CSIRO, Private Bag 33, Clayton South, Victoria 3169, Australia
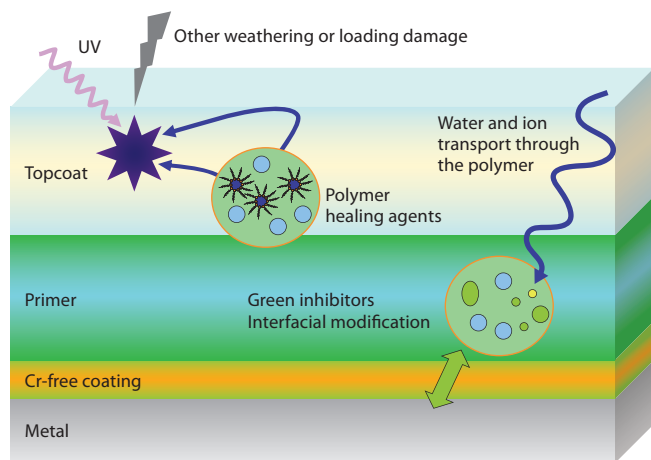
Figure 2. Schematic illustration of a pre-emptive healing system. Water and electrolyte diffusion through the paint coating can generate corrosion reactions at the metal–paint interface. Pre-emptive healing could occur through the trapping of water and corrodents and/or the release of inhibitors from the primer (or from the chromium-free coating), which targets the corrosion reactions and shuts them down. Self-healing agents also heal the polymer from the effects of weathering and other damage.

Figure 3. (a) Soluble fraction of charged species of various inhibitor species such as oxyanions (molybdate, chromate, vanadate), cerium and phosphate (sum of all soluble species for each inhibitor type). (b) Solubility of various aluminum species as a function of pH. Aluminum corrodes at both high and low pH due to destabilization of the oxide. The presence of phosphate in solution broadens the stability regime.

chromium-based oxide (100–200 nm thick), whereas the anodized coating is mostly aluminum oxide (up to a few micrometer in thickness). These coatings are designed to provide a good base for the paint system (Figure 1, left). Chromate conversion and chromic acid anodizing are still used in aerospace applications, but there are also a number of chromate-free processes that have been used in a range of industries for some years [6–8]. The paint system consists of a primer (usually epoxy-based) including an active component for corrosion prevention and fillers, whereas the topcoat (often a polyurethane) contains pigments and fillers and provides a barrier function. For many interior applications, the primer is used without a top coat. The primer contains fillers and poorly soluble forms of chromate such as strontium chromate. Primer layers are typically 20–25 µm in thickness and contain up to 30 % w/w inorganic components, thus providing the majority of active corrosion protection. As chromate is such a good inhibitor [8], this system provides immediate repair in defects and long-term healing (corrosion protection) to the underlying metal through continuous low-level dosing of chromate (post damage) and is considered a self-healing system [7].

The goals of developing 'green', self-healing coatings are to replace the chromate and to incorporate components that regain the functionality in a paint defect (Figure 1, right). In addition, there is a 'pre-emptive' healing role to be played by the inhibitor in order to improve the interfacial properties between the metal and the primer, and by the self-healing components for the repair of weathering damage to the paint system (Figure 2).

Metal treatment and oxide control

All metals undergo oxidation upon exposure to the environment. While many pure metals, such as aluminum, naturally develop protective oxides, industrial metals are usually alloys with heterogeneous microstructures that promote corrosion and inhibit paint adhesion [9]. The development of such microstructures occurs due to precipitation of the alloying elements as intermetallic particles during fabrication. These particles have electrochemical properties that differ from those of the aluminum and so tend to drive localized corrosion.

The ability of natural oxides to form or repair passive layers is controlled by a combination of thermodynamic and kinetic factors, such as oxide solubility, pore structure [10,11], density and charge [12]. For instance, passivity will be more likely where the volume ratio of
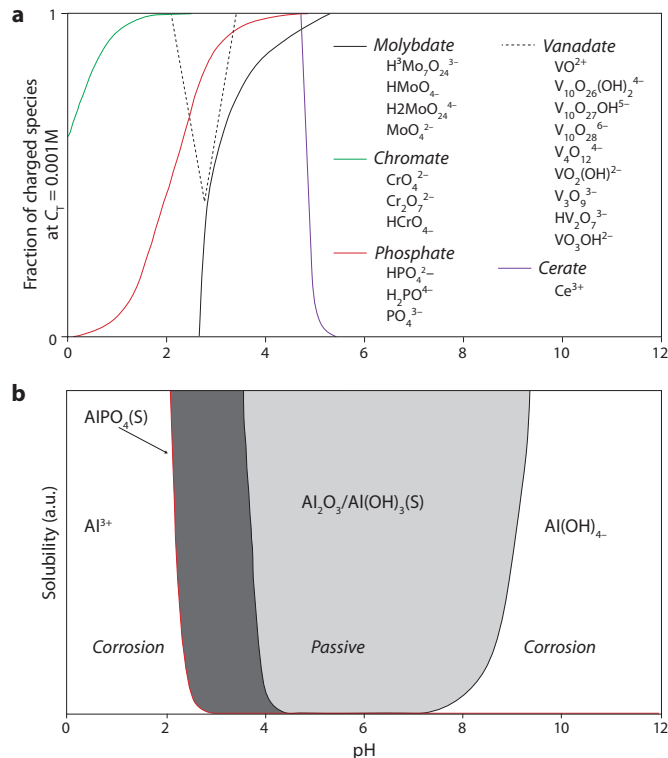
the metal oxide and the metal unit cells falls in the range of 1–2 [13]. As an example, the aluminum stability diagram shows that aluminum forms a passive oxide between pH 4 and 9, and that outside these limits the oxide is susceptible to either acidic or alkaline attack (Figure 3). The presence of soluble ions in solution, which form insoluble aluminum compounds, extends the passive range, in the case of phosphate, to more acidic environments. Oxyanions such as phosphate and chromate are anodic inhibitors and readily adsorb onto the surface of oxides to form insoluble species such as aluminum phosphate and aluminum–chromium(III) oxides [13]. Cerium, along with other species that form insoluble species at high pH, is a cathodic inhibitor since it deactivates the cathodic sites by forming insoluble precipitates. Recent inhibitor design relies on bringing together the inhibiting properties of both anodic and cathodic inhibitors into a single entity, thus providing multifunctionality.

Standard processes

The variable natural passivity of alloys, and the large influence that underlying metal microstructure can have on the structure of the overlying coating [14], have led to the development of multistep treatment processes for metal protection [6,8,9] to eliminate the heterogeneous nature of the metal surface. The end step in these processes results in the deposition or growth of a manufactured oxide via electrochemical (anodizing) or chemical (conversion coating) means. Anodized coatings can be developed on aluminum from solutions that commonly contain chromic acid. These coatings have an outer oxide with a cellular structure that promotes adhesion, and an inner barrier layer. Inhibitors can be incorporated into the outer porous layer of the coating during formation or as a seal after formation. Chromate conversion coatings can be applied to a wide range of metals and provide active corrosion protection and adhesion for overlying paint.
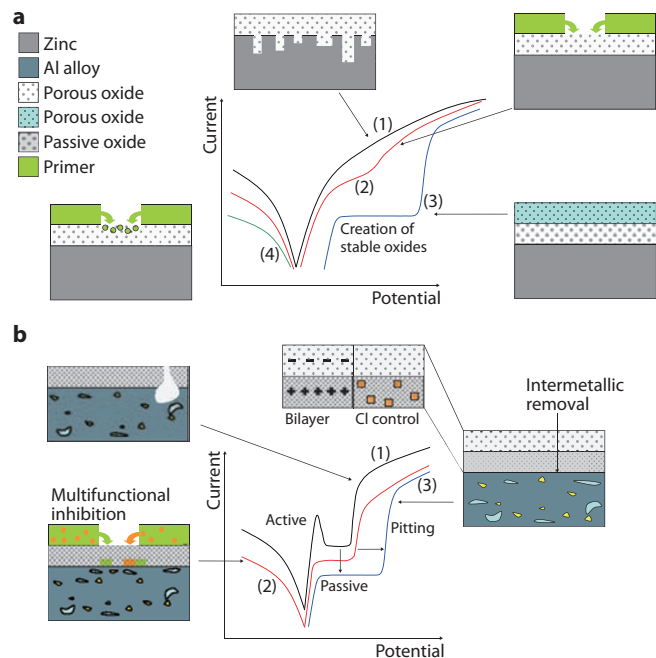
Figure 4. Healing mechanisms of (a) porous and (b) passive metal oxides. (a) Porous oxide (*e.g.* zinc). (1) Zinc typically develops a porous oxide that enables widespread attack across the surface. (2) Anionic corrosion inhibitors are delivered from a primer, competing with aggressive anions (*i.e.* chloride). Sufficient inhibitor release can depress both anodic and cathodic reactions. (3) The formation of stable oxides akin to passive films may be achieved through the formation of charge bilayers via oxide densification and localized pH buffering. (4) The supply of appropriate dopants into ZnO (*i.e.* from primer) may avoid semiconductive properties. (b) Passive oxides (*e.g.* aluminum alloy). (1) The passive film that develops on aluminum alloy contains defects due to intermetallic phases, ultimately leading to pitting corrosion. (2) Where corrosion inhibitors are delivered to the metal surface, passivity can be achieved through inhibition of both cathodic and anodic intermetallic phases. (3) For systems where intermetallics are removed from the alloy surface by etching treatment and oxide barriers are introduced, the solution potential required to pit the aluminum alloys is increased. Potential healing mechanisms against pitting include the repair of surface charge bilayers and the control of aggressive anion (chloride) distribution in the oxide.

Green alternatives

The challenge for the green alternatives is to meet or exceed the performance requirements of the current systems. Alternatives to chromic anodizing such as sulfuric, sulfuric-boric and phosphoric-based processes have been available for a long time. Replacements for CrCCs include a range of treatments based on specifically adsorbing and self-assembling monolayers and hydrotalcite deposition, but chiefly upon sol–gel chemistries such as titanium/zirconium oxyfluorides, rare earth processes, cobalt, vanadium, molybdates and permanganate systems [6–8]. These coatings generally provide only barrier protection, so the challenge remains to design new protective systems based on a fundamental understanding of coating formation, performance and healing mechanisms.

Some of the healing mechanisms being explored by researchers are outlined in Figure 4, where traditional approaches to limiting corrosion (represented as current decrease) by inhibiting anodic (increased potential) and cathodic sites (decreased potential) are extended to the formation of barriers to ion transport through control of surface charge, the densification of pores in oxides, and control of the electrical properties of semiconducting oxides.

At the most fundamental level, a coating on a metal should form a barrier to stop the ingress of corrodents (Figure 4(a)). Many metal oxides are porous [11], allowing transport of oxygen and water, yet they are also ion-selective, limiting the transport of either anions or cations. In some cases, bipolar oxide layers can be developed that limit both anionic and cationic transport [10]. For instance, a fixed charge

developed by hydration and dissociation of the metal oxide results in pH excursion from the isoelectric point where there is no net charge. Therefore, a positive fixed charge will achieve electroneutrality by selectively adsorbing anions to the pore walls. Anion-selective films enhance corrosion and promote local attack, particularly in chloride solution, as ions will accumulate in the occluded electrolyte under the film. In contrast, cation-selective oxides will reduce corrosion because hydrogen ion migration will be promoted across the oxide (from metal surface to solution) while chloride will not cross the oxide resulting in the precipitation of a metal hydroxide. The most effective protection is offered by a bipolar precipitate with the anion-selective electrode on the oxide side and the cation-selective electrode on the electrolyte side.

Where a bilayer of oxides has been deposited such that the two oxides possess vastly differing surface charge characteristics, the barrier properties have been markedly improved [15–18]. Bilayers can be established by natural oxide formation (*i.e.* Fe_3O_4/Fe_2O_3 bilayers on steel) [15] and in conversion coatings (Al_2O_3/CeO_2, Al_2O_3/Cr_2O_3), and most notably anodized coatings have a thick porous layer over a thin barrier layer [17–19]. The naturally passivating oxide on zinc, under near-neutral saline aqueous conditions (solution or drops), develops a bilayer with a thick, porous outer layer of variable composition covering a thinner, compact film of ZnO at the metal interface [20]. Under atmospheric conditions, the porosity of the outer layer, comprised of corrosion products such as gordaite and zinc hydroxyl-carbonate [21], gradually decreases, providing a pH-buffering effect and developing an outer oxide that possesses a negative surface charge in mildly acidic environments [22]. The porosity of the inner layer also decreases over time [20].

Alternative considerations need to be made where the metal oxides possess semiconducting properties. For instance, ZnO is an n-type semiconductor, and cathodic reactions (*i.e.* oxygen reduction) can occur on the oxide pore surfaces rather than penetrating to the metal/oxide interface [22]. Modeling indicates that with zinc overlaid by such a porous oxide, the corrosion current is initially very high (due to the large cathodic area) but rapidly falls as oxygen is consumed within the pores of the oxide. The high availability of zinc and hydroxyl ions promotes precipitation within the pores and densification of the oxide. With appropriate control of oxide growth and dopants (*e.g.* group-I and -V elements), the semiconducting properties of ZnO can be balanced between n- and p-type, thus reducing the conductivity of the oxide film and the flux of cations [23].

For paint applications, good adhesion properties are required of the surface oxide. This can be achieved through mechanical interlocking as well as chemical bonding. For chemical bonding, modification of oxide surface charge has been demonstrated to improve polymeric adhesion [24]. The repair of adhesion between polymeric coatings and oxides has also been demonstrated through the encapsulation of adhesion-promoters into polymer resins, which when fractured migrate to the polymer–substrate surface and repair the defect. The adhesion has been demonstrated to be highly dependent upon the electrostatic interactions between the adhesion promoter and the oxide substrate [24,25].

Paint systems

The focus for self-healing, corrosion-prevention coatings is also slightly different from that of self-healing in coatings for decorative purposes, or self-healing of polymers. In the latter cases, the focus is on providing enough material to repair the volume of the defect, whereas in the inhibited coating case, only the surface of the defect needs to be protected to regain functionality [5]. That is, there is no need to replace all the polymer removed when a defect (*e.g.* scratch) is created.

Current paint systems

The paint system (primer and topcoat in Figure 1) provides continuous protection and repair to the surface for as long as the dose of chromate
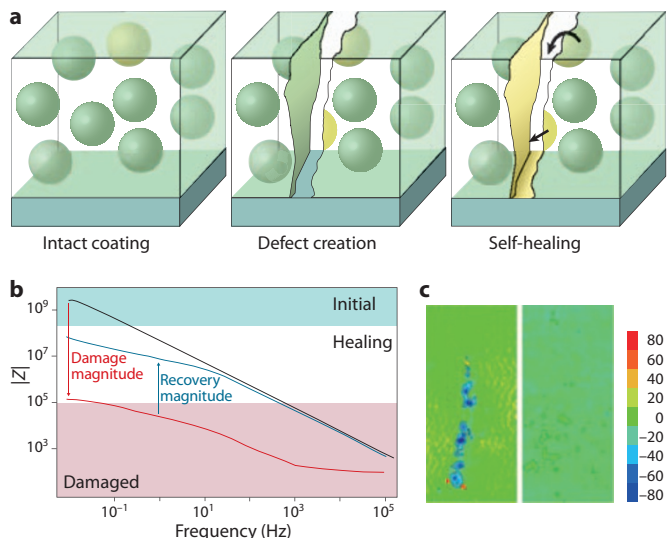
Figure 5. Measuring self-healing responses of paint coatings. (a) Schematic illustrations showing an intact coating, defect creation and the self-healing response. (b) Example of electrochemical impedance spectroscopy results for measurement of the response of the coating to defect formation and recovery. The ratio of the polarization resistance (R_p) after recovery to that prior to damage is the simplest measurement of healing efficiency. R_p is typically the absolute impedance $|Z|$ measured by electrochemical impedance spectroscopy at 0.01 Hz. (c) Example of scanning vibrating electrode measurements, which can also be used to assess healing. These maps show the current density ($\mu A\, cm^{-2}$) 1 h (left) and 2 d (right) after defect creation in an epoxy coating containing encapsulated silyl ester on AA2024-T3. The current density in the defect is suppressed by the flow of the silyl ester over the defect region. Maps were obtained for samples immersed in 0.05 M NaCl solution at room temperature. Maps are courtesy of J. M. C. Mol, S. González-Garcia and S. J. Garcia (Delft University of Technology, Netherlands).

Figure 6. Scheme for the development of self-healing coatings. The development of the inhibitor and its delivery system are depicted on the left and the paint system and its methods of delivery on the right. Approaches that draw together both streams are featured in the center. The types of encapsulation systems for delivery of the inhibitor and the paint repair are quite different. The schematic graphs below show how the system integrity (black) might be viewed with the release of the inhibitor (left, green) and polymeric healing agent (right, blue). With each cycle of agent delivery, the reservoir diminishes, limiting the performance recovery. The intention is to extend the lifetime of the system compared to a situation where there is no recovery.

from the primer remains above the critical concentration, that is, the concentration at which the inhibitor is effective. Sinko [26] describes the level of inhibition I_i as follows.

$$I_i = n \frac{C^i_{sat}}{C^i_{crt}} \qquad (1)$$

where C^i_{sat} and C^i_{crt} are the saturation and critical inhibition concentrations, and n is a stoichiometric factor (generally the valence of the cation). The inhibition should be between 1 and 100 for inhibitors in paints films. The typical chromate inhibitors $SrCrO_4$, $CaCrO_4$, $BaCrO_4$ have I_i values of 5, 141 and 0.2, respectively [26]. The systems forming the simplest class of self-healing coatings are those that incorporate a new inhibitor (satisfying the criterion in Equation 1) as a drop-in replacement. This has been a strategy for many years.

Approaches for performance recovery of paints

In studies of self-healing, measuring the healing efficiency is important. The healing efficiency for bulk materials, from metals to polymers, is often measured in terms of mechanical performance [5,27]. In coatings, regaining the protective functionality of the coating is key. The healing efficiency can be determined using electrochemical techniques such as electrochemical impedance spectroscopy and the scanning vibrating electrode technique (SVET), which measure the degree of protection provided in a defect (Figure 5). Measurements on the defected coating can be compared to measurements on the original coating and the healing efficiency can then be determined. Examples for an epoxy containing a silyl ester encapsulated in urea formaldehyde capsules are shown in Figure 5. Impedance spectroscopy and SVET both show measurable improvements, *i.e.* healing, after defect creation.

Pre-emptive healing refers to protection that occurs in the absence of mechanical damage in response to external triggers and results in the improvement of interfacial properties. The focus of research in
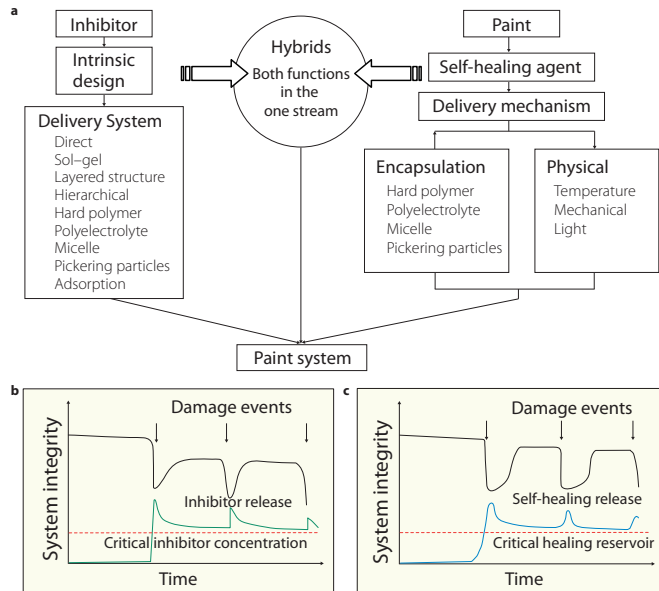
self-healing is generally on repairing defects in paint systems [28–30], but pre-emptive healing is an important and emerging aspect of healing in the coatings field. Obvious triggers for pre-emptive healing are water and chloride ions. Electrolyte ingress and inhibitor dissolution can cause thickness changes in polymer coatings [5,31,32]. For example, swelling of polyurethane has been observed in the presence of chloride and sulfate ions [32]. Water uptake allows soluble inhibitor species to be released into the paint system (Figure 3) and diffuse to the metal/coating interface to provide *in situ* corrosion prevention or repair [28,30]. Ion exchange materials loaded with anions such as vanadate, chromate, nitrate and carbonate also exchange for chloride ions and prevent interfacial damage [33–35].

Alternative approaches for preventing the ingress of water and chloride to the metal/coating interface have been explored. Clay particles have been proposed as water traps for one method of protection in the European MUST program, in which four levels of protection are identifies. Clays have also been used as swelling agents in paints to heal defects [36]. The use of magnesium particles as sacrificial anodes has been reported to protect aluminum alloys and steels, undergoing oxidation instead of the underlying metal [37].

Post-damage healing refers to the release of healing agents from a damaged paint surface into a defect, which then acts to restore functionality. Mechanical damage, water and chloride ions are key triggers resulting from damage creation. Mechanical damage breaks hard capsules that could contain, for example, water-soluble inhibitors. Water dissolves the inhibitor incorporated directly in the primer, and chloride can trigger anion exchange. Droplet formation within defects means that the inhibitor is only released when required, *i.e.* when the defect is moist [31]. The initial high release of inhibitors may be facilitated through atmospheric exposure of the intact paint and penetration of water into the film to prepare the inhibitor, probably via surface hydrolysis reactions within the paint, for diffusion and release into the defect [28–30].

Approaches for post-damage healing have tended to focus on separate response for the inhibitor and the polymer self-healing components.

Figure 6 shows two different pathways for encapsulation-based incorporation of the inhibitor and self-healing agents. The encapsulation techniques are discussed in more detail below.

Green Inhibitors

Direct replacement of chromate relies on finding alternatives with similar chemical properties. This search has resulted in the development of high-throughput electrochemical and corrosion testing techniques for screening of inhibitor performance and even determining the critical inhibitor concentration [38,39].

Needless to say, many promising inhibitors do not have the same inhibitive power at low solubility as chromate. This means that alternatives must be present at higher concentration, leading to the use of more soluble compounds and consequently encapsulation as a method of regulating the response to external or internal triggers (Table 1). Some success has also been achieved in increasing the solubility by replacing methyl groups in organic functionalities with hydroxyl groups [40].

Many current inhibitors are water-soluble salts and thus ionic. Consequently, they exist as either anions or cations in solution and perform the single function of anodic or cathodic inhibition. So the simplest improvement to inhibitor design is to increase the functionality by finding compounds for which both the cation and anion can adopt an inhibitive role. A large range of cations, including zinc, calcium, and rare-earths [7,30, 35,38,39], have been tested independently or combined with either organic (carboxylates, organophosphines, organophosphates and thio compounds) [26,30,38–40,42–44] or inorganic (oxyanions, carbonates, phosphates, phosphites, nitrates, nitrites, silicate [26,35,38,40]) compounds.

Anions with dual functionality, such as transition-metal oxyanions that are both oxidants and anions, have been investigated extensively. The introduction of oxidizing agents or some organophosphates [43] also provides some degree of bio-inhibition, as required for certain applications, to inhibit bacterial and fungal growth, such as in aircraft fuel tanks. Ce(dibutyl phosphate)$_3$ is a good inhibitor and relatively 'green', whereas Ce(di-phenyl phosphate)$_3$, although being a better corrosion inhibitor, also has strong bio-inhibition characteristics, which impart increased environmental and health risks [43].

Functionality for interfacing with the polymer can also be added to organic groups on the inhibitor to provide binding sites to the polymer matrix [30,45]. Matching the inhibitor to both the application needs and the polymer matrix is a complicated challenge, as the transport properties within a multicomponent coating system (most inhibited paints comprise inhibitors fillers, ultraviolet (UV) absorbers, surfactants and the polymer itself) are not well understood or easily predicted. Figure 7

presents several different behaviors for chromate and non-chromate inhibited primers. Under simple Fickian diffusion, inhibitor release into solution would be expected to result in an increase in concentration in proportion to $t^{0.5}$ [46]. However, release behaviors from $t^{0.25}$ to $t^{1.0}$ have been reported [31,46], even for the incorporation of inhibitors into the same paint [47]. The interaction of the inhibitor with fillers, functional components and the polymer matrix are therefore complex. Anomalously low leaching has been attributed to non-uniformity of mixing as well as transport-controlling boundary-layer effects [46]. In the case of paints, the encapsulation of inhibitors is likely to produce a range of leaching behaviors that will depend on the type and homogeneity of the encapsulating system.

The other consideration is the final dose that reaches the defect. Rapid release of a soluble inhibitor might provide immediate protection, but fail to provide long-term protection [29,30], whereas a low initial dose of inhibitor may not provide enough protection to inhibit the corrosion process [30]. Consequently there has been a lot of recent work looking at encapsulation of inhibitors using a range of structures.

Inhibitor encapsulation: from nanocontainers to micelles

The requirements for capsule size and design for coatings are different from those for self-healing of mechanical damage in bulk polymers or composites [27,48,49]. In the latter applications, capsules up to a few hundred micrometers in size can be accommodated [5,27]. However, as can be seen in Figure 1, coating layers are restricted to tens of micrometers in thickness, and thus the large encapsulation systems reported for polymers need to be adapted for coating applications. One adaptation is to modify the aspect ratio of the container to make rods with cross-sections that can deliver larger volumes of material than a sphere of the same cross-section [49]. The role of inhibitors is to prevent surface reactions (corrosion), and therefore the volume of material required is much smaller than that required to actually fill the defect. Consequently, there has been considerable effort looking at 'nanocontainers' [41,42,50].

Table 1 lists a number of encapsulation approaches and most likely triggers for release. All encapsulation systems will respond to extreme excursions of certain triggers (*e.g.* pH). Water is the most obvious trigger because it can permeate most polymers. pH variations are more specific and respond to the pH excursions that occur in corrosion reactions. The presence of chloride ions (and other anions) within the coating can be used as specific triggers for the release of corrosion inhibitors and uptake of corrodents using ion-exchange materials,

Table 1. Encapsulation systems and indicative triggers

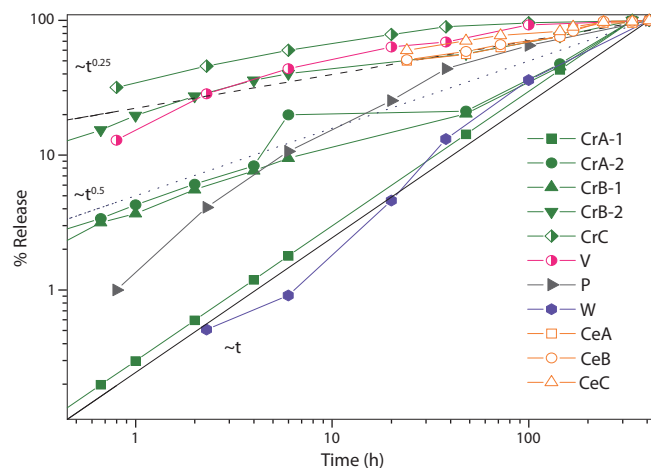| System	H$_2$O	pH	Cl⁻	Light	Temp.	Mech.	Chem.
Direct incorporation	■	■	■				■
Sol–gel	■	■	■				■
Layered compounds	■	■	■				■
Hierarchical	■	■	■				■
Hard polymer	■			■	■		■
Polyelectrolyte	■	■	■		■	■	
Micelle	■	■	■		■		
Pickering particles	■	■	■			■	■

Figure 7. Release of inhibitors expressed as a percentage of total release (typically 17 h) for a range of inhibitors. CrA, CrB, chromate-inhibited epoxy primers used by an aircraft manufacturer [31]; CrC, V (vanadate), P (phosphate), W (tungsten), laboratory-prepared acrylic chromate-inhibited primer [47]; CeA, CeB, CeC, laboratory-prepared Ce(dibutyl phosphate)$_3$-inhibited epoxy coatings with 1.7 (A), 2.3 (B) and 5.2 wt% (C) active agent.
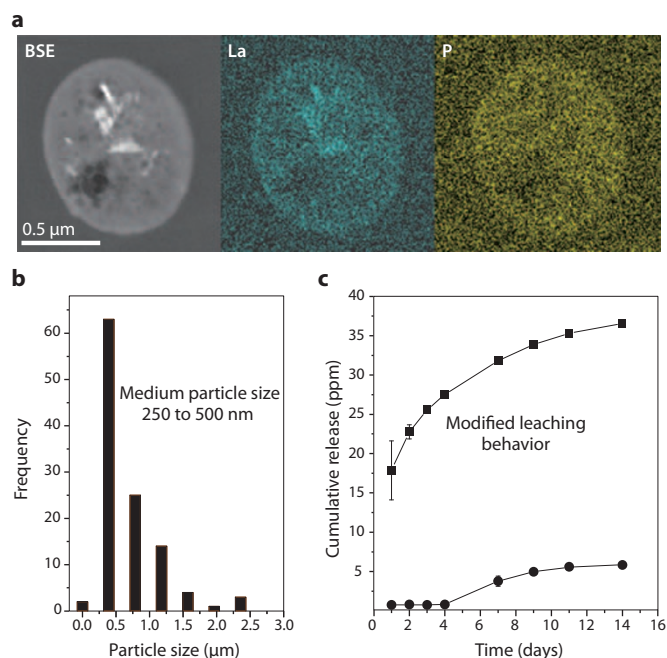
Figure 8. Encapsulation of La(dibutyl phosphate)₃ in oleic acid in an epoxy film. (a) Backscattered electron (BSE) image and lanthanum and phosphorus x-ray maps of a thin section of film mounted on amorphous carbon. The variation in composition within the capsule can be seen in the BSE image. (b) Distribution of encapsulated La(dibutyl phosphate)₃ particle size. (c) Accumulation of lanthanum in solution as a function of immersion time of the film in water.

such as layered double hydroxides (*e.g.* hydrotalcites) [33–35,45,51]. The use of light has also been investigated as a trigger for sol–gel coatings [52], and both light and temperature triggers have been reported for polymers [53,54]. Hard capsules respond to mechanical damage. Chemical triggers have been included here because it is feasible to have secondary triggers derived from the breakdown of the inhibitor/encapsulation system (from the primary trigger), which then trigger release of the polymer-healing function after the inhibitors have been released.

One approach for the development of nanocontainers is via a functionalized sol–gel route using condensation reactions of metal alkoxides and silanes individually or together. This approach has been applied extensively for the development of hybrid coatings that could serve as replacements for at least part of the paint system, *e.g.* pretreatments and the primer [30]. CrCCs are self-limiting and are only able to achieve thin (≤ 200 nm) adhesion-promoting layers [6,7]. Sol–gel coatings, particularly those that incorporate an organic functionality, can provide thick coating, enabling them to store sufficient volume of active corrosion inhibitor [55]. There are an enormous number of possibilities here, which have been reviewed elsewhere [56,57]. Briefly, organic-substituted silicic acid esters of the type $R'_n Si(OR)_{4-m}$ can be polymerized or reacted with metal alkoxides of the type $M(OR)_{m-n}(LZ)_n$, where L has an anchoring function and Z is a general organic group [57]. The R' group can also be compatabilized to improve adhesion to paint overlayers, for example using a glycidoxy group to interface with an epoxy [30,45,58].

These types of coatings have been tested with a range of compounds. Some examples include cerium nitrate [41,42], cerium vanadate [55], cerium acetate [30,55], cerium oxalate, calcium borate and potassium metavanadate [55], polyphosphates [50] and a range of organic inhibitors [42,44,50,55]. The use of pH as a trigger has been tested on sol–gel coatings using methylene orange as the released agent [58]. These types of experiments help in the design of the coating composition and structure.

One variation on the sol–gel route is to put functionalized nanoparticles into the sol–gel. For example, SiO₂ with benzotriazole and multiple polyelectrolyte layers have been incorporated into ZrO₂SiO₂ sol–gel coatings, and the were demonstrated to achieve healing of a defect during the first 24 h of immersion in 0.05 M NaCl solution [59]. Another variation is to form nanoparticles within the aqueous phase and subsequently crosslink them during film formation [42].

Micelle encapsulation offers opportunities to develop small encapsulated particles. Figure 8 shows the encapsulation of La(dibutyl phosphate)₃ in an organic acid through an emulsion process. The particle-size distribution shows that the majority of the particles are between 250 nm and 500 nm in size. The encapsulation process has modified the release profile of the La(dibutyl phosphate)₃ compared to the unencapsulated La(dibutyl phosphate)₃/epoxy system. Without encapsulation, leaching follows a $t^{0.24}$ behavior, whereas with encapsulation, inhibitor release is delayed and does not follow a power law. The encapsulated and unencapsulated inhibitor can therefore be combined into a single system to achieve high initial release as well as sustained ongoing release.

Ion-exchange materials with a high surface area, as discussed above, offer some of the greatest potential for triggered response, specifically in relation to the corrosion process. Both cation- and anion-exchange materials have been reported, and these can be used for a triggered response to the presence of anionic corrodents as well as cations from the corrosion product, such as metal ions [51]. For example, layered double hydroxides such as hydrotalcites have been exchanged with inorganic inhibitors [33,34,51] as well as organic anions [60] and some cations [35]. During corrosion, chloride ions exchange for the anionic inhibitor, thus triggering release of inhibitors in response to chloride. Both anion-exchanged and cation-exchanged materials show good corrosion inhibition depending on the required mechanism of protection.

Solid, high-surface-area materials, often obtained through a sol–gel route, have also been explored as nanocontainers for inhibitors and structural components in films [42,45,52,59]. High-surface-area oxides have already been used successfully for a range of organic inhibitors in sol–gel applications [42,59].

Another approach is the use of hard capsules [5,61,62], such as urea formaldehyde capsules, which have been tested most extensively in self-healing research [5,63–65]. Hard polymer capsules have been used for the incorporation of inhibitors [64], polymer monomers [63] and drying oils [65] to provide a healing function in the coating. These latter approaches simplify the approach to healing in coatings by taking only the right-hand avenue shown in Figure 5. Initial work looks promising [65] for these simplified self-healing approaches, but it remains to be seen whether they have the required corrosion resistance. The longevity of the capsule in the coating may also be an issue that needs addressing [64].

Layered functional materials in which the encapsulated phases are incorporated between the layer have also been researched [66]. In this example, involving a self-healing coating consisting of layers of 8-hydroxyquinoline inhibitor and polyelectrolytes, the creation of a defect resulted in the release of the inhibitor, which pH-buffered the defect due to the weak acid/base activity of the polyelectrolyte and promoted polymer repair through the migration of the polyelectrolytes (polyethyleneimine and polystyrene sulfonate) to the defect.

Self-repairing paints

Once corrosion repair has occurred, it is desirable to provide further protection via a barrier coating. It is not surprising therefore that many strategies are based upon modifying the primer given its proximity to the metallic substrate. However, the incorporation of self-healing mechanisms into the topcoat rather than the primer is also considered, as the topcoat is directly exposed to external environment triggers such as the air, moisture and UV radiation. Many of the strategies developed for composite materials or bulk polymers therefore remain applicable to coatings. In this way, healing of any damage to the topcoat is critical in preventing corrosion, maintaining barrier properties and appearance (Figure 2). As a result, self-healing coatings research tends to be

separated into two approaches: materials that can autonomously heal themselves subsequent to a damage event, and those that require external activation (pathways on the right-hand side of Figure 6). Coatings that are able to heal themselves autonomously tend to be based upon the micro-encapsulation approach pioneered by Dry *et al.* [67], but tuned specifically to coating applications [63,64].

The encapsulation of an epoxy monomer in urea formaldehyde capsules is used extensively in polymer or composite healing [48,68]. Other types of polymer repair include encapsulation for 'solvent welding' of the polymer [69], and drying oils, such as linseed oil [66], with a view to making an alkyd healing of a defect. In work by Cho *et al.* [70], a monomeric siloxane (and catalyst) were used as the healing agents in an epoxy vinyl ester coating, where either the catalyst, or both the siloxane and catalyst, were separately encapsulated. When scratched with a razor blade, the coating provided excellent resistance to corrosion under immersion in saline solution compared to the unmodified formulation.

Mendable coating systems [5,27], activated through external triggers, are another attractive strategy to prevent long-term corrosion because the (virtually) constant presence of atmospheric moisture, UV radiation or even possibly temperature variations means that triggers are continuously available. The specific advantage of these approaches is that the healing arises from the inherent structure of the material, so there is no deleterious impact on material properties. The presence of moisture in the atmosphere has been used to activate healing in various kinds of inorganic organic hybrid polymers. Miccichè *et al.* [36] used the volume expansion of layered silicate clays during moisture absorption for self-healing. In moist environments at elevated temperature, the coatings showed a clear reduction in the depth of a scratch over time, illustrating how a potentially negative environmental factor can be used for positive effect. Liu *et al.* [71] used atmospheric moisture as a healing strategy in inorganic organic hybrid polymers. Moisture-degradable polylactic acid was used to encapsulate $TiCl_4$. When the polylactic acid degraded, the $TiCl_4$ became exposed to moisture and then formed solid titanium dioxide at the surface of the fiber, hence protecting the substrate from the impact of moisture. This strategy has been used successfully to increase the lifetime of organic light-emitting devices by reducing moisture susceptibility.

Hydrogels, colloidal crosslinked networks that undergo reversible swelling in the presence of water, are another class of materials being studied for their application to self-healing coatings. South *et al.* [72] utilized this behavior to construct a multi-layered coating that, after being subjected to multiple impacts with a blunt tip, erased all evidence of damage after the addition of water. In this case, it is the solvated water that is able to restore properties and full functionality.

Ultraviolet-A radiation is another external stimuli that can act as a continuous healing trigger for coatings, although this trigger is potentially dependent on diurnal variations. A recent example is the development of a multifunctional polyurethane coating containing oxetane functional and chitosan groups in the polymer [53]. Upon UV exposure, the oxetane groups open, creating reactive functionality, while the chitosan species provide UV susceptibility via urea and ether linkages. This creates a continuously healing system in the presence of UV irradiation (and damage) because the newly exposed functionality from the oxetane species can form new crosslinks with newly exposed functionality via UV cleavage of the chitosan. The gradual disappearance of a surface scratch with time during UV exposure for this coating elegantly illustrates how different reactive groups can be both dormant and active depending upon the external environment, and if tuned correctly can create truly multifunctional materials (Figure 9).

Another use of UV radiation in protecting coatings from long-term failure is the application of photo-plasticity [73,74]. Failure of network polymers and coatings is often attributed to residual stress induced during processing and the continued build up in stress over time. The ability to intervene through some manual or automatic technique that reduces this stress has enormous potential to producing coatings
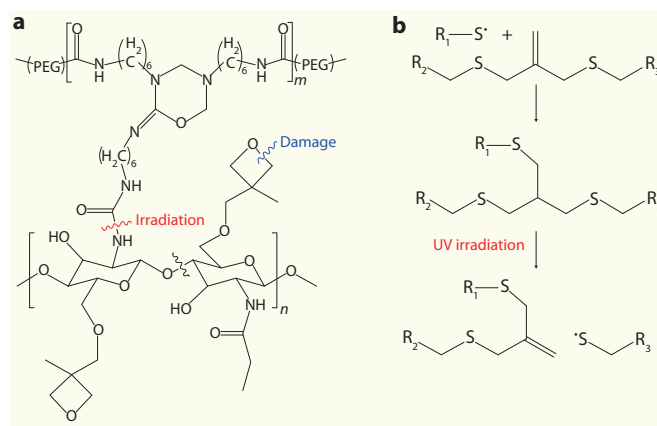

Figure 9. (a) Idealized structure of photo-active polyurethane–chitosan crosslinked coating illustrating the dual functionality available depending on the applied stressor. (b) Schematic representation of photo-induced plasticity illustrating the continuous bond-making and -breaking mechanism that exists in equilibrium during UV irradiation. Bond-breaking occurs at different sites and is not necessarily a reversible reaction.

with enhanced service life. Photo-plasticity has been incorporated into a network coating by Scott *et al.* [74] through a living free radical addition fragmentation process that involves a continuous series of events for making and breaking different covalent bonds. When given sufficient mobility, this process allows the network to re-arrange into a lower energy and lower-stress configuration. As outlined in Figure 9, a radical attacks an unsaturated species, which cleaves a bond to create a new radical and new unsaturated species. The R groups can thus be part of a network polymer undergoing continuous rearrangement to a lower energy structure, rather than the typical, highly brittle one. Another example of how UV radiation can heal coatings is by continuous destruction of a surface through directed phase separation of block co-polymers [75] utilizing fluorinated species in the backbone of a polyurethane coating. In this case, the mobility of the fluorinated tails within the bulk coating enables continuous migration to the surface to minimize the air–film interface and thus restoring its protective role as a coating.

Mendability in polymers and coatings can also be achieved with temperature. The application of the reversible Diels–Alder reaction to self-healing polymers was first demonstrated by Chen *et al.* [54] by creating a crosslinked network from furan and maleimide monomers. The crosslinks, being thermo-reversible, were able to heal a crack when the sample was reheated sufficiently to allow the Diels–Alder reaction to occur. Assuming sufficient molecular mobility and contact between the fracture surface, the crack can be healed in this way. This principle has been demonstrated in polypropylene-based powder coatings [27], where visible damage was repaired over the course of several damage events. The use of different Diels–Alder linkages also provides excellent control over the processing and mechanical properties.

Future systems and approaches

Nanosensors for self-repair or diagnosis

In addition to the autonomous self-repair of a coating, in many instances there is a need for intentional intervention in conducting regular maintenance. The ability to obtain signals from a coating that indicate the presence of corrosive species, the condition of the coating, or the presence of corrosion products is therefore desirable. This could be achieved, for example, by addition of a fluorophore that fluoresces in the presence of metal ions [76] or dye indicators [58,64]. Other approaches involved the introduction of quantum dot materials into a coating to act as environmental indicators based on changes in fluorescence [77]. Some of the greatest challenges in this area relate to measuring the emitted signal.

Conductive polymers, whilst they may not find application as polymeric matrixes, could potentially offer mechanisms to simultaneously release an inhibitor and provide a signalling capability [78].

Arterial networks

A common view of the limits of micro-encapsulation is that it only provides one-off healing at a specific location. A strategy to overcome this is to create a micro-vascular network that provides a continuous supply of healing agent to a damage site through microchannels, thereby allowing multiple healing events to occur. Filled glass fibers have been used in composite materials as an external delivery route to a defect [79]. Soft lithography and direct write assembly methods has been used in composite materials to facilitate the continuous supply of healing agent, and these methods have also been applied to coatings. Toohey *et al.* [80] blended the healing agent catalyst into a coating that was then applied to the surface of a composite substrate containing the micro-vascular system. Upon brittle coating failure, the catalyst initiated polymerization of the healing agent obtained from the microchannels. In a separate experiment, manual insertion of the healing agent had the potential to create autonomous healing of the coating during multiple damage events. One drawback of these types of systems is that they can become blocked with the healing agent and thus become redundant [27].

Conclusions

The objective of this review has been to introduce the broad scope of tools available for the development of a new generation of coatings that incorporate green inhibitors and have the capacity for self-repair. Protection of bare metal is facilitated with a design of the surface oxide, whereby corrosive anions are repelled via the absorption of surface species that change the surface charge. Additionally, the metal–metal oxide interface can have a net positive charge, thus trapping cations for subsequent compound formation to slow ion transport. Self-healing paint systems, particularly primers, can incorporate inhibiting agents in a range of delivery vehicles that release the inhibitor in response to external or internal triggers, resulting in the 'on–demand' repair of corrosion damage. Additionally, there are a range of polymer processes that can be incorporated into the paint system to form functional groups on the polymer itself, providing the encapsulation of monomers or even drying oils. This field is still largely in its infancy and there remain many challenges both in the science related to formulation of the coatings as well as in establishing their durability.

References

1. D. H. Meadows, D. L. Meadows, J. Randers, W. W. Behens, *The Limits to Growth* (Potomac Associates Inc., USA, 1972).
2. L. B. Reynolds, R. Twite, M. Khobaib, M. S. Donley, G. P. Bierwagen, *Prog. Org. Coat.* **32**, 31 (1997).
3. *Mater. Perform.*, supplement, July 2002.
4. S. Pitt and R. Jones, *Eng. Fail. Anal.* **4**, 237 (1997).
5. D. Y. Wu, S. Meure, D. Solomon, *Prog. Polym. Sci.* **33**, 479 (2008).
6. R. G. Buchheit, A .E. Hughes, in American Society for Materials, Vol. 13A, S. D. Cramer, B. S. Covino eds (2003).
7. M. W. Kendig, R. G. Buchheit, *Corrosion* **59**, 379 (2003).
8. R. L. Twite, G. P. Bierwagen, Prog. Org. Coat. 33, 91 (1998).
9. T. H. Muster, A. E. Hughes, G. Thompson, in *Corrosion Research Trends*, I. S. Wang ed. (Nova Publishing, USA, 2007).
10. N. Sato, *Corrosion*, **45**, 354 (1989).
11. M. Sakashita, N. Sato, *Corros. Sci.* **17**, 473 (1977).
12. J. Zhao *et al.*, *Surf. Coat. Tech.* **140**, 51 (2001).
13. T. H. Muster, I. S. Cole, *Corros. Sci.* **46**, 2319 (2004).
14. T. H. Muster, W. D. Ganther, I. S. Cole, *Corros. Sci.* **49**, 2037 (2007).
15. K. Asami, M. Kikuchi, *Corros. Sci.* **45**, 2671 (2003).
16. F. Presuel-Moreno, M. A. Jakab, N. Tailleart, M. Goldman, J. R. Scully, *Mater. Today* **11**, 14 (2008).
17. A. E. Hughes *et al.*, *Surf. Interface. Anal.* **36**, 290 (2004).
18. Y. Hayashi, M. Masuda, J. Lee, M. Kojima, *Mater. Sci. Eng A* **198**, 71 (1995).
19. N. Sato, *Electrochim. Acta*, **41**, 1525 (1996).
20. I. S. Cole, T. H. Muster, D. Lau, N. Wright, N. S. Azmat, *J. Electrochem. Soc.* **157**, C213 (2010).
21. I. S. Cole, T. H. Muster, S. A. Furman, N. Wright, A. Bradbury, *J. Electrochem. Soc.* **155**, C244 (2008).
22. C. B. Tay, S. J. Chua, K. P. Loh, *J. Phys. Chem. C* **114**, 9981 (2010).
23. T. A.. Markley *et al.*, *Corros. Sci.* **52**, 3847 (2010).
24. S. Lee *et al.*, *Tribol. Lett.* **24**, 217 (2006).
25. J. Tedim *et al.*, *Appl. Mater. Ins.* **2**, 1528 (2010).
26. J. Sinko, *Prog. Org. Coat* **42**, 267 (2001).
27. H. Fischer, *Nat. Sci.* **2**, 873 (2010).
28. I. M. Zin, R. L. Howard, S. J. Badger, J. D. Scantlebury, S. B. Lyon, *Prog. Org. Coat.* **33**, 203(1998).
29. S. A. Furman *et al.*, *Corros. Sci.* **48**, 1827 (2006).
30. J. H. Osborne *et al.*, *Prog. Org. Coat.* **41**, 217 (2001).
31. S. A. Furman, F. H. Scholes, A. E. Hughes D. Lau, *Prog. Org. Coat.* **56**, 33 (2006).
32. R. M. Souto, Y. G.-García, J. Izquierdo, S. González, *Corros. Sci.* **52**, 748 (2010).
33. S. P. V. Mahajanam, R. G. Buchheit, *Corrosion* **64**, 230 (2008).
34. G. Williams, H. N. McMurray, *Electrochem. Solid. St.* **6**, B9 (2003).
35. S. Bohm, H. N. McMurray, S. M. Powell, D. A. Worsley, *Mater. Corros.* **52**, 896 (2001).
36. F. Miccichè, H. Fischer, R. Varley, S. van der Zwaag, *Surf. Coat. Tech.* **202**, 3346 (2008).
37. D. Battocchi, A. M. Simões, D. E. Tallman, G. P. Bierwagen, *Corros. Sci.* **48**, 2226 (2006).
38. S. R. Taylor, B. D. Chambers, *Corrosion* **64**, 255 (2008).
39. T. H. Muster *et al.*, *Electrochim. Acta* **54**, 3402 (2009).
40. F. Blin, P. Koutsoukos, P. Klepetsianis, M. Forsyth, *Electrochim. Acta* **52**, 6212 (2007).
41. M. L. Zheludkevich *et al.*, *Electrochim. Acta* **51**, 208 (2005).
42. N. N. Voevodin, V. N. Balbyshev, M. Khobaib, M. S. Donley, *Prog. Org. Coat.* **47**, 416 (2003).
43. S. J. García *et al.*, in *Green Inhibitors* (Maney Publishing, UK, in press).
44. A. N. Khramov, N. N. Voevodin, V. N. Balbyshev, M. S. Donley, *Thin Sold Films* **447**, 549 (2004).
45. M. L. Zheludkevich, I. M. Salvado, M. G. S. Ferreira, *J. Mater. Chem.* **15**, 5099 (2005).
46. D. R. Jenkins, A. D. Miller, *Proc. 18th World IMACS*, 323 (2009).
47. A. Nazarov, D. Thierry, T. Prosek, N. Le Bozee, *J. Electrochem. Soc.* **152**, B220 (2005).
48. T. Yin, M. Z. Rong, M. Q. Zhang, G. C. Yang, *Compos. Sci. Technol.* **67**, 201 (2007).
49. S. D. Mookhoek, H. R. Fischer, S. van der Zwaag, *Comp. Mater. Sci.* **47**, 506 (2007).
50. D. Raps *et al.*, *Corros. Sci.* **51**, 1012 (2009).
51. R. G. Buchheit, H. Guan, S. Mahajanam, F. Wong, *Prog. Org. Coat.* **47**, 174 (2003).
52. E. V. Skorb, D. V. Sviridov, H. Möhwold, D. G. Shchukin, *Chem. Commun.*, 6041 (2009).
53. B. Ghosh, M. W. Urban, *Science* **323**, 1458 (2009).
54. X. Chen *et al.*, *Science* **295**, 1698 (2002).
55. Y. J. Du *et al.*, *Prog. Org. Coat.* **41**, 226 (2001).
56. R. L. Ballard, J. P. Williams, J. M. Njus, B. R. Kiland, M. D. Soucek, *Eur. Polym. J.* **37**, 381 (2001).
57. C. Sanchez *et al.*, *Chem. Mater.* **13**, 3061 (2001).
58. A. J. Vreugdenhil, M. E. Woods, *Prog. Org. Coat.* **53**, 119 (2005).
59. D. G. Shchukin *et al.*, *Adv. Mater.* **18**, 1672 (2006).
60. G. Williams, H. N. McMurray, *Electrochem. Solid. St.* **7**, B13 (2004).
61. M. Samadzadeh, S. H. Boura, M. Peikari, S. M. Kasiriha, A. Ashrafi, *Prog. Org. Coat.* **68**, 159 (2010).
62. F. J. Rossier-Miranda, C. G. P. H. Schroën, R. M. Boom, *Colloid. Surface. A* **343**, 43 (2009).
63. S. R. White *et al.*, *Nature* **409**, 794 (2001).
64. A. Kumar, L. D. Stephenson, J. N. Murray, *Prog. Org. Coat.* **55**, 244 (2006).
65. C. Suryanarayana, K. C. Rao, D. Kumar, *Prog. Org. Coat.* **63**, 72 (2008).
66. D. V. Andreeva, D. Fix, H. Möhwald, D. G. Shchukin, *Adv. Mater.* **20**, 2789 (2008).
67. C. Dry, *Comp. Struct.* **35**, 263 (1996).
68. Y. C. Yuan *et al.*, *Macromolecules* **41**, 5197 (2008).
69. S. D. Mookhoek *et al.*, *Adv. Eng. Mater.* **12**, 228 (2010).
70. S. H. Cho, S. R. White, P. V. Braun, *Adv. Mater.* **21**, 645 (2009).
71. H. A. Liu, B. E. Gnade, K. J. Balkus Jr, *Adv. Funct. Mater.* **18**, 3620 (2008).
72. A. B. South, L. A. Lyon, *Angew. Chem. Int. Edit.* **49**, 767 (2010).
73. W. D. Cook *et al.*, *Polym. Int.* **57**, 469 (2008).
74. T. F. Scott, A. D. Schneider, W. D. Cook, C. N. Bowman, *Science* **308**, 1615 (2005).

75. T. Dikic, W. Ming, R. A. T. M. van Benthem, G. de With, International Patent Application WO/ 2007/046687 (2007).
76. A. Augustyniak, J. Tsavalas, W. Ming, *Appl. Mater. Int.*, **1**, 2618 (2009).
77. K. J. Davis, N. L. Dehuff and M. Safai, International Patent ApplicationWO/2010/077930 (2010).
78. M. Kendig, M. Hon, L. Warren, *Prog. Org. Coat.* **47**, 183 (2003).
79. J. W. C. Pang, I. P. Bond, *Compos. Part S-Appl. S.* **36**, 183 (2005).
80. K. S. Toohey, N. R. Sottos, S. R. White, *Exp. Mech.* **49**, 707 (2009).

Author profiles

Anthony Hughes

Tony Hughes is a leading coatings and corrosion scientist specializing in aerospace coatings and the corrosion of high-strength aluminum alloys. His recent work focuses on developing environmentally friendly inhibitors and delivery systems as well as self-healing coatings. He has a background in surface analysis, catalysis, solid oxide electrolytes and metal finishing. He was awarded the Royal Society of Chemistry (UK) 2004 Corrosion Prize and the BAE Systems Silver Award (2002) for a corrosion prediction management project. He has managed a number of large international projects in the aerospace industry and now in catalysis. He is a science leader in the catalysis area at CSIRO's Division of Materials Science and Engineering, and is a member of NACE and the ASM.

Ivan Cole

Ivan Cole is a leading corrosion scientist specializing in modeling atmospheric corrosion and passivation systems for metals. His recent work has focused on the development of oxides on aluminum and zinc, combining fine-scale models of electrochemical processes with experimental studies to develop strategies to promote self-repair in oxides. He has led major international projects in the aerospace and Infrastructure sectors to predict the lifetime of structures and develop non-chromate passivation systems. He is a chief research scientists at CSIRO's Division of Materials Science and Engineering and a visiting professor at Manchester University, UK.

Tim Muster

Tim Muster leads the Functional Interfaces Team in the CSIRO Division of Materials Science and Engineering. He obtained his PhD in colloid and surface chemistry at the University of South Australia, and has undertaken postdoctoral research at Bristol University and CSIRO. Since joining CSIRO, his efforts have focused on understanding the links between metallic microstructure and electrochemical processes, including the development of new metals and coatings, and structural health sensing technologies for maintaining existing materials and structures.

Russell Varley

Russell Varley has worked in polymers and coatings for over 15 years, investigating the structure–property relationships of the matrix and the fiber–matrix interface. More recently, he has been applying molecular modeling to gain insights into the origin of polymer properties. He is also investigating novel self-healing materials to develop more durable materials. He received his PhD from Monash University, Australia, in 1998 for research on toughening high-performance epoxy resin systems.