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Fundamentals of Smart Corrosion Protection Coatings

1.1 Introduction of Corrosion Protection Coatings

Metal materials are ubiquitous due to their good mechanical and processing properties, which have been widely applied in industrial production and daily life [1, 2]. However, they are vulnerable to corrosion under the influence of chloride ions, water, oxygen, atmospheric pollutants, etc., causing both economic loss and safety issues [3–5]. According to a survey by the Chinese Academy of Engineering in 2017, the annual cost of corrosion in China is more than 2100 billion yuan, accounting for 3.34% of the gross national product [6].

Many methods and materials have been developed to retard corrosion, with organic coating being one of the most widely used [7–9]. The principle of organic coating is to create a dense covering layer that can effectively isolate the metal substrate from corrosive media, preventing or slowing down the electrochemical reactions on the underlying metal substrate [10, 11]. Corrosion protection coatings account for approximately two-thirds of all anticorrosion measures. However, these coatings can become damaged or cracked by the harsh environment during transportation and service. Unless effectively repaired in time, such damage will seriously weaken the adhesion between the coating and the metal substrate, and the barrier properties of the coating will also decline to some degree.

Organic coating primers provide corrosion protection in multilayer systems because they have high adhesion strength with the metal substrate, good barrier properties, and can be loaded with large amounts of pigments and fillers. Chromate is often used as an anti-rust pigment in the organic primer layer due to its excellent corrosion inhibition properties. In recent years, more nontoxic and harmless new corrosion inhibitors have been developed to improve the corrosion resistance of coatings. The limited solubility of the corrosion inhibitor in the coating substrate causes the corrosion inhibitor to be exhausted in a certain period, thus reducing the corrosion protection effectiveness. The disadvantages of directly adding the inhibitor as a pigment can now be overcome by using microcapsules or nanocontainers that store both organic and inorganic inhibitors without any negative impact on the organic material matrix. The top paint should not only have good weather resistance and aging resistance but also must have the necessary decorative effects. It can provide a protective layer for the primer layer. Therefore, the top paint

Smart Protective Coatings for Corrosion Control, First Edition. Lingwei Ma and Dawei Zhang.

used outdoors must be selected with excellent weather resistance, such as alkyd, polyester, fluorocarbon, polysiloxane, polyacrylate, and polyurethane polymers.

1.1.1 Mechanisms of Corrosion Protection Coatings

The corrosion of metal materials involves three basic processes that occur in parallel: metal dissolution, the reduction of the cathode depolarizing agent, and the conduction of electronic and ionic currents in the cathode and anode [12]. As long as one of the processes is blocked, the metal corrosion rate decreases and the corrosion is suppressed. The protection mechanism of organic coatings is achieved by inhibiting one or more of the abovementioned steps. Some generally recognized anticorrosion mechanisms of coatings are listed below [13]:

(1) Shielding effect: The corrosion reaction of metals requires the presence of water, oxygen, and ions. When these corrosive media penetrate the coating to the coating–metal interface and accumulate at a certain concentration, metal corrosion occurs. The significance of the existence of organic coatings is to effectively prevent or slow down the direct contact between water, oxygen, and the metal matrix, thereby preventing or slowing down the occurrence of corrosion, which requires the coating to have good water resistance, oxygen permeability resistance, and wet adhesion [14]. When there is less water and oxygen on the substrate surface, the anode and cathode reactions of corrosion are slow, and the corrosion current is reduced. At the same time, flake pigments, such as mica powder and peeling scales, can be added to the coating. These flake pigments can cut off the pinhole channels in the coating and shield the diffusion of water, oxygen, and ions to the metal substrate [15]. Coatings can effectively block the mutual diffusion of corrosive ions, effectively preventing the generation of corrosion products by their moist-resistant adhesion.

(2) Cathodic protection: When added to the coating, a large amount of metal powder can function as a sacrificial anode in the corrosion process, while the metal substrate acts as the cathode. The metal powder contained within the coating corrodes as a sacrificial anode in the corrosion process of the organic coating/metal system, thus delaying the initiation and development of matrix metal corrosion and effectively protecting the cathode metal [16, 17]. For example, Zn powder can be used for this purpose because Zn has a more negative electrode potential than common metals, such as iron, steel, and aluminum alloys. Moreover, the corrosion products of Zn (the basic zinc chloride and zinc carbonate) can fill pores in the coating, tighten the coating layer, and further reduce the corrosion rate.

(3) Coating adhesion: Coating adhesion is an important characteristic that affects the performance of the corrosion resistance [18]. When the adhesion becomes weaker at the coating–metal interface, more corrosive media can leak into the area, and the coating may even fall off. Therefore, stronger coating adhesion (especially after encountering water) can significantly enhance the corrosion resistance of metals.

1.1.2 Failure Type and Failure Mechanism of Corrosion Protection Coatings

Serious coating defects, such as peeling, cracks, loss of mechanical strength, and foaming, occur between the coating and metal interface, which not only affect the aesthetics but also compromise the protection [19]. Figure 1.1 shows the microstructure of corrosion products formed at defects in organic coatings in different systems. The four samples were corroded to different degrees owing to surface defects.

The failure of the organic coating itself does not involve electrochemical corrosion or produce electrical current; rather, it occurs through aging caused by physical and chemical changes. To fundamentally strengthen the protective performance of organic coatings, accurately predict the coating life, and reduce the occurrence of accidents, it is important to find out the failure mechanism of the coating. The microscopic failure mechanism of organic coatings can be divided into four categories:

(1) Aging: Physical aging refers to the deterioration of a coating's protective properties. Swelling, infiltration of corrosive media, and cracking may occur under the action of environmental media and external stress during the coating's service [20]. In chemical aging, macromolecules in the chain or network structure are gradually degraded into smaller units, cross-linked, or undergo other chemical reactions under the actions of light, heat, acid, alkali, and oxygen during the coating's service. Aging facilitates the penetration of external corrosive media and degrades the chemical and physical properties of the coating.

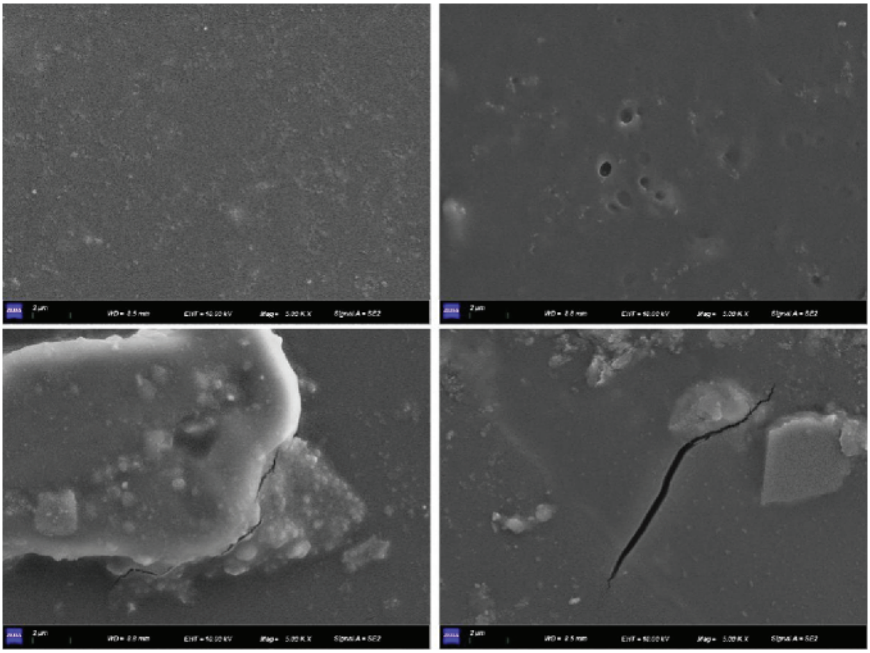

Figure 1.1 Microstructure of corrosion products on defects in organic coatings of different systems.

(2) Hydrolysis: When exposed to external corrosive media, organic coatings expand, causing bubbles or layer damage due to decomposition reactions. Hydrolysis is a typical decomposition reaction [21, 22]. The water resistance of organic coatings depends strongly on their molecular structures.
(3) Photo-oxygen degradation: The organic coating in outdoor service is subjected to the double action of sunlight and oxygen, and the organic coating will undergo photo-oxygen aging. Photons with enough energy from light will trigger a light reaction, causing polymer excitation or bond breakage, and the second energy of the light wave will be absorbed.
(4) Thermal failure: When the coating is exposed to high temperatures for a long time, decomposition, aging, and weight loss can easily occur [23]. These changes are mainly caused by the destruction of molecular chains and the cross-linking of film-forming materials. After the destruction of the molecular chains, the length and molecular weight of the polymers decrease, the film becomes soft and thin, and its resistance to permeability decreases. On the other hand, molecular cross-linking makes the polymer less elastic, which also tends to diminish the coating's protective effects, especially under the combined actions of environmental media and stress.

Common failure modes of coatings include peeling, foaming, burst holes, cracking, and pulverization. (i) Peeling: When adhesion between the coating and metal substrate falls below the tensile strength of the coating, the coating peels from the substrate or separates into layers [24]. This phenomenon is mainly due to poor pretreatment of the metal substrate, mixed pollutants between the primer layer, middle layer and top coating, and other reasons. (ii) Foaming: Foaming is the main form of coating failure and is more likely to occur for coatings in marine environments due to the presence of abundant corrosive ions [25]. It usually starts with water reacting with hydrophilic groups and soluble salts in the coating, forming channels for ions to diffuse to the metal surface. Corrosion reactions on the metal surface enhance the alkali content in the cathode region and reduce the adhesion strength of the coating. With the gradual accumulation of corrosion products, the coating expands in volume, and bubbles are formed. (iii) Burst holes: Foaming is the formation of bubbles on the coating surface. If the bubble breaks without the coating supplement and flattens, this phenomenon is called burst hole, and pinholes are small burst holes. When the temperature rises, the solution volatilized by the underlying coating cannot penetrate into the air through the high-viscosity surface layer, resulting in bubbles within the coating [26]. As the temperature continues to increase, the bubbles expand and exert pressure on the coating. When the expansion pressure exceeds the binding force of the surface coating film, the coating film breaks and forms a burst hole. (iv) Cracking: Cracks include both visible cracks and fine cracks that are generally invisible to the naked eye. They are mainly caused by a mismatch between the coating resin and additive fillers. Stress causes existing cracks to deepen. (v) Pulverization: Pulverization occurs when cross-linked macromolecules, such as resins, are severely degraded, leaving only a layer of filler on the surface [27].

This phenomenon is caused by ultraviolet (UV) radiation from the sun, while moisture and air pollutants also participate in the formation of powder. The presence of pigments in the coating also affects pulverization. Flaky aluminum powder and micro filler can reflect sunlight and thus retard pulverization.

1.2 Smart Self-healing Coatings

At present, artificial repair or replacement is the main treatment method for damaged coating, which is complicated and costly. Due to the limitations of site construction conditions, the surface state of repaired coatings is difficult to meet the requirements of related performance parameters. Therefore, the development of anticorrosion coatings with self-healing functions to realize active repair after coating damage is of great significance to extend the service life of coatings and reduce maintenance costs. Smart self-healing coatings have emerged, which can effectively repair the damage with no or little external intervention [28, 29]. Due to the great economic value and good development prospects in improving corrosion protection performance, many domestic and international scholars have focused on self-healing anticorrosive coatings in recent years [10, 30, 31]. These coatings can be classified into intrinsic and extrinsic types. Intrinsic self-healing coatings can be repaired by restoring internal chemical bonds and/or physical conformations in the polymer network [32]. Extrinsic self-healing coating generally loads healing agents or corrosion inhibitors into the coating and can recover the corrosion protection performance based on the adsorption of these species [33]. Compared to intrinsic self-healing coatings, extrinsic ones are more widely used in production and daily life because of their simple preparation and more options for loading species. Microencapsulation technology is often used to enhance their stability to avoid the premature release of film-forming substances and corrosion inhibitors and the occurrence of side reactions.

1.2.1 Intrinsic Self-healing Coating

Instead of film-forming substances or corrosion inhibitors used in extrinsic self-healing, intrinsic self-healing occurs by restoring internal chemical bonds and/or physical conformations in the polymer network, with little relationship with the metal substrate. Thermal energy and light radiation may provide sufficient activation energy for the formation or breakage of chemical bonds. Thermal stimulation can effectively improve the fluidity of polymers, allowing the atoms to closely approach each other and restore broken bonds. Thermal energy may be supplied artificially (e.g. using a heat gun) or from the environment (such as heating by sunlight). Ultraviolet, near-infrared, and sunlight have all been used as light stimuli. By adding corrosion-sensitive components, the stimulated response in the coating can be effectively promoted to repair the coating defect. Thus, the coating can be positioned and healed in a more timely and efficient manner.

1.2.1.1 Self-healing Based on Dynamic Bonds

The first type of intrinsic self-healing mechanism relies on dynamic bonding, such as hydrogen bonds, dynamic covalent bonds, and ionic interactions [34]. For instance, a thermoreversible bond breaks above a certain temperature, which allows the polymer chains to gather, cross-link at the defect, and heal the defect [35]. The main merit of this healing system is that no other healing agent and the healing process can theoretically be repeated endlessly.

A typical reaction used for dynamic bond repair is the Diels–Alder reaction (DA), which is achieved through a [4+2] cycloaddition between conjugated dienes and dienophiles (such as furans and maleimides) [36]. Wouters et al. [37] and Tian et al. [38] showed that by fabricating furfuryl glycidyl ether and *N*,*N*-diglycidyl furfuryl amine and doping reversible furan and maleimide bonds in epoxy coatings, self-healing can be achieved under heating. Wang et al. [39] synthesized UV-curable polyurethane based on a thermoreversible DA structure by copolymerizing an isocyanate monomer with a polycross-ester diol (Figure 1.2). The thermal characteristics of these materials were verified using differential scanning calorimetry and dynamic mechanical analysis. Surface scratching and subsequent healing tests have shown that the scratches on the polyurethane film surface can be repeatedly healed in as little as 100 seconds under heating conditions at 120 °C.

Light can also be used to trigger the formation of dynamic bonds [40, 41]. For instance, UV-sensitive self-healing polymers have been designed based on dynamic covalent bonds (such as S—S bonds) and cross-linking reactions (such as the cycloaddition of cinnamyl or anthracene derivatives). Compared with heat-induced self-healing, light-induced self-healing can be triggered instantly, remotely, and on demand [42]. It is also easier to limit stimulation to a specific area, preventing possible side reactions and degradation during the healing process and preserving the integrity of the coating. For coatings used in outdoor practical environments, sunlight-triggered self-healing is a convenient way. However, in addition to the need for photosensitive bonds, the coating must be sufficiently stable to withstand long-term sunlight exposure and maintain its overall chemical composition and performance. Moreover, light stimulation can be combined with other self-healing mechanisms, such as the controlled release of corrosion inhibitors in micro-/nanocontainers and damage repair by monomer polymerization [43, 44].

1.2.1.2 Self-healing Based on Shape Memory Effect

Shape memory materials, including shape memory alloys (SMAs) and shape memory polymers (SMPs), are novel self-healing materials that can recover from a temporarily fixed deformation state to the original state under external stimuli [42]. For SMAs, such as NiTi and Cu–Zn–Al, their shape memory effect is controlled by transitions among three phases: twinned martensite, detwinned martensite, and austenite [45]. SMA fibers can assist microencapsulated composites containing polymerizable restorers in achieving complete closure of cracks [46]. For SMPs, the viscoelastic transition occurs mainly through the polymer chains during the thermal transition temperature (T_{trans}) cycle, and therefore, the glass transition temperature (T_{g}) and melting temperature (T_{m}) are important factors (Figure 1.3).

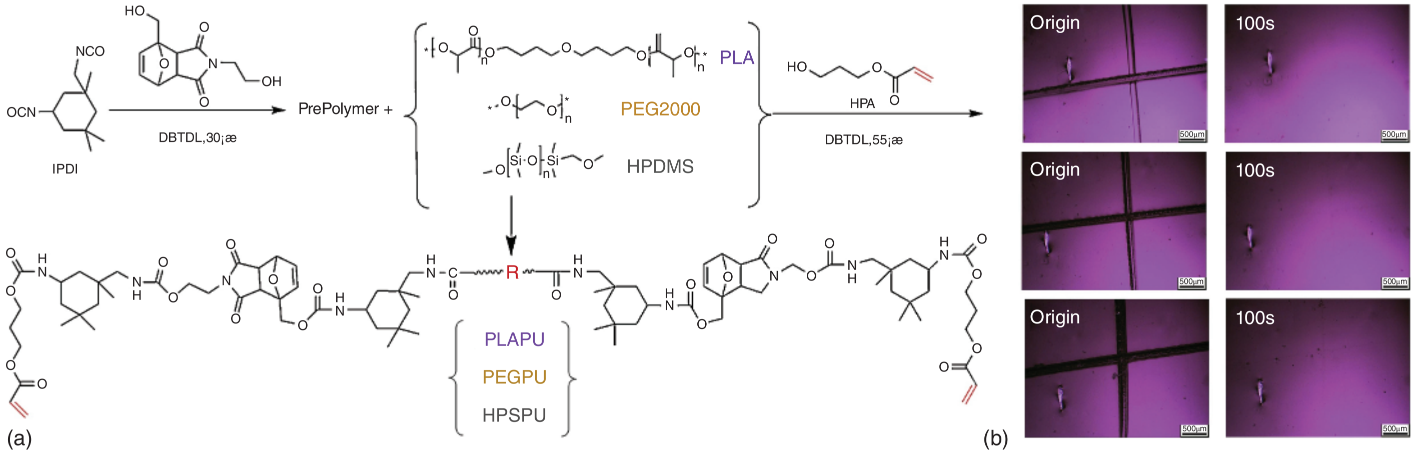

Figure 1.2 (a) Synthesis of UV-curable polyurethane coating with Diels–Alder structure, (b) optical microscope images of polylactide diol polyurethane coating with artificial scratches in three different areas and healed at 120 °C. Source: Wang et al. [39]/with permission of Elsevier.

For example, an SMP deformed at $T < T_g$ is "frozen" because the polymer chains are locked. Heating above T_g returns the polymer to its original shape, defined by chemical or physical cross-linking, and the polymer chains regain mobility and return to the random coiling state, where the entropy is most stabilized [48]. Recently, a novel self-healing coating based on SMP was developed to prevent corrosion. Compared with other types of self-healing coatings, SMP coatings have a strong strain-recovery ability and can effectively close larger physical damages. This is very meaningful in self-healing applications since this feature could significantly reduce the amount of corrosion inhibitors and film-forming agents required for the damaged parts of the coating.

Li and coworkers [49, 50] designed a clever strategy of sealing-and-then-healing to recover physical cracks in a polymer composite. The composite consisted of a shape memory matrix and a polyester thermoplastic filler. The shape memory effect narrows the scratches, and then the cracks are further filled and sealed by melting the polyester thermoplastic filler. Subsequent research on self-healing corrosion protection coatings employed the same principle. Luo and Mather [51] synthesized self-healing coatings by injecting SMP epoxy resin into a polycaprolactone (PCL) fiber scaffold (Figure 1.3). When the temperature reached 80 °C, the shape memory effect of the resin was triggered (above the T_g of epoxy) to close scratches in the coating, and the PCL fiber melted and flowed to seal the defect (above the T_m of PCL). Linear scanning voltammetry was used to confirm that the shielding properties of the coating recovered well after thermal healing. However, this process could not restore coating adhesion near the scratches. Wang et al. [47] developed a similar but more effective approach by applying carnauba wax microcapsules as restoratives in SMP coatings. After heating for 60 minutes, the effects of molten SMP and wax on the self-healing performance were determined. The best self-healing was observed at 15 wt% carnauba wax microcapsules. When this ratio was increased to 20 wt%, the molten wax oozed from the coating substrate after heating, which made the coating surface more hydrophobic and reduced the adhesion strength at the coating–steel interface.

1.2.2 Extrinsic Self-healing Coating

One of the most direct ways to realize extrinsic self-healing is to embrace the coating with a healing agent, mostly stored in micro- or nanocapsules [52, 53]. When subjected to mechanical impact, the coating breaks, causing the capsules to break and release the healing agent, which can polymerize to form a protective film to repair the coating and restore its barrier function and integrity. In addition, there is a class of extrinsic self-healing coatings that use the corrosion inhibition effect of inhibitors [54]. In this repair process, the corrosion inhibitor oozes from the micro- or nanocapsules to form a complex with metal ions through adsorption or chemical reaction that inhibits the corrosion behavior of the metal substrate. Such coatings often need to interact with the specific environmental factors in which they are located. Compared with intrinsic self-healing mechanisms, these extrinsic self-healing coatings have more extensive applications in aerospace, construction, medical, and electronic fields.

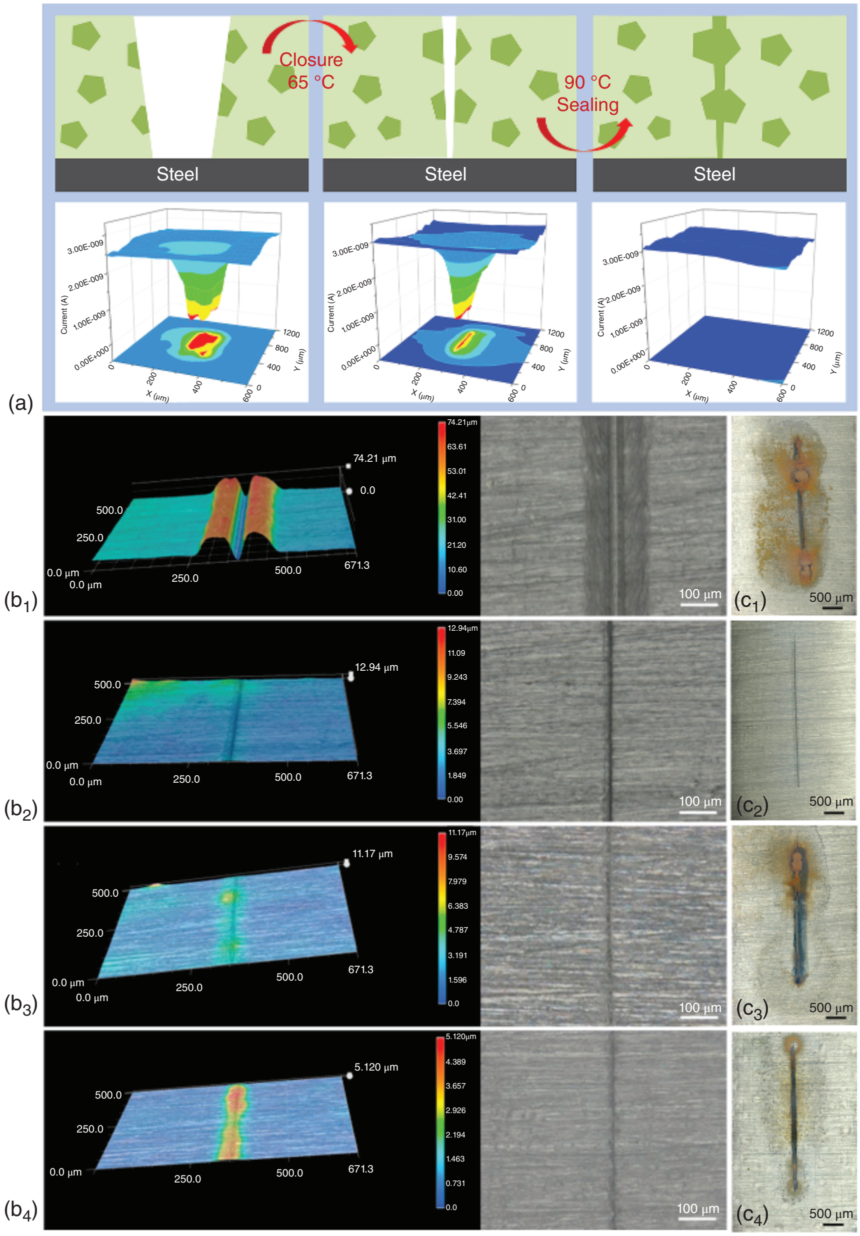

Figure 1.3 (a) Optical images during self-healing of damaged coating: (b_1) original defect, (b_2) after the first healing step at 65 °C, (b_3) after the second healing step at 90 °C, and (b_4) wax-free coating after two-step healing. Optical images of samples after seven days of immersion in 3.5 wt% NaCl solution: (c_1) scratched SMC coating, (c_2) healed SMC coating, (c_3) scratched wax-free coating, and (c_4) healed wax-free coating. Source: Wang et al. [47]/with permission of Elsevier.

1.2.2.1 Self-healing Coating Based on Defect Filling

Mechanical damages in coating require the construction of a new film to restore barrier performance. The film used to fill the defects must possess a certain strength and thickness [15, 55]. In self-healing coatings based on defect filling, polymerizable healing agents are spontaneously released and form a film under the catalytic effect of substances (either already contained in the coating or provided by the corrosive environment). The proper encapsulation of healing agents can extend their service life and reduce their interactions with the coating matrix.

Because of the fast curing rate, good fluidity, and high reactivity of dicyclopentadiene (DCPD), White et al. [56] designed urea–formaldehyde resin microcapsules coated with DCPD, which is a typical first-generation self-healing system. The authors prepared urea–formaldehyde resin microcapsules (>200 μm in size) and used them to store the DCPD monomer. These microcapsules were dispersed on the coating substrate and isolated from a Grubbs catalyst that could polymerize the monomers. When the coating was damaged, the monomer was released from the microcapsules and underwent catalytic polymerization to bond with the fracture interface, thus restoring the protective performance of the coating.

To rebond the crack interface, the healing agents must have an ideal chemical composition and provide sufficient bonding strength between the coating and metal interface. Epoxy resin is regarded as an excellent choice owing to its high adhesion strength and wide use [57]. Attaei et al. [58] developed a variety of microcapsules and selectively enclosed isophorone diisocyanate (IPDI) (Figure 1.4), hexamethylene diisocyanate, and the less toxic hexamethylene diisocyanate trimer as single-component healing agents in the coating. The microcapsules at the

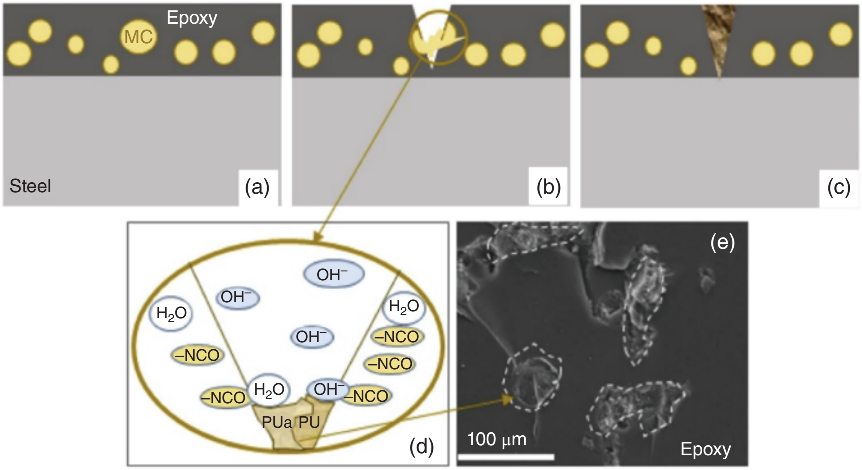

Figure 1.4 Diagram of self-healing process of microcapsule coating containing isophorone diisocyanate as a healing agent: (a) intact coating with added microcapsules, (b) damaged coating containing a scratch, (c) filling of the healing agent after polymerization, (d) self-healing reaction, (e) SEM micrographs of artificially damaged epoxy coating after immersion in 0.005 mol l^{-1} NaCl for seven days. Dashed lines indicate polymer formed by the reaction of IPDI released from microcapsules. Source: Attaei et al. [58]/with permission of Elsevier.

coating–damage interface expand and break due to water infiltration, prompting the healing agent to polymerize and fill the damage. However, because of the limited storage capacity of the microcapsules and reaction losses at the damaged area, the self-healing effect can only be effective for cracks with a width below 30 μm [59]. In actual applications, moisture from the environment inevitably penetrates the whole coating and reacts with the healing agent, and there may not be sufficient healing agent by the time the coating becomes damaged, which reduces the self-healing performance [60].

Among existing self-healing coatings based on defect filling by healing agents, the healing ability is directly affected by the mechanical and chemical properties, size, and quantity of microcapsules [61]. Ideally, the microcapsule wall should have sufficient stiffness; meanwhile, it must also be brittle to ensure that the microcapsules are broken when coating healing is needed [62]. Good compatibility and strong adhesion between the microcapsule wall and the coating substrate help to minimize water seepage through the capsule–coating interface. To provide durable self-healing capacity, the capsule material should also be stable against water, oxygen, and other corrosive media in different environments. Currently, the size of microcapsules used for storing polymerizable healing agents (often ranging from tens to hundreds of microns) is relatively large, which leads to difficulties in the practical application of corrosion protection coatings with thin thickness. Recently, oil-loaded smaller capsules (hundreds of nanometers in size) based on the sol–gel technology have been successfully applied to thinner coatings [63]. To ensure complete self-healing performance, a sufficient number of microcapsules have to be broken to fill the damaged area completely; otherwise, the damaged coating will have difficulty achieving the expected self-healing effect. To seal the coating defects effectively, the microcapsules were evenly mixed with the primer and coexisted close to the metal substrate. Although this design somewhat reduced the adhesion between the primer and metal, the researchers controlled the loading of capsules to reach a good compromise between the coating's adhesion strength, barrier properties, and self-healing performance [64].

1.2.2.2 Self-healing Coating Based on Corrosion Inhibitors

Another method to achieve extrinsic self-healing is to embed corrosion inhibitors in the coating [65]. Corrosion inhibitors can be classified into three categories according to their mechanisms: oxide film-forming, precipitation film-forming, and adsorption film-forming inhibitors [66]. Generally, there are many types of inorganic corrosion inhibitors used in self-healing coatings, including nitrite, molybdate, phosphate, and rare-earth salts [17]. Organic corrosion inhibitors contain adsorption centers (electron-rich regions) with an affinity to the metal surface [67]. The typical adsorption center is a relatively unstable unsaturated bond, such as $C{=}C$ (alkenes), $C{\equiv}C$ (alkyne), $C{=}O$ (carbonyl), $C{=}N$ (imine), and $C{=}S$ (carbonyl-sulfur) [68]. The selection of corrosion inhibitors depends on the metal substrate that needs protection. For aluminum alloys, benzotriazole, mercaptobenzothiazole, and 8-hydroxyquinoline have good effects [69]. For steels, the choice also depends on the solution conditions. For instance, precipitation film-forming inhibitors in neutral solutions include zinc salts, cerium salts, and phosphate salts that can be applied [70]. Most adsorption film-forming inhibitors are organic compounds and are typically used in industrial acid pickling processes, such as ionic liquids, Schiff base derivatives, amine-based organic molecules, and imidazoles [71]. In the protection mechanism of film-forming inhibitors, the corrosion inhibitor released from the coating can quickly inhibit the anodic dissolution and cathodic reduction reactions at the defects [72]. In the anodic dissolution inhibition mechanism, inhibitors are adsorbed onto the metal surface and form a dense passivation film, whereas the cathodic reaction may be inhibited by the deposition of oxides and hydroxides by the corrosion inhibitors [73]. In addition, mixed-type corrosion inhibitors function via a combination of chemical reactions, physical adsorption, and/or complexation [74]. The majority of studies on self-healing coatings are based on various corrosion inhibition mechanisms because the design concept is simple and the inhibition action is direct.

Corrosion inhibitors can be mixed directly with the coating matrix to induce self-healing. For instance, cerium nitrate and phosphate have been directly incorporated into organic coatings to achieve the self-healing effect of coatings on zinc, steel, and aluminum alloy surfaces [75–77]. Lithium salts have also been added to organic coatings as corrosion inhibitors to protect aluminum alloys. The lithium salt created an alkaline environment in the striated area of the coating and induced the formation of three layers of alumina/alumina hydroxide films (including dense, porous, and columnar layers). Compatibility has always been the most important consideration for corrosion inhibitors and coatings, and it has an important impact on the self-healing process. The corrosion inhibitors must be properly leached from the coating into the damaged area. Undesirable side reactions between the corrosion inhibitors and coating should be avoided to ensure good corrosion inhibition efficiency of inhibitors, and agglomeration of the inhibitor should also be prevented because it creates more channels for water penetration, which is fatal for the barrier properties of coatings.

In view of these factors, there is increasing attention on the use of microcontainers or nanocontainers to load corrosion inhibitors and ensure their release in a sustained or controlled manner. Using organic microcapsules, corrosion inhibitors can be released either with or without breaking the capsules [78]. For nanocontainers, the commonly used ones include nanoparticles, nanotubes, and porous nanofibers [79]. These have great advantages in thin organic coatings or sol–gel layers and can be evenly distributed in the coating matrix because such particles are sufficiently small and disperse easily. However, organic nanoparticles are often unsuitable for applications because of their poor stability, low mechanical properties, and vulnerability to solvents or heat during service. Inorganic nanoparticles with more stable chemical properties are often used instead. In self-healing coating applications, the micro- or nanocontainers usually release their content in response to specific conditions according to their own characteristics, surface grafting, modification, or intelligent functional group modification, as illustrated in Figure 1.5 [80].

Self-healing will be unsatisfactory if corrosion inhibitors cannot completely cover the exposed metal substrate in the damaged area. Therefore, the inhibitor is mainly

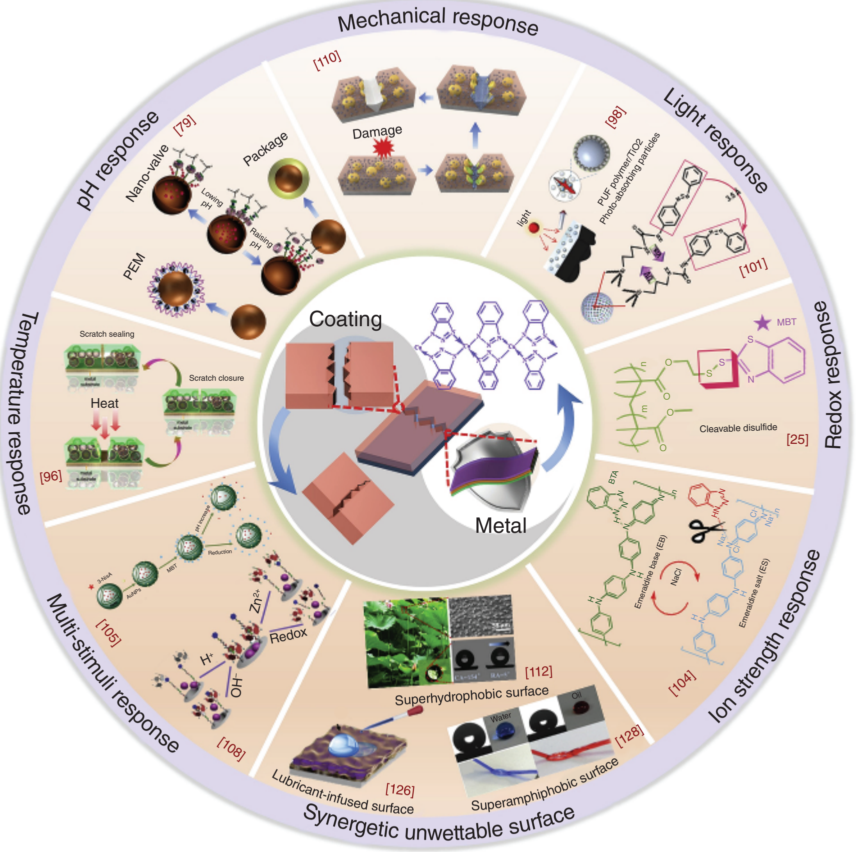

Figure 1.5 Release of corrosion inhibitors from containers in response to different stimuli. Source: Fu et al. [80]/with permission of Elsevier.

doped into the primer or pretreatment layer to be as close as possible to the metal substrate [81]. It should be noted that excessive use of corrosion inhibitors (or their containers) should be avoided to maintain overall good barrier properties and adhesion to the metal substrate. Containers with a high loading capacity for corrosion inhibitors and corrosion inhibitors with high performance are the best choices [82]. Once these conditions are satisfied, the next priority is evenly dispersing the corrosion inhibitor or container throughout the coating.

To achieve long-term restoration capacity, the corrosion inhibitors should be carefully screened with consideration of the types of corrosive media at the damage site and the electrochemical reactions during corrosion. Second, the compatibility between the container and coating should be optimized by design. Third, the environmental stability of the container should also be considered. The self-healing properties of a coating can only be confirmed after prolonged simulation or corrosion tests in an actual service environment. Although studies have demonstrated the release of corrosion inhibitors from the container in response to external stimuli, a better understanding of their release from the coated substrate or container and transport to the damaged site will help achieve long-term self-healing.

Self-healing coatings based on extrinsic healing mechanisms have great potential in industrial applications, and the healing of coating defects can be achieved without external energy. The addition of microcapsules to the substrate can play a toughening role, delay the expansion of fatigue cracks, and increase the fatigue life of the coating. However, the variety of microcapsules or nanocontainers currently available for coating is still limited, and the preparation process of most of them is complex and cumbersome, which is difficult to use in large-scale industrial production. After the release of corrosion inhibitors or healing agents, the empty microcapsules or nanocontainers provide a new infiltration route for corrosive substances. The corrosion resistance and durability of the coating depend on the amount of healing agent/corrosion inhibitor carried. If the coating has only a few healing cycles, the corrosion resistance in harsh environments is far from meeting the required requirements. Therefore, the volume of microcapsules or nanocontainers should be enlarged to improve their loading capacity of corrosion inhibitors and healing agents. Moreover, these additives should be designed and arranged according to the most needed positions in the coating to reduce their random distribution. For intrinsic coatings, the dependence on healing agents or corrosion inhibitors is reduced, and in theory, the coating can be repaired countless times, with the potential for rapid and large-scale repair of coating damages. However, this coating is only suitable for specific resin systems, and it has some drawbacks, such as environmental pollution for some coating systems, poor mechanical properties, and weak fracture resistance. The healing condition usually requires high temperatures or other severe conditions. For the optimization measure, multiphase polymer systems can be developed by binding multiple chemical bonds to achieve a balance between high mechanical properties and high self-healing properties of coatings.

1.2.3 Characterization Methods of Self-healing Properties

The characterization methods of self-healing properties in coatings are broadly categorized into visualization and quantitative techniques. Visualization methods encompass optical microscopy (OM), scanning electron microscopy (SEM), atomic force microscopy (AFM), confocal laser scanning microscopy (CLSM), and other methods. OM, being straightforward to operate and cost-effective, is widely accessible in most laboratories. It is used to monitor variations in the size of coating damage, release of healing agents, and peeling phenomena in coatings. However, its magnification capability is limited to about 1500 times, with a restricted depth of field. SEM, on the other hand, offers magnifications up to 100 000 times, enabling detailed investigation of surface topography and morphology at the coating damage area and on the underlying metal substrate. SEM, coupled with energy dispersive spectrum (EDS) analysis, provides insights into the morphologies and composition of microcapsules, nanocontainers, and nanofibers, their distribution in coating systems, and the release of healing agents and corrosion inhibitors. It also facilitates the comparison of corroded morphologies between traditional and self-healing coatings to analyze the self-healing mechanism. SEM is instrumental in studying nanoparticle migration and intrinsic healing of minor cracks. AFM, a nanotechnology tool, is used for detailed analysis of metal substrates and coating surfaces due to its excellent resolution, minimal sample preparation needs, and the ability to preserve the original sample state. It can in situ monitor scratch closure, changes in Young's modulus, and adhesion strength of coatings in response to external stimuli, such as pH, heat, and water. CLSM, offering higher resolution than OM, does not require probe contact with the coating surface, thus preventing sample damage and preserving sample integrity during imaging. It is useful for studying the self-healing performance of cracks on coating surfaces. Localized electrochemical measurements, including scanning vibrating electrode technique (SVET), scanning kelvin probe (SKP), localized electrochemical impedance spectroscopy (LEIS), and scanning electrochemical microscopy (SECM), can also be applied for analyzing the self-healing behaviors of coatings. SVET is utilized to study potential gradients generated by reaction currents on sample surfaces in solution environments, pinpointing sites of anodic oxidation and cathodic reduction reactions at the micron scale on corroded sample surfaces. The technique involves a probe vibrating at a fixed frequency, driven by a piezoelectric unit, and an AC signal monitored through a phase-locked amplifier to enhance the signal-to-noise ratio. SVET is extensively used in corrosion systems, including corrosion inhibitors and self-healing coatings. SKP can acquire surface morphology and work function distribution of samples in atmospheric environments or with a single microdrop without direct contact. It aids in studying coating peeling kinetics, such as accelerated peeling rates in polypyrrole membranes due to small cation penetration. LEIS, which measures the ratio between applied AC voltage and the tested AC current, provides high-precision information, such as pitting or scratches. Although a powerful tool for studying under-coating reactions, the distance between the probe and sample is crucial for result resolution. SECM, combining high electrochemical sensitivity and spatial resolution, analyzes electrochemical reactions in different coating systems, sensitively detecting localized oxygen reduction, metal ion oxidation processes, and pH changes. These advanced characterization methods are pivotal in the ongoing development and refinement of self-healing coatings.

For quantitative analysis, common methods include electrochemical impedance spectroscopy (EIS), potentiodynamic polarization tests, oxygen or water permeability tests, and water contact angle (WCA) measurements. In EIS studies, variations in impedance modulus, phase angle, and fitting parameters are indicative of a coating's self-healing properties. The efficiency of self-healing can be gauged using the values of charge transfer resistances (R_{ct}) of both the damaged ("blank") coating and the healed one. This technique offers a deep insight into the electrical characteristics of coatings and their changes post-healing. Potentiodynamic polarization testing, as an electrochemical approach, involves scanning the potential of the working electrode while concurrently measuring the current density. This method is particularly suitable for examining the release of healing agents and evaluating the effectiveness of corrosion inhibitors in protecting the underlying material. Oxygen and water permeability tests are critical for assessing the barrier properties of polymer films. In the context of self-healing coatings, these tests can be used to gauge the extent of healing, especially for coatings relying on intrinsic healing mechanisms. Additionally, measuring the WCA on both damaged and healed coating surfaces is a straightforward approach to observe changes in surface structure and composition. This method provides a visual and quantitative assessment of the coating's hydrophobic or hydrophilic nature before and after healing. These methods collectively contribute significantly to the development and industrial application of self-healing coatings by elucidating the mechanisms of self-repair and providing both qualitative and quantitative means of assessment. However, it is important to note that, despite the availability of various evaluation techniques, there is still a lack of standardized and universally established methods for assessing self-healing performance in coatings. Therefore, the introduction of relevant standards is imperative, as it will facilitate the comparison of self-healing performances across different research works and aid in the advancement of this field. Establishing these standards will provide a consistent framework for evaluating and comparing the efficacy of various self-healing coatings, thereby promoting their development and application in various industries.

1.3 Smart Self-reporting Coatings

Organic coatings can effectively extend the service life of metal substrates. However, even nano- or micron-scale damage to the coating surface would destroy the integrity of the coating matrix. If not detected in time and firmly repaired, the spread of corrosion can lead to catastrophic consequences and pose serious economic and safety problems. Therefore, there is an urgent need to develop self-reporting coatings that can detect coating damage at an early stage of corrosion so that maintenance can be carried out before the materials show serious corrosion or aging performance [83].

Self-reporting coatings are primarily divided into pH-sensitive type, metal-ion-sensitive type, and aggregation-induced luminescence material (AIE)-fluorescent type [84]. Zhang and Frankel [85] developed a new self-reporting coating on an aluminum alloy. Two pH indicators, phenolphthalein and bromothymol blue, were directly added to the acrylic resin. After immersion in the NaCl solution for eight days, the resin with phenolphthalein indicator showed pink spots while that with bromothymol blue indicator turned overall dark orange in color. Between these two, phenolphthalein performed better for early self-reporting in the coating. Dhole et al. [86] introduced modified 5-acrylamide-1,10-phenanthroline into acrylic polymer segments. After reacting with ferrous ions, the polymer changed its color from light yellow to bright red, as a sign of corrosion in steel substrates.

Self-reporting functional materials can be prepared by directly dispersing or modifying responsive dye molecules or fluorescent molecules into the coating matrix. However, these small molecules or their functional groups are prone to react with active groups in the coating matrix, resulting in photobleaching or degradation under UV light. To better protect the dye or fluorescent molecules, microcapsules or nanocontainers have been used to prevent their direct contact

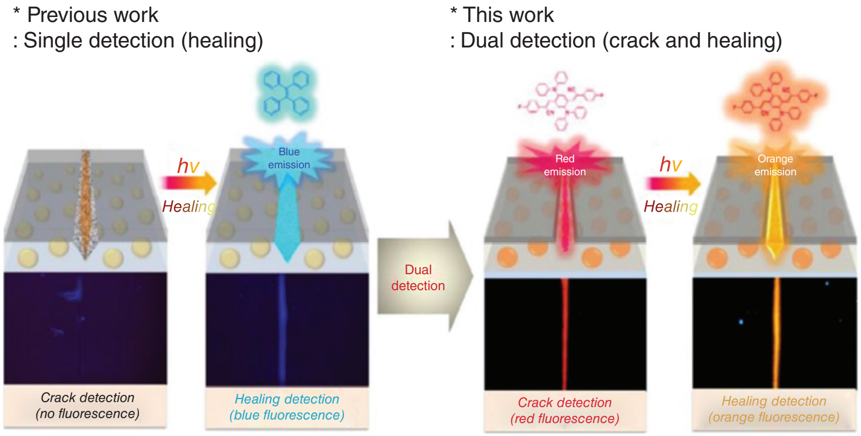

Figure 1.6 Schematic diagram of AIE-based self-reporting and self-healing mechanism. Source: Song et al. [88]/with permission of Elsevier.

with the coating matrix [21]. Song et al. [87, 88] conducted extensive research on self-reporting coatings based on the aggregation of fluorescence quenching (ACQ) and AIE (Figure 1.6). In their early research, AIE and ACQ fluorescent agents and liquid healing agents were encapsulated in urea–formaldehyde resin microcapsules. When microcapsules in the coating were destroyed, the liquid healing agents flowed out from the collapsed microcapsule, and the ACQ dye showed yellow fluorescence signals. Under UV irradiation, the fluorescence of the ACQ dye was inhibited by photoradical polymerization, and the blue fluorescence of the AIE dye was significantly enhanced. However, these microcapsules loaded with two dyes still have some limitations, such as adjusting the loading ratio owing to the different solubilities of the ACQ and AIE dyes. Further optimization is needed for the AIE- and ACQ-based self-reporting coatings.

1.4 Superhydrophobic Coatings

Inspired from “biological bionics,” many researchers have studied superhydrophobic coating surfaces, which have great potential in self-cleaning, antifog, antifreeze, low-viscosity, reducing resistance, and other applications. Superhydrophobic surfaces are also useful for minimizing corrosion in atmospheric and marine conditions, soils, and even industrial environments [89, 90]. Therefore, the development of superhydrophobic coatings with comprehensive properties, such as self-cleaning, corrosion resistance, and wear resistance, is an important research direction.

An increasing number of superhydrophobic surfaces with microscale roughness have been used to protect metals from corrosion [91]. However, there has been no thorough discussion on how these surfaces improve the physical barrier effect and inhibit corrosion initiation. It is generally believed that the micro- and nanostructures of superhydrophobic surfaces can trap a large amount of air and greatly increase the contact angle of water droplets on the superhydrophobic surface [92]. The water droplets have difficulty staying on the substrate, and it also reduces the contact time between the water droplet and the surface. When superhydrophobic surfaces are immersed in water, the trapped air forms a gas film, which somewhat enhances the physical barrier effect against water and other corrosive media. A biomimetic superhydrophobic surface has also been applied to prevent ice formation. The formation of an ice layer on a surface is very complicated and involves both the environment and the phase transition of water. By reducing the contact area between water droplets and substrate, the superhydrophobic surface lowers the heat transfer rate and delays the freezing of water droplets. During icing, the formation of heterogeneous ice nuclei is delayed, the generation of surface fog/frost becomes slower, and the transformation of water droplets from the Cassie to Wenzel state on the superhydrophobic surface is prevented. The probability of droplets sliding on the surface also increases, and the adhesion strength at the ice–solid interface decreases, both of which are beneficial for achieving the anti-icing effect.

Making the surface more hydrophobic often reduces the corrosion rate of metals, mainly because the hydrophobic coating limits the interaction of water or other corrosive particles with the substrate material [93]. Organic anticorrosive coatings can effectively prevent the diffusion of water molecules and extend the time required for water to reach the metal surface. As mentioned above, hydrophobicity depends mainly on the inherent chemical properties of the materials and the surface microstructure. The most obvious way to improve surface hydrophobicity is by using low-surface-energy materials. For instance, the surface energy of silicone resins can be as low as $22\,\mathrm{mN\,m^{-1}}$, whereas that of fluorinated resins is even lower ($10\,\mathrm{mN\,m^{-1}}$). Nevertheless, the WCA of coatings prepared using these materials does not exceed 120°. On the other hand, a designed rough surface could increase the WCA to above 150° to realize a superhydrophobic state [94].

As mentioned above, a microstructured superhydrophobic surface can trap a thin film of air, which significantly reduces the contact between water droplets and the surface [95]. Therefore, such surfaces are expected to reduce corrosion by preventing the generation of electrolyte films. These properties of the superhydrophobic surface will facilitate the future development of anticorrosion coatings in rainy environments. However, the water resistance of a superhydrophobic surface also depends on the droplet size [96]. Ultrafine droplets in the actual environment, such as water vapor, can directly condense onto the surface microstructures, precluding the formation of a protective gas film. To solve this problem effectively, it is recommended to use materials with finer dimensions or higher aspect ratios to prepare the superhydrophobic surface. The mechanical durability of the microstructure should also be considered in the manufacturing process.

A superhydrophobic surface prepared by Zhang and coworkers has prevented atmospheric corrosion caused by deliquesced salt [97, 98]. Such a surface makes it difficult for a deliquesced salt solution to diffuse. Instead, the salt solution remains a spherical droplet until the salt is completely dissolved. Salt particles on an inclined and highly lubricated substrate surface are extremely easy to fall off owing to the presence of the surface air film, thus reducing the corrosion of the substrate by

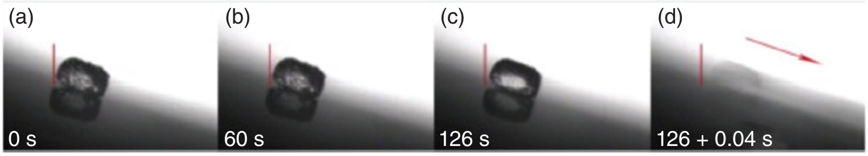

Figure 1.7 Time-lapse photographs of a NaCl particle dissolving under atmospheric environment at RH = 90% on an inclined superhydrophobic surface: (a) 0 s, (b) 60 s, (c) 126 s, and (d) 126 + 0.04 s. Source: Lu et al. [97]/with permission of Elsevier.

the dissolved salt (Figure 1.7). However, this effect depends on the microstructure of the superhydrophobic coating. For example, the brine in a deliquesced salt solution will roll off a surface with smaller microstructures (~5 μm); however, it penetrates another one with larger microstructures (~30 μm) [99]. In addition, fine salt particles deposited in the marine environment can easily enter the surface microstructure. Therefore, the microscale structure of superhydrophobic coatings should be fully considered when the application environment contains brine droplets or salt particles.

In superhydrophobic surfaces immersed in water, the air layer in the microstructure can form a barrier that somewhat protects the surface from the surrounding moisture, enhancing the overall corrosion resistance [100]. The superior corrosion inhibition performance of the superhydrophobic surface is also directly reflected by the corrosion current density from the polarization curve. After prolonged soaking, water inevitably penetrates the air layer. In other words, the Cassie contact may change to a Wenzel contact, and the corrosion resistance of the superhydrophobic surface decreases. In a previous study, Wang and coworkers eliminated the residual air captured on the surface of superhydrophobic copper by changing the solvent from ethanol to water [101]. Unlike the conventional superhydrophobic surface, the degassed surface formed a Wenzel contact with the surrounding water. In the absence of the air barrier, both the potentiodynamic polarization curve and EIS data confirmed a dramatic reduction in corrosion resistance.

The protective effect of a superhydrophobic surface in an immersed environment largely depends on the stability of the air film in water, which also rapidly decays at a higher hydraulic pressure, high flow rate, or high salinity of the surrounding fluid [102, 103]. To achieve hydrophobicity, a highly porous microstructure with a large surface area is required. However, the microstructure also renders the material more vulnerable to a corrosive environment. By comparing the hydrophobic and superhydrophobic surfaces of TiO_2/ZnO structures, Yu and Tian [104] found that the superhydrophobic TiO_2/ZnO layer has high porosity, good self-cleaning properties, and good corrosion resistance in an atmospheric environment. Nevertheless, a porous superhydrophobic surface is more susceptible to the intrusion of corrosive media during immersion, making this surface less resistant to corrosion than a hydrophobic one. Further studies are required to fully elucidate the relationship among the microstructure, surface roughness, and corrosion resistance of the generated superhydrophobic surfaces [105].

1.5 Conclusions

This chapter provides a brief introduction to corrosion protection coatings and smart design approaches for intelligent corrosion control. The degradation process of coatings and the corrosion process of metals are discussed in detail so that the reader can gain a basic understanding of the corrosion protection techniques. The concepts of self-healing coatings, self-reporting coatings, and superhydrophobic coatings are also explained. Compared to traditional corrosion protection coatings, smart coatings can ensure the lifetime safety of coatings, greatly reducing the repair costs for damaged coatings and sending warnings of coating damage at a very early stage. Therefore, smart coatings with self-healing, self-reporting, and superhydrophobic functions have broad application prospects in concrete, marine shipment, automotives, 3C products (computer, communication, and consumer electronics), and biomedicine. The following chapters will discuss in detail the different types of smart coatings to inspire further development in this area.

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