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Smart coatings for corrosion protection by adopting microcapsules

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1 Introduction

For decades, iron and steel have been two of the most important materials in our daily lives due to their good mechanical properties, availability and relatively reasonable cost. However, iron does not exist in nature as iron, but as a compound such as iron oxide. In order to get a usable material, these compounds must be refined and processed from their natural state. The conversion process (reduction, eq. 1) of iron from iron ore is undertaken by heating, therefore providing energy, with carbon under careful control, in order to prevent the reverse reaction.

$$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2 \tag{1}$$

According to the second law of thermodynamics [1, 2], there is a strong tendency for the system to move from order to disorder: its energy tends to be transformed from high energy states into lower levels energy states available, in order to reach the state of complete randomness and be unavailable for further work. Corrosion occurs due to this tendency of metals to recombine with components of the environment to reach its low energy state. In the case of iron, the metal tends to be oxidized into a reddish oxide, commonly known as rust, leading to a gradual destruction or deterioration of the metal [Figure 3–Figure 7]. All metals, with a few exceptions such as gold and silver, show this natural tendency to return to their lower energy state to form oxide and hydrate and therefore are prone to corrosion. Corrosion degradation is one of the main reasons for large industrial losses. One of the most suitable methods to protect metal for the external environment is the application of coatings on the metal's surface. Coatings are designed to protect the metal by physically isolating and preventing the diffusion of aggressive species towards the metal surface. However, coatings are prone to degrade, either because of the long exposure time – processes commonly known as weathering and ageing (e.g. moisture, UV radiation, thermo-oxidation, etc.) – or mechanical factors (e.g. damage due to impacts, scratches, defects, etc.). These chemical and mechanical degradation processes will eventually lead to the formation of microcracks and premature failure of the coating system. When the coating fails, the corrosion of the substrate is greatly accelerated. Repairs and maintenance of failed coatings are well-known to be both expensive and time consuming. Therefore, an *active protection* in addition to the time-limited passive protection is required. In order to prolong the service life of the metallic structures, scientists have developed a new class of intelligent polymeric coatings able to fully or partially regenerate their structural integrity resulting from external damage, without the help of any external factors. These new class of coatings are known as "smart coatings". This chapter aims to cover the latest state-of-the-art developments in the field of smart coating, focusing the attention exclusively on the use of microcapsules loaded with functional active species autonomically activated by different external stimuli, namely mechanical damage and microcrack propagation as a result of thermal cycling or UV exposure, pH change, etc.

2 Basic principles: electrochemical nature of corrosion

Corrosion can be defined as a deterioration of the metal by reaction with its environment [3–7]. It is possible to distinguish the corrosion processes in two major areas [3–7]: dry and wet corrosion. In dry corrosion, the

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corrosion reactions take place in high-temperature dry gaseous environments, and so are referred to as gaseous or oxidation corrosion. While in wet corrosion, the process involves the exposure of the metal to an electrolyte (normally a liquid). As most of the corrosion processes occur in aqueous environments and the electrolyte involved is, usually, an aqueous solution, wet corrosion is also commonly referred to as aqueous corrosion. Which is, in turn, classified on the base of the apparent morphology in six others types of corrosion [3–7]: general corrosion (uniform, quasi-uniform, nonuniform, galvanic); localized corrosion (pitting, crevice); metallurgical corrosion (intergranular, dealloying); mechanically assisted corrosion (erosion, fatigue, wear); microbiological corrosion and environmentally induced cracking (stress-corrosion cracking, embrittlement, etc.).

A metal surface is composed of a network of local galvanic cells short-circuited by the metal itself (Figure 1). As long as the metal is dry, corrosion processes are not observed. The corrosion process is triggered when an electrical circuit is established between these local cells (Figure 2), involving the generation and transport of electrons from the metal (negative or anodic sites) to active species present in the aqueous solution in contact with the metal (positive or cathodic sites). This established circuit leads to a continuous degradation of the metal [8–10]. As the process occurs through two distinguished reactions taking place at the surface of the metal, i.e. anodic and cathodic reactions, corrosion in aqueous media is often defined as an electrochemical process. The anodic process or oxidation-dissolution reaction (eq. 2 and eq. 3) involves the oxidation of the metal, and thus the generation of the electrons as a result of the changing from the metal, or some of the metals present in the alloy state, into metallic ions.

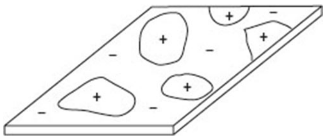

Figure 1: Surface network of local galvanic cells short-circuited by the body of the metal itself.

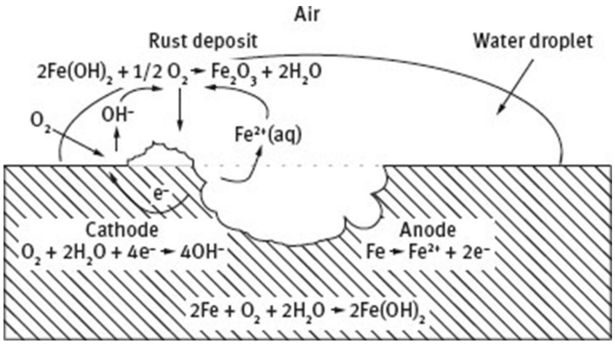

Figure 2: The electrochemical corrosion of iron under a drop of water.

$$\mathrm{Me} \rightarrow \mathrm{Me}^{n+} + ne^{-} \tag{2}$$

$$\mathrm{Me} + n\mathrm{OH}^{-} \rightarrow \mathrm{Me}\,(\mathrm{OH})\,n + n\mathrm{H}^{+} \tag{3}$$

where n is the valence of the ion and the number of electrons produced, Me^{n+} and $\mathrm{Me(OH)}_n$ are the metallic ion and hydroxide, respectively. Equations 2 and 3 refer to anodic reactions that involve soluble and insoluble corrosion products, respectively.

As the system does not produce any net charge [8–10], the electrons generated by the electrochemical anodic reaction must be consumed by another electrochemical reaction, called the cathodic process. Therefore, the anodic and cathodic processes are inseparable. Corrosion of the metal is a process that requires the presence of three important elements: anodic and cathodic reactions and a conductive liquid, the electrolyte, which is the medium surrounding the anode and the cathode, closing the circuit. In aerated or an in contact with air aqueous solution, where a significant amount of dissolved oxygen is available for reduction, the following cathodic reactions are very common [3–10]:

- Reduction of oxygen dissolved reactions in acid and in neutral or basic environments:

$$\mathrm{O}_2 + 4\mathrm{H}^{+}_{(\mathrm{aq})} + 4\mathrm{e}^{-} \rightarrow 2\mathrm{H}_2\mathrm{O}_{(1)} \tag{4}$$

$$\mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O}_{(1)} + 4\mathrm{e}^{-} \rightarrow 4\mathrm{OH}^{-}_{(\mathrm{aq})} \tag{5}$$

- In acid and neutral and/or basic deaerated environments, the main cathodic process involves the evolution of molecular hydrogen, as result of the proton and water reactions:

$$2H^{+}_{(aq)} + 2e^{-} \rightarrow H_2 \tag{6}$$

$$2H_2O_{(1)} + 2e^{-} \rightarrow 2OH^{-} + 2H_2 \tag{7}$$

If, for example, the oxidized metal is iron and the electrolyte is water, the presence of oxygen lead to the formation of a corrosion product layer of ferrous hydroxide that, in the presence of excess of oxygen reacts to form the final reddish corrosion product layer of hematite (Fe_2O_3) (eq. 8–10), commonly known as rust [, , , , , , , , , , , 10]:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \tag{8}$$

$$2Fe + O_{2(g)} + 2H_2O_{(1)} \rightarrow 2Fe^{2+} + 4OH^{-} \rightarrow 2Fe(OH)_2 \tag{9}$$

Thus, the overall reaction, which proceeds through a series of intermediate steps, is given by:

$$2Fe(OH)_2 + 1/2O_{2(g)} \rightarrow Fe_2O_3 + 2H_2O_{(1)} \tag{10}$$

2.1 Thermodynamics of corrosion

As stated above, metals try to lower their energy by spontaneously reacting with the external environment to form a compound or solution with a greater thermodynamic stability [1, 2]. The tendency of a metal to corrode into its own corrosion product is thermodynamically indicated by the free energy change of the reaction or Gibbs free energy, ΔG. When ΔG is negative (i.e. reaction products having a lower energy than the reactants) the reaction will proceed spontaneously. The more negative the free energy value is, the greater the tendency of the reaction to proceed. The free energy change associated with an electrochemical reaction may be related to the electrode potential and is given by the following equation:

$$\Delta G = -nF\,(\mathrm{emf}) = -nF\,(E_{cat} - E_{an}) \tag{11}$$

where n is the number of electrons or equivalents exchanged in the reaction, F is Faraday's constant (96,500 C/mole) and E_{cat}/E_{an} = electrode potentials (V), respectively form the cathodic and anodic reactions. Therefore, there are three possibilities for a process in which the initial state of the system is given by G_I and the possible final state is given by G_F:

i. $G_F - G_I = 0 \rightarrow \Delta G = 0$, the process is at equilibrium and no net change in components will occur.

ii. $G_F - G_I > 0 \rightarrow \Delta G > 0$, the process will not occur spontaneously as the final energy state is higher.

iii. $G_F - G_I < 0 \rightarrow \Delta G < 0$, the process may occur spontaneously depending on the activation energy of the process and at a rate dependent on the kinetics system of the process.

In addition, the electrode potentials, E, for a single reaction can be calculated from the Nernst equation, that for e generic reaction (eq. 12) is described by the following equation:

$$aRd + bH^{+} + ne^{-} \leftrightarrow cOx + dH_2O \tag{12}$$

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{\{Ox\}^{c}\{H_2O\}^{d}}{\{Rd\}^{a}\{H^{+}\}^{b}} E^{\circ} - \frac{0.05916}{n} \log \frac{[Ox]^{c}[H_2O]^{d}}{[Rd]^{a}[H^{+}]^{b}} \tag{13}$$

where: R is the universal gas constant (8.314 J/K mole), T is Kelvin temperature (298 K), E° is the standard electrode potential (V) and {i} is the activity of the species. At low concentrations, the activities are replaced with the concentrations. At 25 °C, *RT/F* can be treated like a constant and in changing the natural logarithm in the one of base 10, we have the coefficient 0.05916. The standard electrodes potential are calculated at standard condition for each metal (Table 1). The electrochemical series consists of the arrangement of metals in order of electrode potential, the more negative the single potential is, the more active the metal is, i.e. there is a greater tendency of the metal to corrode [3–7]. If we set up a galvanic cell, e.g. zinc and iron with a generic electrolyte, based on the potential listed in Table 1, zinc will act as the anode and is therefore prone to corrode, whereas iron will be the cathode.

Table 1 Standard electrode potentials in aqueous solution at 25 °C [11].

Electrode reactions	E° (V) at 25 °C vs. SHE
$Au^{3+}_{(aq)} + 3e^- \rightarrow Au$	+1.498
$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)}$	+1.230
$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu$	+0.337
$2H^+_{(aq)} + 2e^- \rightarrow H_2$	0.000
$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni$	−0.250
$Fe^{2+}_{(aq)} + 2e^- \rightarrow Fe$	−0.440
$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn$	−0.763
$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH-_{(aq)}$	−0.830
$Al^{3+}_{(aq)} + 3e^- \rightarrow Al$	−1.662
$Mg^{2+}_{(aq)} + 2e^- \rightarrow Mg$	−2.363

The application of thermodynamics to corrosion can be generalized by means of potential-pH plots or a Pourbaix diagram. Figure 3 and Figure 4 show the Pourbaix diagram for the solution systems Ni-H_2O and Cu-H_2O at 25 °C, respectively [12]. The Pourbaix diagram grants useful thermodynamic information on the feasibility of a generic corrosion reaction. The diagram provides a graphical representation of the relations between the pH of the aqueous system and the equilibrium potential of the electrochemical species involved. Such diagrams are temperature-dependent and are constructed using a Nernst equation (eq. 13) on the basis of the solubility for various metal compounds. The continuous lines delimit the stability domains of the metal species involved in the electrochemical process whereas the two dashed lines (a and b) indicate the proton and water reduction reactions. The area between the dashed lines delimits the stability domain of water. So, below line A water is unstable due to hydrogen evolution and above line b water is unstable due to the evolution of oxygen. Horizontal lines describe reactions that are dependent only on potential (e.g. eq. 8), vertical lines describe reactions that are dependent only on pH (eq. 9), whereas the angled lines correspond to reactions that depend on both potential and pH (eq. 9).

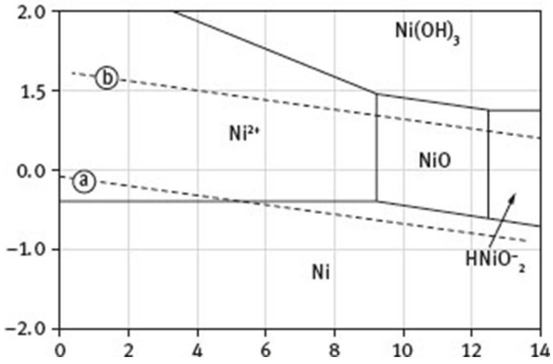

Figure 3: Pourbaix diagram for Ni-H_2O at 25 °C.

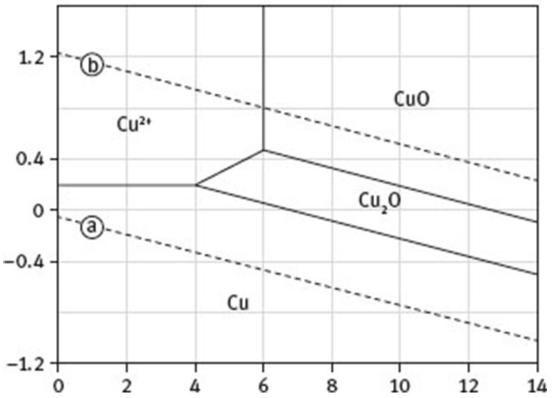

Figure 4: Pourbaix diagram for Cu-H_2O at 25 °C.

In the Pourbaix diagram it is possible to distinguish three regions:

i. Corrosion: where the metal will dissolve into its soluble species.
ii. Immunity: where the metal is thermodynamically stable and therefore, will not corrode.
iii. Passivity: where the metal is covered by a solid compound thermodynamically stable and it prevents its dissolution activity.

If, for example, the oxidized metal is nickel in equilibrium with its own specie (Ni^{2+}) at concentration of 10^{-4} M in acid solution, using the Pourbaix diagram it is possible to predict the species thermodynamically stable at different pH. The standard potential of nickel calculated in standard condition is $E° = -0.250$ V (Table 1), with the Nernst equation it is possible to calculate the potential of the following anodic and cathodic reaction in acid deaerated solution.

The anodic reaction corresponding to the dissolution reaction of the nickel is:

$$\mathrm{Ni} \rightarrow \mathrm{Ni}^{2+} + 2e^- \tag{14}$$

$$E_{\mathrm{Ni}^{2+}/\mathrm{Ni}} = E°_{\mathrm{Ni}^{2+}/\mathrm{Ni}} + \frac{0.059}{n}\log\left[\mathrm{Ni}^{2+}\right] = -0.250 + \frac{0.059}{2}\log 10^{-4} = -0.368\,\mathrm{V} \tag{15}$$

The cathodic reaction in acid solution is represented by eq. 16. From Table 1 $E°_{H^+/H_2} = 0$ V with partial pressure $P_{H_2} = 1$ atm, the Nernst equation will be:

$$E_{\mathrm{H}^+/\mathrm{H}_2} = E°_{\mathrm{H}^+/H_2} + \frac{0.059}{n}\log\frac{[\mathrm{H}^+]}{\mathrm{P}_{\mathrm{H}_2}} = 0 - 0.059\mathrm{pH} = -0.059\,\mathrm{pH} \tag{16}$$

From pH = 1 to pH = 6, the equilibrium potential of the species H^+/H vary from –0.059 to –0.368 V (eq. 16), and –0.368 V for the species Ni^{2+}/Ni (eq. 15), respectively. As the corrosion reaction involves the generation and consuming of the electrons, the electrons flow from the specie with equilibrium potential more negative (nickel; –0.368 V) to the one with equilibrium potential less negative (hydrogen). The mixed potential of the two reactions will be a value between the nickel and hydrogen equilibrium potential, and for pH ranging from 1 to approximately 6 it is located in the region of Ni^{2+} stability and below the dashed line A, in the region of H_2 stability (Figure 3). Therefore, in an acid solution ions of nickel are thermodynamically stable and nickel is prone to be corroded (oxidized) into Ni^{2+}, (eq. 1), while H^+ is reduced into hydrogen gas (eq. 6). However, when increasing the pH, e.g. from 6 to 8, the equilibrium potential of the species Ni^{2+}/ Ni will be less negative than the hydrogen one, therefore in this case, the electrons will flow from hydrogen (oxidized) to Ni^{2+} (reduced). Hence, under these conditions nickel behaves as a noble metal and it is no longer susceptible to corrosion. For a further increase of pH, e.g. higher than 8, the thermodynamic stable specie is the oxide of nickel. In this case the metal surface will be covered by a protective oxide layer and the metal is said to be in the passive state. This oxide can protect the metal by physically blocking the aggressive species and preventing or reducing further corrosion phenomenon. This is the reason why nickel and nickel-based alloys are widely used in modern industry: both are ductile and tough and easily processed using conventional methods and can withstand a variety of extreme corrosive environments [5, 13]. Another interesting metal worth mention and extensively used in the industry due to its conductive and mechanical properties is copper and its alloys. Figure 4 shows the Pourbaix diagram for the system Cu-H_2O. At first sight of the diagram, it is clearly noticeable that the equilibrium potential of the species Cu^{2+}/Cu (+0.337 V; Table 1) is above the line of the equilibrium potential of the species H^+/H_2 (dashed line A) for a wild range of pH. The H^+ ions are thermodynamically stable in contact with copper; therefore, metallic copper is thermodynamically stable in deaerated solution with respect to the other dissolved species. However, in the presence of oxygen the equilibrium potential of the species O_2/H_2O is higher than that of the Cu^{2+}/Cu (+1.230 and +0.337 V, respectively; Table 1), thus copper is prone to corrode in acid media. At neutral and alkaline pH values, the thermodynamically stable species is the copper oxide (Cu_2O). As in the case of nickel, the metal's surface will be passivated with a protective layer. Due to these excellent corrosion properties, copper is broadly used as metallic coating on metals such as iron and iron-based alloys, Figure 7(b).

3 Corrosion protection

Every year, corrosion processes cause $US billions of damage [6, 14]. The National Association of Corrosion Engineers [15], jointly with the Federal Highway Agencies (FHWA) [16], conducted a study on the cost of corrosion and found that the direct cost was estimated to be around 276 billion $US – approximately 3.1% of the national GDP. Therefore, understanding the mechanisms of the corrosion processes can facilitate analysis of material loss and help to develop a predictive model of material lifetime. Even with a well-designed system, together with a carefully choice of the materials used, there is no absolute way to eliminate this process. It is possible nevertheless to mitigate and control the effects of these corrosion processes. As the system does not produce any net charge [Figure 8–[10], in order to ensure the electroneutrality of the system the rate at which the electrons are generated must be equal to the rate at which the electron are consumed. It is therefore possible to control the rate of the corrosion process by controlling the rate of one these reactions. The control can be achieved by a number of different methods and sometimes, when the structure is placed in severe environments, with multiple methods applied together such as, cathodic protection, corrosion inhibitors, coating, etc.

3.1 Cathodic protection

Cathodic protection (CP) together with protective coatings is one of the most effective methods widely used in the oil and gas industry and provides an effective way of preventing corrosion on substrates that are immersed or buried in an electrolyte. Cathodic is broadly used to protect large infrastructure, pipelines and reinforced concrete structures, with its first application dating back to 1824 [6].

CP can be achieved by supplying an external current to the buried or submerged structure. According to Le Châtelier's Principle [17], if a change occurs in one of the factors under which a system is in equilibrium, the system will tend to adjust itself so as to annul, as far as possible, the effect of that change. Taking as an example the dissolution reaction of iron (eq. 8), by supplying additional electrons (external current) the equilibrium will move to the left in order to decrease the "concentration" of electrons, and so reducing the dissolution rate of the metal.

Figure 5(a), shows the sketch of a pipe cathodically protected, in which a direct current (dc) source is connected with its positive terminal to the auxiliary electrode buried some distance from the structure to be protected, and its negative terminal to the structure itself; in this way the pipe becomes the cathode and the auxiliary electrode the anode with the current flowing from the auxiliary electrode through the soil to the structure. As long as the current is applied the metal cannot corrode. The most common auxiliary electrode used is composed either of scrap iron or graphite. Scrap iron is relatively cheap but is consumed at the rate of 15 lb/A per year, and therefore needs to be restored periodically. Conversely, graphite is more efficient and is consumed at the rate 2 lb/A per year, but is more expensive and fragile compared to scrap iron and must be installed with greater care [5].

There are, however, cases in which is not economical to install power lines and is preferable to protect the structure by setting up a galvanic cell using a "sacrificial anode". Basically, the sacrificial anode, with a potential more negative (so, more active in the galvanic series [11]) than the metal being protected, is consumed in this galvanic process (Figure 5). It is important to point out that the sacrificial anode, coupled with the metal of the structure, must provide a sufficient driving voltage to generate sufficient current in order to adequately protect the structure. One of the most-used sacrificial anodes is magnesium, a metal that with a standard potential of $E°= -2.38$ V, coupled for example with iron pipe $E°= -0.41$ V, provides the crucial driving voltage required to protect the pipe. Besides magnesium, others metals are used as anodes and are capable of ensuring an adequate driving voltage, such as zinc ($E°= -0.76$ V) or aluminum ($E°= -1.66$ V).

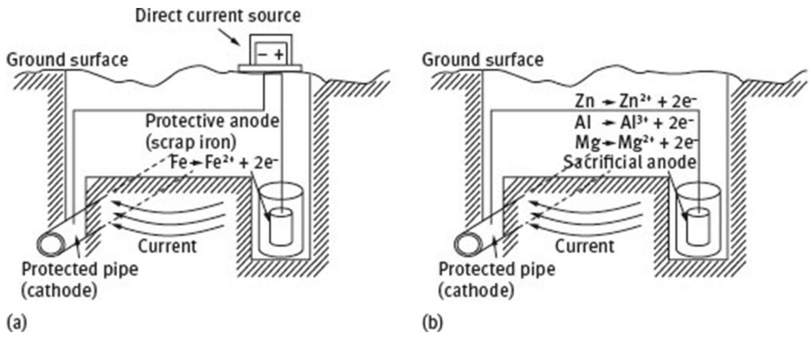

Figure 5: Sketch of the pipe cathodically protected: (a) with a direct current source; (b) with a sacrificial anode.

When the structure to protect is in an extremely corrosive environment, e.g. seawater, CP is sometimes not really economic. In fact, large infrastructures, i.e. offshore, long oil pipelines, would require a prohibitively high current. Therefore, in order to increase the level of protection of the system, CP is often used together with other protection methods. The most common method, and rather economical, is the use of organic coatings. The combined use of CP system and barrier coatings reduce the amount of current needed for CP, however, in the case of failure of the coating the CP system will protect the bare metal from corrosive attack.

3.2 Anodic protection

Anodic protection is a method of corrosion control relatively newer than CP, but nevertheless less frequently used. Anodic protection, similar to the CP, is an electrochemical means of corrosion control but is based on a different electrochemical principle. As its name suggests, this form of protection is achievable by the formation of a passive film on the surface of the anodic electrode (the metal to be protected) with the application of an electrical current (Figure 7), therefore, bringing the structure into the regime of thermodynamic immunity in the Pourbaix diagram. One of the reasons why this method is less frequently used than CP is that only certain metals in specific environments can be anodically protected, whereas all metals can be protected with the CP. Anodic and CP, are sometimes confused even though they are essentially two different techniques. In practice, the difference involves the electrode that is protected: the cathode is protected in CP, and the anode is protected in anodic protection.

3.3 Corrosion inhibitors

Another practical method to protect the metal dissolution from aggressive environments is the use of corrosion inhibitors. Corrosion inhibitors are chemical substances that are added to the corrosive environment in small amounts, reducing the corrosion rate to an sufficient level [18]. It is generally accepted that the inhibitor interacts with the metal surface, inhibiting the corrosion reactions that take place at the cathodic or anodic sites of the corrosion cell, e.g. either by blocking the reduction of the oxygen to form hydroxide ions at the metal's surface (eq. 5) or by keeping the metal from dissociating into ions (eq. 2). By its adsorption on the metal surface, the inhibitors form a protective film or barrier layer, which isolates the metal from the corrosive environment and therefore is able to inhibit the corrosion processes [18–20] (Figure 6). On the basis of which reaction is suppressed, the inhibitors are classified as cathodic, anodic or mixed-type.

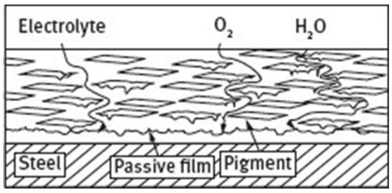

Figure 6: Corrosion protection provided by inhibitors pigments.

3.4 Corrosion protection by coatings

The most common and relatively economical method used to prevent the corrosion of metallic structures is via coating. This provides long-term protection under a broad range of corrosive conditions by isolating the structure from the aggressive external environment. Based on the types of coatings produced, coatings can be classified in three different ways [21–23]:

i. nonmetallic inorganic coatings such as conversion layers, anodized layers, glass and ceramic chemical vapor deposition (CVD) and physical vapor deposition layers;

ii. metallic coatings;

iii. organic coating such as paints and polymer sheets.

While the organic coatings essentially act as a barrier protecting the metal from the surrounding environment, metallic coatings provide their protective action by functioning either as a sacrificial anode or as cathodic protector, therefore changing the surface properties of the substrate. This chapter focuses only on the latter two types of coatings.

3.4.1 Metallic coatings

Metallic coatings basically utilize the same mechanism as the classic cathodic and anodic protections described above. A less noble metal, so more active in the galvanic series [11] than the substrate to protect, is used as coating and therefore acts as an anode under corroding conditions, whereas the substrate supports the cathodic reaction (Figure 7a). The most common coatings utilising this mechanism are zinc, aluminum, manganese, cadmium, and their alloys that, due to their more negative standard potential, are used to protect iron and steel substrates. The deposition is usually obtained either by wet chemical processes or by new alternative techniques such as thermal spraying, hot dipping, CVD, etc.

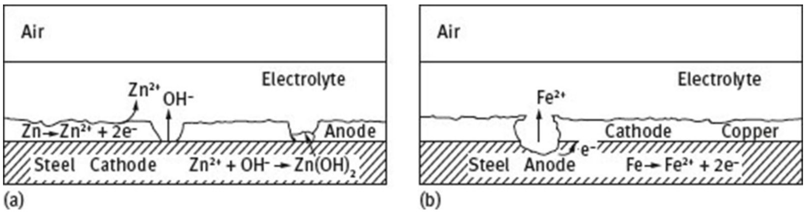

Figure 7: Schematic illustration of the cathodically protection coating (a) and anodic protection coating (b).

It is also possible to employ metal coatings more noble than the metal of the structure e.g. copper (Figure 7b). Several metals can be used as metallic coatings in addition to copper, such as nickel, tin, chromium, lead, etc., under the condition that the applied layer covers the entire surface of the substrate with a total absence of defects and pores. In fact, the presence of pores and defects in the coating may lead to the corrosion of the metal, as the result of the diffusion of water throughout the coating. The diffused water will establish the electric connection required to start the corrosion process between the substrate, the less noble metal (the anode electrode) and the coating, in which, as more noble metal, will act as the cathode. Conversely, with a less noble metal, in the presence of defects, the exposed portion of the substrate will trigger a galvanic process between the substrate (in this case, the cathode) and the surrounding coating (anode), with the formation of corrosion products. The corrosion products formed by this galvanic action may also lead to the formation of a second barrier that will fill up the defect itself [5] (Figure 7a). Other noble coatings, such as gold, silver, platinum etc., due to the their high cost are usually used in the field of jewelry and watches, etc., when the aesthetic aspect of the surface is the dominant factors, or are also used in electrical equipment due to their good conductive properties.

3.4.2 Organic coating

Three elements are necessary for the corrosion process to occur: cathode, anode and a conductive media that allows the electrons to flow from the anode to the cathode establishing an electric circuit [, , , , , , , , 10]. It is possible to interrupt this electric circuit by providing a protective barrier of coating between the metal and the external environment. Therefore, the main function of an organic coating is to insulate the metal from the external environment, by decreasing the diffusion of water, oxygen and aggressive ionic species towards the surface of the metal.

As the cathodic and anodic reaction are inseparable, preventing the oxygen from reaching the metal/coating interface deprives the cathodic reaction of the necessary fuel, thus reducing the corrosion rate of the metal.

However, for years it was believed that the corrosion prevention provided by the coatings was only owing to the effect of the barrier that hindered the permeation of water and oxygen.

It is important to point out that – although water and oxygen are necessary to the corrosion processes to take place – their permeation is not the rate-controlling step [24]. In fact, most of the coatings (with the exception of a few) are permeable in some degree to water and oxygen, and therefore it is not the barrier that prevents them from diffusing through the coating. For example, the corrosion of steel in pure water is very slow, due to the formation of ferrous hydroxide, $Fe(OH)_2$. Ferrous hydroxide has a low solubility in water, and therefore precipitates, forming a corrosion product layer on the surface that retards the diffusion of the oxygen and water necessary to continue the corrosion process [23, 24]. Conversely, the presence of water and oxygen, combined with aggressive species, e.g. chloride ions (Cl^-), leads to an autocatalytic process dissolution of the metal with formation of localized corrosion spots. Thus, it is important to prevent the permeation of water and oxygen, but also the diffusion of these aggressive species [25–27]. This method is accomplished by using resistive coatings.

The theory of ionic resistance or resistance inhibition, suggests that by creating a path of high electrical resistance between the anode and the cathode areas, the flow of current available for cathode and anode is reduced. In other words, the resistance to ionic current flow isolates anodic and cathodic areas and thereby corrosion is slowed down.

In summary, the coating efficiency and its service life, strongly depend upon the composition (high electrical resistance), structure and chemical bonds of the metal/polymer interface as well as the precautions taken during its application on the substrate [24, 28, 29]. Defects or pores may occur during the application of the film (Figure 8) as well as the result of abrasion or damages. Damage could be mechanical, e.g. the impact of solid objects or chemical by exposure to acids or solvents and high-temperature exposure or exposure to light [10]. The presence of defects lower the diffusion barrier effect provided by the coating, thereby promoting the penetration of the electrolyte through the coating itself. In particular, the reduction of oxygen generates hydroxyl ions that will promptly attack the chemical bonds between the film and the substrate [23, 30–34]. Therefore, above all, the coating must provide a good adhesion with the substrate. Poor adhesion could lead to the formation of blistering and coating failure (Figure 9).

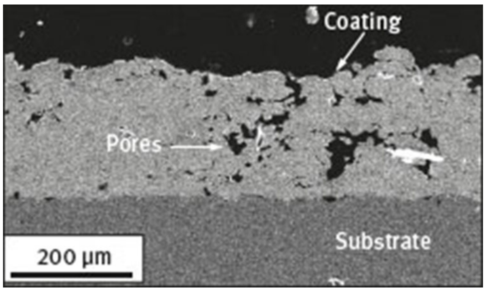

Figure 8: Pores or defects generated during the application of the coating (adapted from [35] and reprinted with permission from Elsevier).

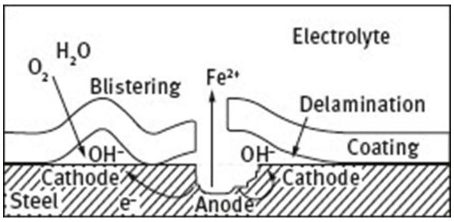

Figure 9: Schematic illustration of the blistering and delamination mechanism.

On the basis of their composition, coatings may be divided into solvent-borne, water-borne and solvent-free (solid). For the water and solvent based coatings, their deposition is usually done by spray-gun. However, in the last few decades, new technology are developed, e.g. electrostatic-sprays, utilizing solvent-free powder coating. In particular, powder coatings provide more environmental benefits than traditional coatings, meeting the stringent environmental regulations limiting the emissions of VOCs [36, 37]. Regardless of the physical form – either liquid or solid – the major constituents of coating are binders, pigments, fillers and additives [21, 24, 38, 39]. The binder, usually a polymer, is the matrix of the coating in which all the others components are integrated to form a dense, tight film, Figure 10. The binder can be a resin (epoxy, polyurethane etc.) or inorganic compound.

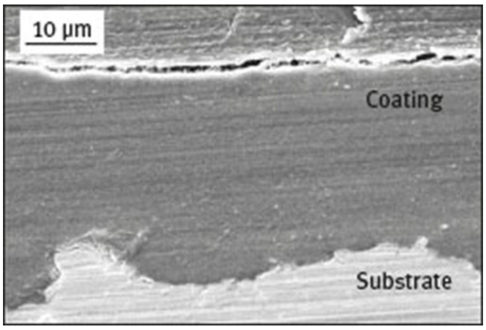

Figure 10: Compact coating free of defects and pores.

Pigments are basically dry powder added to the coating either to improve the corrosion protection properties, e.g. chemical and moisture vapor transfer resistance, or purely for aesthetic reasons, e.g. by providing color to the coating. There are different ways by which the pigments can enhance the corrosion action of the coating and they can be classified by the way they work: chemical (active pigments) or physically (barrier pigments). One of the most effective methods is achieved by using flake-shaped pigments parallel to the surface of the metal (Figure 11). They can increase the barrier effect of the system by retarding the diffusion through the coating (i.e. barrier pigments). Figure 12 shows the effects of the pigments on the oxygen and water permeability through the coating and how the permeability of both decreases by increasing the percentage of pigments on the coating. Occasionally, water permeation is desirable to a certain degree in order to activate inhibitive pigments (i.e. active pigments) (Figure 6). Sometimes the application of a single layer is not enough to protect the substrate, especially in aggressive environments, and in some cases the application of a second or third layer is required. Figure 11 shows a schematic example of a multilayered coating, in which each layer aimed for specific functionalities, namely: adhesion to the metal or adhesion between layers, water resistance, corrosion inhibition, and et cetera.

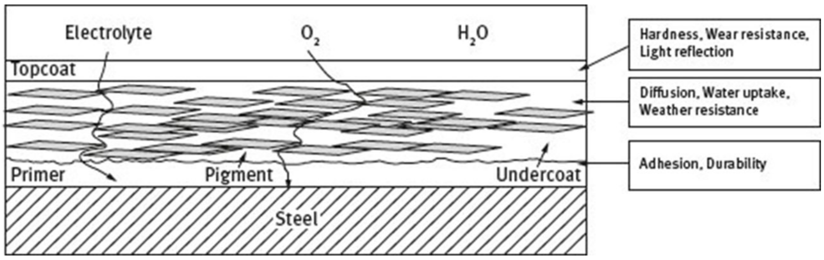

Figure 11: Barrier protection provided by the coating with flake-shaped pigments in a multi-layered system.

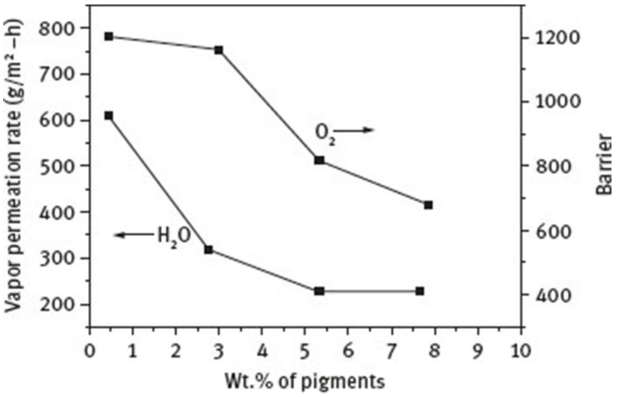

Figure 12: Permeability of the H_2O and O_2 as function of the pigments content in the coating (adapted from [40]).

The first layer of this multilayered system, the primer, is usually applied on the clean metal surface, providing long-lasting adhesion properties between the metal and the finishing coating, better than if it were used alone. In fact, in a multilayered system the use of a poor quality primer may compromise the efficiency of the entire system, even in the presence of a high performance finishing coating on top, and it will eventually lead to the formation of blistering and thus disbonding of the coating. After the primer layer, an intermediate coat or undercoat might be present. The main function of the undercoats is essentially to increase the thickness, thus the protection, of the overall system with the pigments embedded on the undercoat itself. The thickness can range from a few μm to up 1 mm, depending on the application of the structure. The finishing coat, sometimes called topcoat, is the last layer to be applied and provides the first line of defense against the external environment. The main function of the topcoat can be vary; they can provide toughness and wear resistance, enhancing the resistance towards light, chemical agents, etc. of the surface or be merely decorative.

4 Smart coatings

Coatings are designed to provide long-lasting protection against most chemical aggressive environments. There are different reasons for the failure of a coating: misapplication, defects, or simply a long period of exposure to aggressive elements, e.g. high temperatures, light, acids, etc. Furthermore, with the exception of a few coatings, most of them are permeable to the water to some degree. In fact, during its service life, the properties of the coating will eventually change as a result of the penetration of the water, oxygen and other aggressive species through the coating. In addition, defects or the combination of mechanical damage resulting from the impact of solid objects may lead to the formation of microcracks on the coating surface, providing pathways by which the aggressive species may diffuse towards the metal surface. Whatever the reason, the failure will eventually lead to disbonding of the coating and flake formation from the metal coating interface (Figure 9).

Maintenance and repair of the damaged coatings are known to be very expensive, especially on large structures, e.g. offshore oil rigs, ships, etc. Moreover, the conventional repair procedures are generally time consuming and it is mainly appropriate to repair the external damage rather than the internal microcracks. Dry and Sottos performed the first successful attempt at a self-healing material in 1993, using fibres as healing agent carriers [41]. In 2001, White et al. published in *Nature* [42] a landmark paper entitled "Autonomic healing of polymer composites" with the first successful attempt at an encapsulated healing agent combined with a dispersed encapsulated catalyst agent within a polymeric matrix. In the last few decades, as witnessed by the increasingly number of scientific papers [43, 44], textbooks published [22, 45–47] and four international conferences on self-healing materials held in Netherlands (2007) [48], USA (2009) [49], UK (2011) [50] and Belgium (2013) [51], self-healing materials have become an intense field of research. Since then, different approaches have been researched and tested; to date the most common approach and the most successful is the one proposed by White and Sottos [42], which involves the encapsulation of a self-healing reagent within microcapsules incorporated in the coatings (Figure 13).

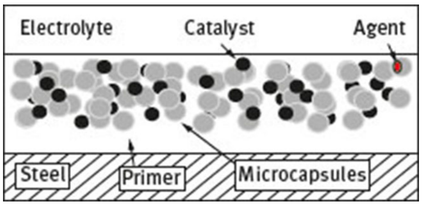

Figure 13: Schematic representation of the microcapsules incorporated within the coating matrix.

The encapsulation of reactive agent has been widely used in the agriculture, food [52] and pharmaceutical industries [53, 54] as a delivery device. In the context of corrosion protection it has proved to be an effective means of increasing the life-span of the coating, enhancing the compatibility of the active agent with the coating matrix and sustaining, prolonging and controlling the release rate of the agent itself. In particular, as will be discussed later, the process of encapsulation has proved to be very useful in the case of corrosion inhibitors because it allowed coating scientists to solve some problems related to their chemical activity and solubility in water [18, 55–58].

This new class of coatings are commonly referred as "smart coatings" due to their ability to respond to physical, chemical or mechanical external stimuli, namely temperature, UV light, and pH changes, and they can be considered as an alternative mean to further enhance the corrosion protection and thereby the durability of metallic structures. Based on the type of microcapsules content, three major release mechanisms were proposed: mechanical rupture of the microcapsule wall, diffusion through the wall, and erosion. In mechanical rupture, upon rupture resulting from microcrack or sudden damage of the coating, the encapsulated self-healing agent is released into the damaged region, and by acting as a healant prevents further propagation of the crack, allowing the recovery of the barrier property of the coating (Figure 14). In particular, corrosion inhibitor microcapsules present all of three mechanisms above mentioned, depending on the type and final use of the coating. The release can be achieved either upon rupture of the capsules themselves [44, 59] or by localized pH changes as a result of the corrosion process. Changes towards acidic and alkaline pH may lead the inhibitors either to diffuse through the shell of the capsule into the coating or by a spontaneous leakage due to the erosion of the embedded capsule [60–62]. In both cases the released agent can react with the environment, forming a thin protective layer on top the metal surface [44, 59, 63]. There are basically two different methods to incorporate the microcapsules into the coating, mostly depending on the final use of the coating: blending them within coating matrix [43, 64, 65], or electrolytically co-depositing the microcapsules on the substrate with metal ions in order to produce metal-matrix composites (MMCs) [66–77] (Figure 15).

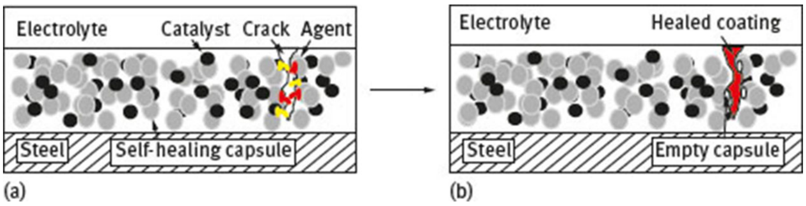

Figure 14: Schematic representation of self-healing coating; (a) before and (b) after healing.

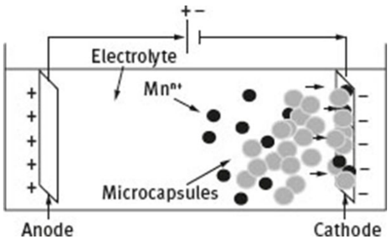

Figure 15: Schematic representation of the microcapsules incorporated within the coating matrix applied by electrolytic codeposition with metal ions.

4.1 Self-healing coatings

As White et al. showed [42, 78–82], it is possible to design polymer composite to self-heal autonomically from external damage by embedding liquid-containing microcapsules in a polymeric matrix. One of the first successful attempts to incorporate microencapsulated agent into commercial epoxy coating for corrosion prevention was made by Kumar and co-workers [83] in 2003. The corrosion study as well as the self-healing behavior was carried out by using poly(urea-formaldehyde) (PUF) microcapsules loaded with several types of self-healing agents (tung oil and spar varnish) and corrosion inhibitors (camphor and alkylammonium salt of 2-benzothiazolylthio succinic acid in xylene) incorporated into the coating. The coating was then applied on a steel hand scribed and exposed for 12 weeks to a cycle treatment of salt-fog/UV. The results demonstrated that, after scribing the coating surface, the undercutting corrosion and the growth of the artificial scribe were reduced, but not fully recovered, resulting in the release of the healing agent and corrosion inhibitor. Although the experimental results displayed only partial recovery of the artificial damage, nevertheless this approach showed the effectiveness of the microcapsule as a suitable route to increase the service life of the coating. Suryanarayana et al. [84] were able to achieve full recovery of the artificial damage using PUF microcapsules as shell material loaded with linseed oil as self-healing agent. The finding reveals that after exposed both self-healing and the control scribed coatings specimens to the spray chamber, no sign of undercutting corrosion was found for the self-healing coating, unlike the control coating. Figure 16 displays the healing process of the initial scratch shrinking gradually with the time until it is completely healed, showing no visual corrosion evidence. Linseed oil, upon rapture of the microcapsule, was released into the crack and through oxidation with atmospheric oxygen was able to heal the damage efficiently.

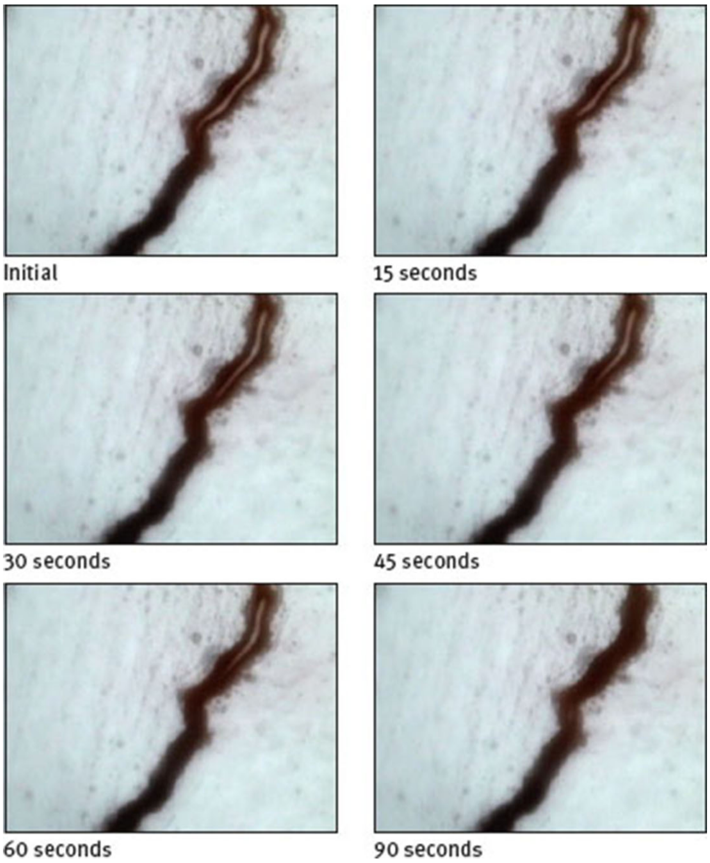

Figure 16: Optical microscope photos of self-healing coating films process as a function of the healing time (reprinted from [84] with permission from Elsevier).

White et al. [79] also achieved full recovery from the artificial damage by individually encapsulating reactive siloxanes and tin, as self-healing and catalyst agents, respectively, in polyurethane (PU) microcapsules. Both microcapsules were then incorporated into epoxy-based coatings and characterized by means of morphological and electrochemical techniques. The results showed that upon the artificial damage a polymerization reaction took placed within the damage, resulting in the release of healant and catalyst agents, preventing further propagation and therefore restoring the barrier properties of the scribed coating.

Samadzadeh et al. [85] synthesized by *in situ* polymerization, tung oil liquid core PUF microcapsules, without the presence of any catalyst agent. The self-healing action was evaluated through corrosion testing of damaged and healed coated steel systems compared to control samples in 3.5% of NaCl. The morphological results confirmed full recovery of the artificial scribe (Figure 17) resulting from the release of the healing agent tung oil. The recovered barrier property was also confirmed by electrochemical impedance spectroscopy (EIS) results. Figure 18 shows the EIS data for the scratched tung oil microcapsule incorporated epoxy coating compared with the neat epoxy coating with and without the scratch performed in 3.5% of NaCl after 14 days of exposure. Generally speaking, the higher the value of the impedance $|Z|$, the better the anticorrosive properties. It is clearly visible that microencapsulated scratched coating shows better corrosion resistance properties than the scratched neat epoxy coating, confirming the effectiveness of the healing agent by the full recovery of the artificial damage. Moreover, the corrosion resistance of the microencapsulated scratched coating displays high value of impedance, almost comparable to the unscratched neat epoxy coating, indicating that even after a long exposure in an aggressive media the recovered damage area still provides good barrier properties.

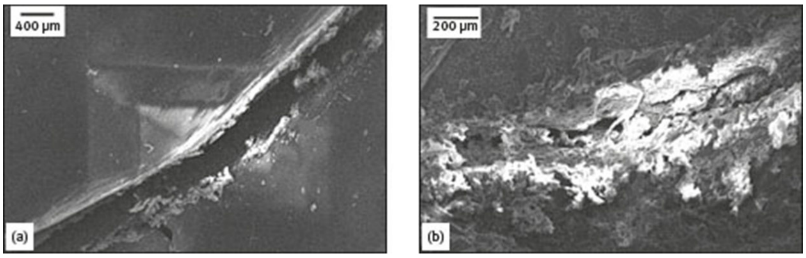

Figure 17: Scanning electron microscope (SEM) image of artificial scratch after exposure of the specimens for 14 days in 3.5% of NaCl solution. (a) control epoxy coating, (b) healed scratch on self-healing coating (reprinted from [85] with permission of Elsevier).

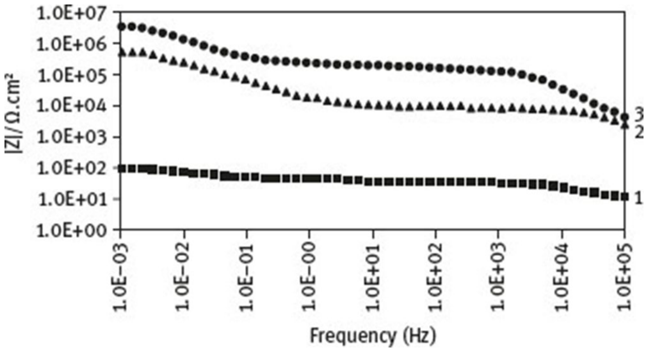

Figure 18: EIS plot of samples after 14 days of immersion in 3.5 wt. % NaCl aqueous solution. (a) scratched neat epoxy coating, (b) scratched Tung oil microcapsule incorporated epoxy coating; (c) neat epoxy coating without scratch (reprinted from [85] with permission from Elsevier).

Following the promising results obtained with the one-step intelligent self-healing approach proposed by Samadzadeh et al., Huang and co-workers [86, 87] investigated the anticorrosive property of examethylene diisocyanate (HDI) PU microcapsules dispersed in epoxy resin coating. Even though the work was more focused on the optimization of the process parameters, the anticorrosion performance undertaken in 1 M of NaCl solution showed the excellent corrosion protection achieved. No undercutting corrosion signs for the self-healing coating were noticed after exposing the specimens for 48 h in the test solution (Figure 19). On the other hand the control specimen is characterized by severe undercutting corrosion.

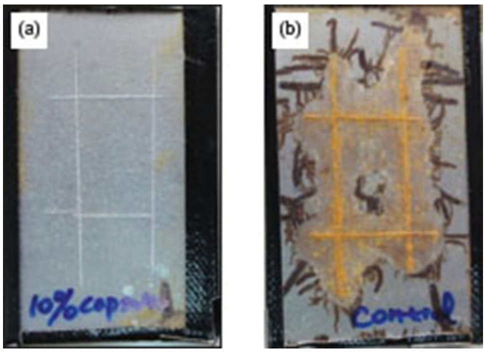

Figure 19: Corrosion test results after exposure in 1 M NaCl solution for 48 h. (a) Self-healing coating, (b) control epoxy coating (modified and reprinted from [87] with permission from Elsevier).

All the approaches mentioned so far are based on the idea of closing the gap generated during the damage and therefore restoring the barrier effect loss. More recently, new interesting and different approaches were proposed. These approaches tend to isolate rather than fill the local damaged area, by incorporating microcapsules loaded with environment-reactive healing agent (Figure 20). García and co-workers [44] used silyl ester as a healing agent in a single healing component. Silyl ester was encapsulated in PUF microcapsules incorporated into an epoxy resin coating and then applied to aluminum alloy. Fourier transform infrared spectroscopy (FTIR) and contact angle measurements showed the formation of a tightly adhered hydrophobic barrier layer on top of the metallic surface caused by the reaction of the silyl ester with the water/humidity presented in the coating. The corrosion protection performance of the formed layer were also characterized by means of EIS, comparing the performance of a scratched coatings with and without the presence of the encapsulated agent. The result displayed in Figure 21 clearly shows a well-defined distinction between the two scratched coatings. An increase in the module of impedance upon a long exposure time for the coating containing the encapsulated silyl ester was observed, confirming the formation of the hydrophobic protective layer. This work demonstrated that the silyl esters were able not only to wet the damaged surface but also the cut edge of the coating, avoiding further leakage of the inhibitor from the coating, Figure 21.

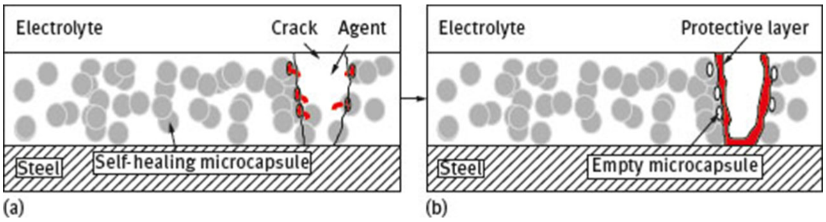

Figure 20: Schematic representation of the anticorrosive hydrophobic layer of the self-healing coating; (a) before and (b) healed.

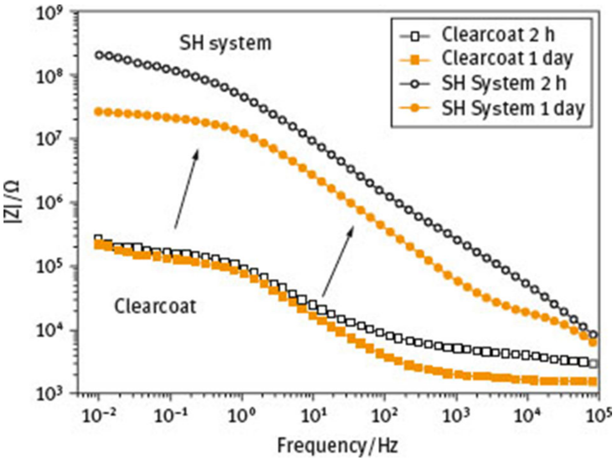

Figure 21: EIS plot of scratched coating at different immersion time in the presence and absence of the encapsulated agent (reprinted from [44] with permission from Elsevier).

Latnikova et al. [88] used microcapsules loaded with alkoxysilanes in PU. The applied coating was then tested in 0.1 M NaCl solution for 6 h. Accordingly, alkoxysilanes possessing a long hydrophobic tail were found to display better corrosion resistance than those without a tail, as a result of the water-repelling properties of the tails [88]. Huang et al. [89] successful incorporated 1H,1H,2H,2H-perfluorooctyl triethoxysilane (POTS) containing microcapsules in epoxy resin matrix.

Figure 23 shows the optical and SEM-EDX analysis for the neat scribed epoxy and the self-healing scribed coatings after exposing the specimens in 1 M NaCl for 48 h. The presence of the undercutting corrosion on the scribed neat epoxy coating denoting the poor corrosion resistance provided by this coating as result by the diffusion of the electrolyte through the scribe. Conversely, no sign of undercutting corrosion was found on the self-healing coating (Figure 23a,b). Moreover, SEM analysis on the scribed area clearly shows that the gap generated by the artificial scribe has been partially sealed, resulting in leakage of the silane agent (Figure 23c,d). EDX analysis undertaken on the bulk of the coating and in the scribed area for the self-healing coating showed that both areas share the same composition, i.e. silicon (S) and fluorine (F). As only the healing agent is comprised of these two elements, the analysis confirmed that leakage occurred from the microcapsule. On the contrary, the EDX analysis performed on the scribed neat epoxy coating only displayed the presence of iron (Fe), sodium (Na) and chlorine (Cl) from the electrolyte solution, without any signs of silicon (S) and (F) fluorine. The presence of sodium and chlorine indicated the diffusion of the electrolyte through the artificial scribe, while the presence of iron could be ascribed to the formation of iron oxide Fe_2O_3 on the metal surface, indicating that corrosion process occurred (eq. 10). Both the presence of these elements and the absence of any traces of the latter two elements lend the conclusion that no leakage process occurred. The corrosion resistance of the scribed self-healing coating was also investigated by the electrochemical technique shown Figure 22; the figure shows the current density vs. the potential of the specimen – the higher the value of current density the higher the corrosion rate of the metal. It is clearly visible that after 48 h exposure in an aggressive media the scribed control self-healing coating displays lower current density compared with the control coating. The lower current, thus the lower corrosion rate, is the result of the barrier effect provided by the coating, which isolates the metal from the external electrolyte, impeding the current flow. This electrochemical experiment once more confirmed that the self-healing coating has recovered its barrier properties during the immersion process.

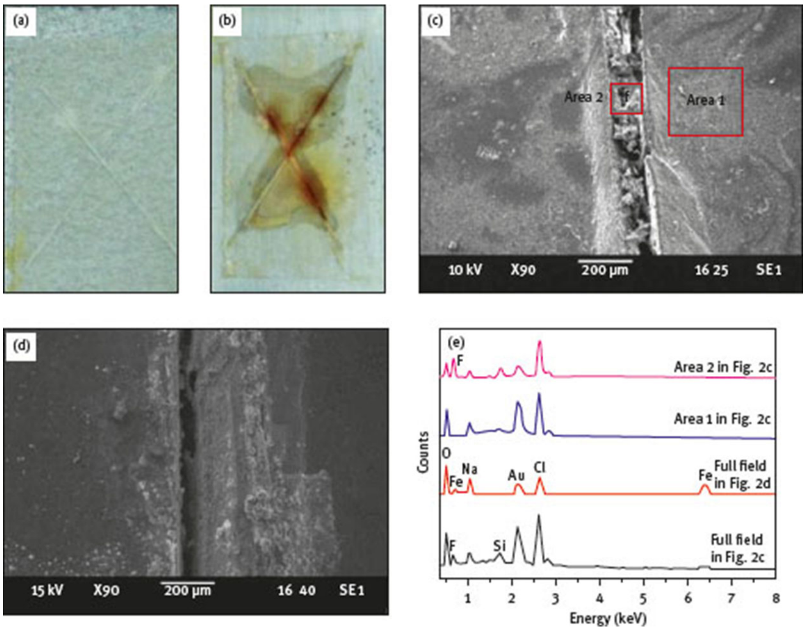

Figure 22: Optical images of the scribed coatings: (a) self-healing coating, (b) neat epoxy control coating. Scanning electron microscope (SEM) of the (c) self-healing scribed coating and (d) neat epoxy control scribed coating. (e) EDX analysis of the areas of the control coating and self-healing coating. The figures were taken after the the specimens were exposed for 48 h in 1 M NaCl solution (reprinted from [88] with permission from Elsevier).

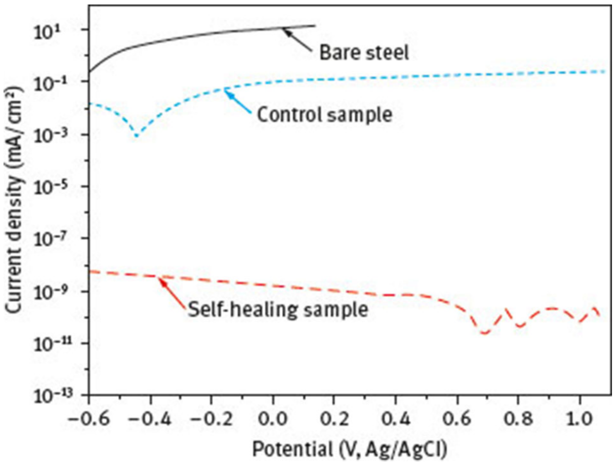

Figure 23: Electrochemical plot comparing the behavior of the bare steel panel, scribed control and self-healed specimens (adapted from [88] and reprinted with permission from Elsevier).

All those approaches, in addition to the aforementioned corrosion protection effect, present another interesting advantage that is not present with other methods so far discussed. These methods use single self-healing microcapsules, rather than the conventional two microcapsules method, i.e. a self-healing agent containing microcapsules and the catalyst microcapsules necessary to accelerate the polymerization of the healing agent.

As will be detailed below, this two-step self-healing approach may pose a serious drawback. In fact, the presence of a second phase decreases the likelihood of having both phases present at the same time and in the required ratio in the region of the scratch, hindering the restoration of the barrier properties of the coating itself [44].

However, this probability can be enhanced by increasing the concentration of microcapsules within the coating, which in turn, can negatively affecting the adhesion between the metal and the coating [85, 90]. What instead makes these materials a catalyst-free self-healing additive is their ability, once released, to react with the environment and form a hydrophobic film on the surface of the metal or to reduce the growth of the damage. For example, the self-healing approach proposed by García and Huang utilising silane is able to react with the hydroxyl groups present on the metal surface, producing a hydrophobic layer able to passivate the surface, according to the reaction showed in Figure 24 [44, 88, 89, 91]. The new formed hydrophobic layer will repel the electrolyte solution from the metal, therefore restoring corrosion protection. Linseed oil [84, 90, 92, 93] and tung oil [85] have comprehensibly demonstrated their capability to form a protective layer on the metal surface by their oxidation in contact with air, and thus no catalyst is needed. Isocyanates also have proved their effectiveness as catalyst-free healing agents due to the higher reactivity with water [87, 89] (Figure 25).

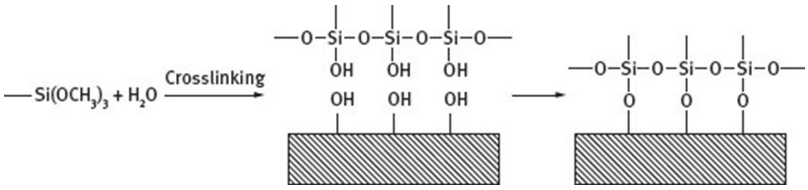

Figure 24: Reaction of silanes agent with water from ambient medium. The surface becomes passive and hydrophobic resulted by binding of silanes with the metal.

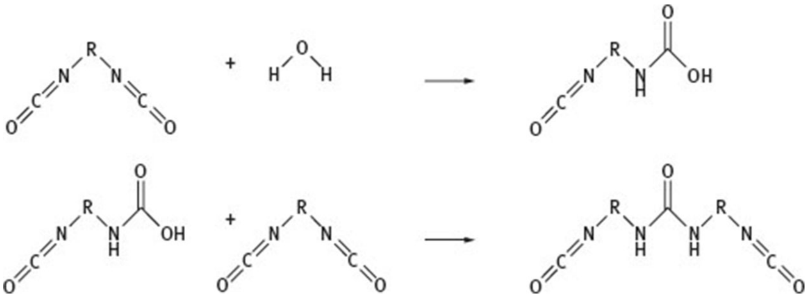

Figure 25: Reaction of diisocyanate monomer with water.

One major disadvantage overlooked by all the studies so far mentioned is that once the system has recovered itself from the damage by the released healing agent,corrosive species may still be trapped between the healed coating layer and the substrate. Therefore, further electrochemical reactions can take place at the coating/substrate interfaces and that eventually may lead to disbonding of the coating itself. This shortcoming can be addressed by the combination of self-healing and self-releasing microcapsules containing inhibitors. While the active component in ruptured embedded self-healing microcapsules is released into damaged coating (Figure 15), allowing the recovery of the barrier property, the released inhibitor forms a protective layer due to the reaction of the inhibitor and the entrapped aggressive species (Figure 27).

4.2 Self-releasing inhibitor coatings

As discussed so far, there are essentially three suitable routes to protect the metal for the external environment and therefore hinder its degradation:

i. by using the electrochemical properties of the metal, i.e. cathodic and anodic protection;

ii. by isolating the structures by means of an appropriate coating;

iii. by the incorporation of corrosion inhibitors into coating formulations in order to confer active protection when the coating barrier property fails.

As has been stated above, regardless of the best coating system designed it is just a matter of time before oxygen, water and others species diffuse through the coating towards the metal substrate. The inhibitor protection action is achieved via the formation of a passive layer on the metal surface. For isolating the metal from the external environment, chromate conversion coatings (CCCs) were widely used as corrosion inhibitors, providing additional long-term corrosion protection for both the bare and coated metal by not only providing a thick barrier of oxide/hydroxide layer, but also improving the adhesion between the metal and the primer [94, 95].

Furthermore, CCCs can provide self-healing properties to the system in the case of chemical and mechanical damage. In fact, hexavalent chromium [Cr(VI)] contained in certain types of CCCs can leach from the coating into the surrounding solution and migrate to the coating damage, where it may prevent further corrosion activity and therefore act as a self-healing material [96–98].

However, chromate compounds are highly toxic and carcinogenic due to their high potential to oxidase organic molecules [99, 100]. As a result of these drawbacks they were banned in Europe in 2007 and worldwide shortly afterwards by the Environmental Protection Agency (EPA) [101, 102].

Because of this, scientists have focused their research on finding more environmentally friendly, but nevertheless effective organic corrosion inhibitors in replacement of the chromate-based inhibitors in industry. Organic inhibitors, e.g. salicylaldoxime, tolyltriazole (TTA), benzotriazole (BTA), etc. have shown great potential as corrosion inhibitors of commonly used aerospace aluminum alloys [103]. However, the addition of corrosion inhibitors to coating formulations is not straightforward. Due to the functional groups present on their structure they can react with the coating material, causing coating degradation and/or inhibitor deactivation.

Another issue that must be taken into consideration during the formulation of a corrosion-resistant coating is the solubility of the inhibitors themselves. In fact, corrosion inhibitors can only provide the effectiveness if their solubility is in the right range, the so-called "window of solubility" [18, 55–58]. Corrosion inhibitors with too low solubility cause a lack of sufficient inhibiting ions available to diffuse from the matrix to the metal surface to protect. Conversely, upon higher solubility inhibitors may leach out from the coating and are thereby lost, providing the ability to protect the substrate for only a limited period of time. The leaching is the result of the diffusion of the inhibitors through the coating, and being replaced by water molecules that in turn diffuse into the coating from the coating surface, lead to osmotic blistering (Figure 9) [32–34]. All these factors can modify the leaching rate, i.e. the amount of inhibitor that is available for corrosion control, thus they cannot be used directly as pigments in the organic coating.

One approach to extend the life-span of the coating is to incorporate high amounts of inhibitors, but this may not be economically, environmentally and practically viable. A strategy that has attracted considerable interest among corrosion scientists in the last decade is the encapsulation of corrosion inhibitors in hosting systems into the coating matrix. These containers will store the inhibitors, preventing the inhibitors themselves from interacting with the matrix, where they can act as slow release pigments similar to chromate pigments, extending the corrosion protection effectiveness of the coating. Sometimes – either due to their toxicity or otherwise potential harm when used alone – it is preferable to encapsulate these types of inhibitors.

Therefore, the encapsulation process provides a potential environmentally acceptable and controlled means of prolonging inhibitor activity in coatings. In addition, controlling their release leads to a reduction in the threshold levels of inhibitors commonly used to prevent the corrosion process. Once encapsulated, the inhibitor-loaded microcapsules can be incorporated in the coating in the same manner by which the classic inhibitors are used. In order to solve these shortcomings, Khramov et al. proposed to encapsulate organic inhibitors such as mercaptobenzothiazole (MBT) and mercaptobenzimidazole (MBI) in cyclic oligosaccaharides and then incorporates them in hybrid organo-ceramic coatings [104, 105]. The study compared the anticorrosive performance of the coating applied on aluminum alloy AA 2024-T3, with the corrosion inhibitors directly dispersed in the matrix with the encapsulated one. The coating were characterized by means of EIS, an electrochemical technique widely used to test the anticorrosion properties of coatings over a long exposure time (Figure 26) [10, 106–108]. The results showed that for short immersion times the coatings displayed similar behaviors. However, upon higher immersion times the nonencapsulated inhibitors showed a remarkable decrease whereas the encapsulated inhibitors exhibited stable anticorrosion properties, as the result of the slow and long-term releasing rate of the inhibitors in coating.

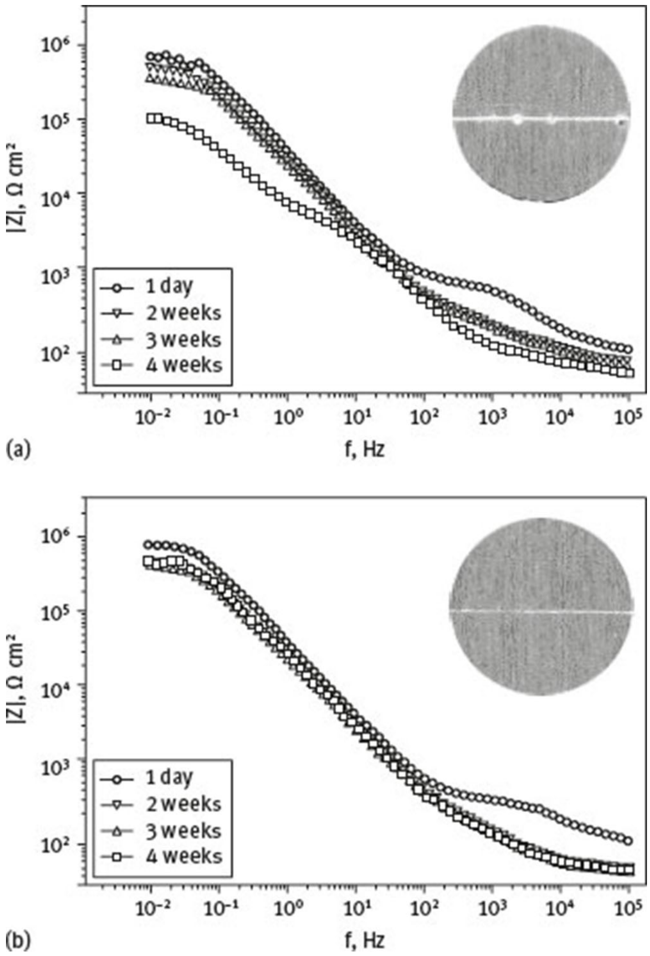

Figure 26: EIS plots for the scribed coatings at different immersion times in dilute Harrison's solution (a) without inhibitor and (b) with MBI/β-cyclodextrin complex (adapted from [105] and reprinted with permission from Elsevier).

The cyclodextrin is a truncated cup-shape structure with a hydrophilic exterior surface and a hydrophobic interior cavity in which the inhibitor is allocated, forming an inclusion complex with the cyclodextrin itself. Although the method proposed by Khramov and co-workers back in 2004, strictly speaking, does not involve the encapsulation of the inhibitors within closed structures (capsule), nevertheless the novelty of this study clearly shows the effectiveness of this approach as a suitable route to ensure long-lasting release rate of the inhibitors within coating thereby, opening new opportunities for increase corrosion protection of the substrate.

Kuang and co-workers encapsulated the inhibitor thiurea within microcapsules by using thermal phase separation method together with vigour Finestran drying bath method. The microcapsules were comprised a shell polyvinyl alcohol (PVA) sealed by alginate natrium [58]. The electrochemical results showed that the releasing times of the encapsulated inhibitor almost tripled and the corrosion rate, initially decreased with the release of the microcapsules, remained stable after the inhibitor was released completely upon higher immersion times.

Another interesting approach was proposed by Yang and van Ooji [103]. In an attempt to decrease the negative effects associated with highly soluble corrosion inhibitors, they used a plasma polymerization technique to encapsulate triazole inhibitor particles in a one ultrathin polymer layer comprised either of a single shell of perfluorohexane or of two ultrathin polymer layers comprised of an interior shell of perfluorohexane and an exterior shell of pyrrole. The authors found out that the inhibitor release and degradation performances of capsule were closely related to the shell material.

High hydrophobic capsules may render it difficult to disperse the capsule into paints, however high hydrophilicity leads to an increase in adsorption of water and formation of blisters. Plasma polymerization is a technique generally used to change the hydrophilicity, hydrophobicity as well as other anticorrosion properties of materials [109, 110]. The inhibitors were then applied on aluminum copper alloy as a water-based epoxy coating and immersed in 3.5% NaCl solution. The result shown that the introduction of the outer layer of pyrrole enhanced the compatibility of the capsules with the coating and that the inhibitors were able to reduce the corrosion rate of the metal by acting as cathodic inhibitors, i.e. suppressing the cathodic reaction. The presence of the second layer increased the thickness of the microcapsule, allowing the inhibitor to be slowly released by diffusion through the microcapsule to the coating, therefore lowering the corrosion rate of the substrate.

Polyurethanes (PUs) are widely used in coating industries due to their excellent chemical, mechanical and physical properties. However, a direct addition of an inhibitor like MBI or MBT will yield the deactivation of the inhibitors themselves as a result of the reaction between the isocyanate groups of the PU coating and the thiol groups of the inhibitors, through a thiol-isocyanate coupling reaction. Marathe et al. [111] encapsulated 2-MBI and 2-MBT inhibitors in UF microcapsules dispersed in acrylic-based PU coatings in order to enhancing anticorrosive properties of PU coatings. The anticorrosive properties of the self-releasing inhibitor PU coating were carried out by exposing the specimens in 0.5 M HCl and 3.5% NaCl solutions for up to 240 h. The electrochemical and immersion results showed that self-releasing PU coatings performed better than the nonencapsulated coating microcapsules. Moreover, the anticorrosion property of the coating increased increasing the loading of UF microcapsules in the coating.

4.2.1 pH-sensitive self-release microcapsules

There is no doubt that self-healing materials would offer enormous possibilities, in particular for the applications with long-term reliability in severe environments. However, it would be preferable to detect corrosion processes at an early stage, so that action can be taken to prevent and/or to correct the problem to avoid failures. Over time, many corrosion sensors or probes based on electrochemical or nonelectrochemical theory have been developed and applied to corrosive environments in industry [112–115]. One suitable route to prevent the failure of the structure is the using of a corrosion control coating filled with pH-sensitive carriers [60–62, 116–121]. The main cathodic reaction in the presence of oxygen involves the reduction of oxygen with formation of hydroxide ions that lead an increase in the local pH (eq. 5). In this sense, these pH-sensitive carriers loaded with inhibitors act at early corrosion stages by releasing the inhibitor *on demand* into the system, resulting in pH changes, stabilising the local pH gradients and preventing the propagation of the corrosion process. Once the pH returns to a more suitable value, i.e. a pH value in which the capsules are stable, the release of the inhibitor is stopped (Figure 27). However, at present the literatures contains only studies related to the use of nanocontainers as pH-trigger release inhibitors, e.g. inhibitor-loaded silica nanoparticles and inhibitor-loaded halloysite nanotubes, and only few of them are related to the use of microcapsules [116–118].

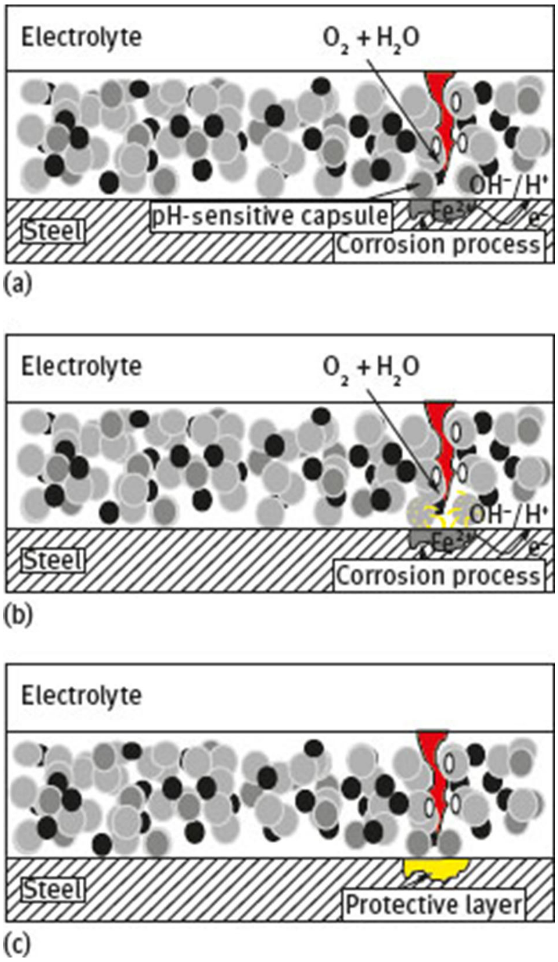

Figure 27: Schematic representation of microcapsule-based on pH-sensitive release releasing agent. (a) Onset corrosion process, (b) respond, (c) formation of a protective layer.

The literature reports some interesting attempts to formulate corrosion control coatings based on pH indicators incorporated in the coating that are able to detect the increased pH (alkaline) associated with the local cathodic activity under the coating, through colour changes by visual inspection [60–63, 119, 122, 123] or fluorescence changes [124–126]. This concept is easy to understand using a simple laboratory demonstration shown in Figure 28. Placing an iron nail in agar in which ferricyanide ions ($[Fe(CN)_6]^{3-}$) and phenolphthalein (PhPh) indicator have been previously placed, the ends of the nail will turn blue and the middle of the nail will turn pink. The pH indicators show which part of the exposed nail tends to be acid (anodic) or basic (cathodic). The blue colour (Prussian blue), is the result of the reaction between the ferricyanide ions indicator with the iron ions released during the oxidation reaction (anodic regions, eq. 8), while the pink colour is due to the reaction hydroxide ions released during the oxygen reduction reaction (cathodic regions, eq. 5) with phenolphthalein. Zhang and co-workers proved the effectiveness of this approach back in 1999 by mixing several color changing pH indicators, namely phenolphthalein (PhPh) or bromothymol blue, to a transparent acrylic-based coating, thereby conferring sensing functionality to the coating [122]. At that time this approach showed great promise from an industrial standpoint and soon others scientists followed this interesting route [121]. PhPh is a good pH indicator because of its intense colour that displays at a pH higher than 8.2 (pink) and also that it is colourless at pH values below 8.2, which is useful for the indication of corrosion process and avoiding false-positive corrosion indications [60–62, 119–122, 127]. However, unlike with the inhibitors, some technical challenges associated with the solubility and possible interaction between the indicators and coating system had to be considered. Once again these negative effects were overcome by encapsulating the indicator into containers [60–62, 119, 120].

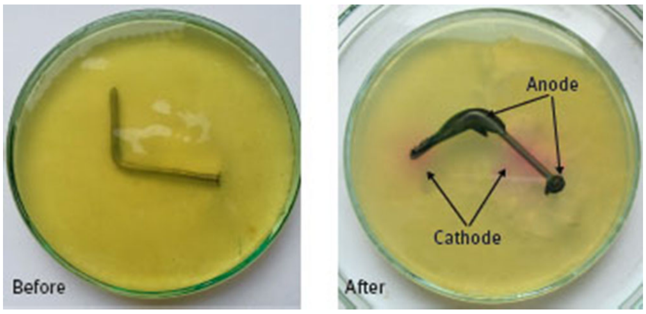

Figure 28: Iron nail in agar gel enriched with ferricyanide ions $[Fe(CN)_6]^{3-}$ and phenolphthalein indicator. The blue color (Prussian blue) indicates the anodic regions while the pink color indicates the cathodic regions.

To date, to the knowledge of the author, the literature reports few successful attempts to discuss the incorporation of encapsulated pH indicators microcapsules in functional coatings used as coating sensing [60–62, 120, 128]. The microcapsules filled with inhibitors described above are actually only inert containers that do not respond to any trigger mechanism but they are simply used to increase the compatibility between the coatings and to reduce the release rate. The main difference between the self-releasing and pH-sensitive microcapsules, essentially, is the release mechanism; in the first the healing contents is released by its diffusion through the microcapsule shell whereas, the latter will release their contents in response to the erosion of the shell as result of hydrolysis reaction catalyzed by local change of pH associated with the corrosion process (Figure 29). The chemistry of these approaches resides on the use of PhPh as the pH indicator encapsulated in microcapsules based on the combination of film-forming monomer and pre-polymers such as urea–formaldehyde and melamine–formaldehyde with crosslinking agent such as pentaerythritol tetraki (3-mercaptopropionate) [60–62]. The microcapsule, being sensitive to an alkaline pH, breaks down and releases the indicator.

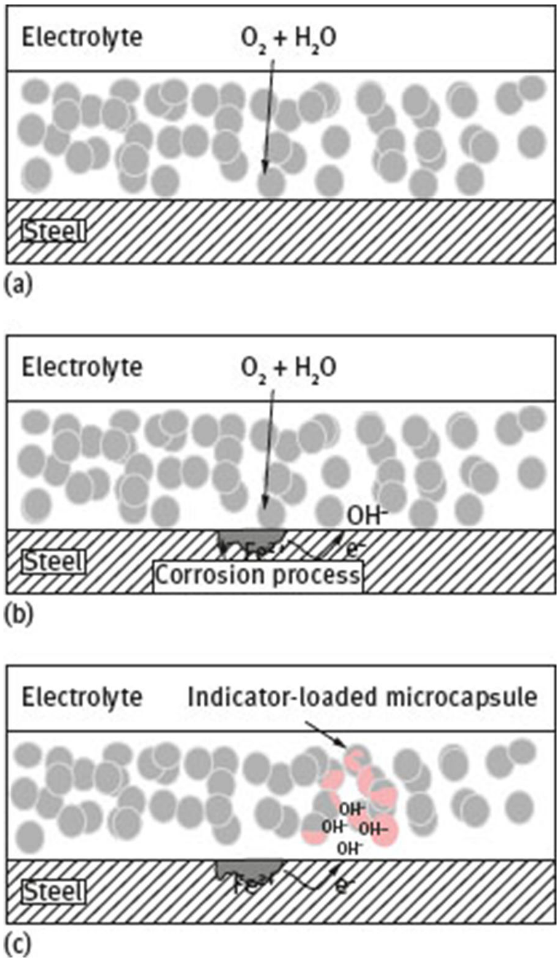

Figure 29: Schematic representation of indicator-loaded microcapsuled coating. (a) Diffusion of water and oxygen, (b) onset corrosion, (c) response.

Maia et al. developed a sensing coating by encapsulating PhPh in silica nano-containers. The authors discovered that PhPh, instead of being released in to the coating, reacts with the hydroxide anions diffused within the capsule and turns them from colourless to pink [119]. Later, the same authors encapsulated PhPh in polyurea microcapsules dispersed in polyurethane based coating [120]. The corrosion onset ability of the sensing coating was investigated by applying the formulation onto an aluminum sample and then exposing it to 3.5% of NaCl solution. The applied coating successfully detected the early stage corrosion through the formation of pink coloured spots scattered on all over the surface as a result of the reaction of the PhPh with the hydroxide ions generated in the cathodic areas (eq. 5). Another interesting aspect of this work is the combination of microcapsules of polyurea and polyurethane matrix. In fact, as both microcapsules and coating share a similar chemical nature, their adoption has allowed for enhancing the compatibility between the shell and matrix, obtaining uniform and homogeneous sensing coating and therefore, increasing the barrier properties of the coating itself.

5 Metal/liquid microcapsule composite coatings

Composite coatings can be prepared by mixing microcapsules in a paint formulation, or by electrodeposition (or co-deposition). Electrolytic co-deposition is a technique (Figure 15) used to embed small particles into a metal or alloy matrix, to which they impart special properties, in order to produce composite coating. Composite coatings produced by electrolytic co-deposition are broadly used in the automotive and aerospace industries due to their better wear, friction and corrosion properties [66, 67]. In addition to the co-deposition of small particles, it has recently been shown that by embedding encapsulated liquids products into the metallic matrix they can be released gradually, forming a protective film on the matrix surface [66, 68, 70–77] (Figure 30b). One of the first attempts to embed liquid microcapsules on metallic matrix dates back to 1994 and was performed by Alexandridou and co-workers. The study focused on the influence of the synthesis parameters, e.g. type of encapsulated, size, distribution etc., of an oil liquid core and polyamide microcapsules obtained by interfacial polymerization as a self-lubricating metallic coating deposited from Watts nickel plating baths. Depending of the type and concentration of the monomers used in the deposition bath, a coverage as high as 40% was obtained. Several studies showed that, based on the type of liquid embedded, several properties such as abrasion, friction, and corrosion resistance can be achieved. For example, by encapsulating corrosion inhibitor liquid, upon local surface damage, the slow release of the liquid inhibitor can either partially repair the damage and/or protect the surface from corrosion by the formation of passive layer on the metallic surface. Conversely, the release of encapsulated oil liquid products leads to the formation of a low surface energy hydrophobic layer on the metal surface enhancing the corrosion resistance of the coating [71, 75–77] (Figure 36d).

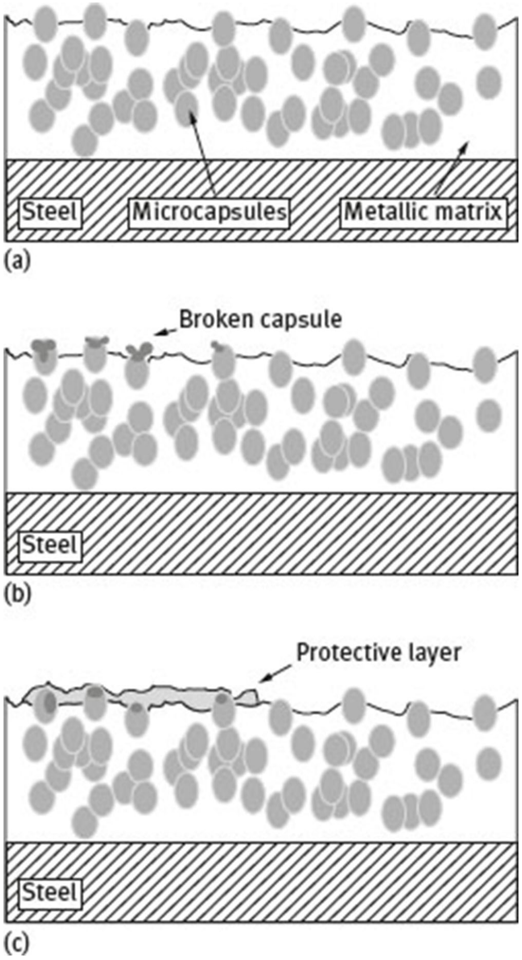

Figure 30: Cracking of microcapsule with formation of the protective layer. (a) Intact coating, (b) broken capsules, (c) protective layer.

This new protective layer can provide long-term protection under a broad range of corrosive conditions either due to chemical stability or excellent water-repellent properties. The literature also reports others' successful attempts to co-deposite encapsulated liquid core microcapsules on others metallic matrix, e.g. nickel [66, 67, 69], tin [73], etc. Masayuki et al. successfully prepared embedded microcapsules containing abietic acid as a liquid core, (i.e. welding agent, incorporated with a tin matrix in order to improve the weldability of the final composite coating [73]) and lube oil-containing microcapsules in Watts nickel plating baths and co-deposited on nickel metallic [69]. Copper is a metal widely used in the chemical and microelectronics industries due to its high electrical conductivities and lower cost than gold or silver as protective layer. However, one of the major disadvantages of copper coating, as we have seen from the Pourbaix diagram, is that in aerated acid solutions copper is prone to corrode. In recent decades, different methods were used to try to increase the corrosion resistance of plated copper coatings, such as surface passivation [68], self-assembly technology [72], and different coatings were used for protection, e.g. by creating hydrophobic surfaces [71, 76]. At present, Cu/liquid microcapsules composite coatings, prepared by electrolytic co-deposition with hydrophobic surfaces, have attracted increasing attention [70–72, 74–77, 129]. In order to improve the corrosion resistance of plating copper coatings, Zhu and co-workers [71, 75–77] synthesized Cu/microcapsule composite coatings using BH-102 hydrophobic agent and 1H-Benzotriazole inhibitor as core and methyl cellulose as shell, by electrolytic co-deposition with metal ions in an acidic copper-plating bath (Figure 31). The hydrophobic protective layer and corrosion resistance of the composite was investigated by means of water contact angle, electrochemical and morphological techniques. Morphological and contact angle analysis showed that a thin hydrophobic film was formed on the composite surface as a result of the slow release of the encapsulated liquid (Figure 32). Hydrophilic surfaces are characterized by contact angles of 0°, while complete hydrophobicity surfaces display contact angles of 180°. For a good hydrophobic surface, the angle must be around 160°. Figure 32 depicts the contact angle at different exposure days; it is clearly visible that the angle increases with an increase of time, resulting in the formation of hydrophobic layers. Moreover, the findings displayed in Figure 34 for the immersion test performed in 0.1 M H_2SO_4 solution show that the copper composite coating, compared with a copper coating, exhibits excellent corrosion resistance, which it is ascribed to the hydrophobic nature of the film on the composite surface. The formed film also presented good stability over a long period of time, as suggested by the polarization curve for the composite coating stored in air at 25 °C and by the stable contact angle value of around 160° obtained after a long exposure time (100 days) (Figure 33).

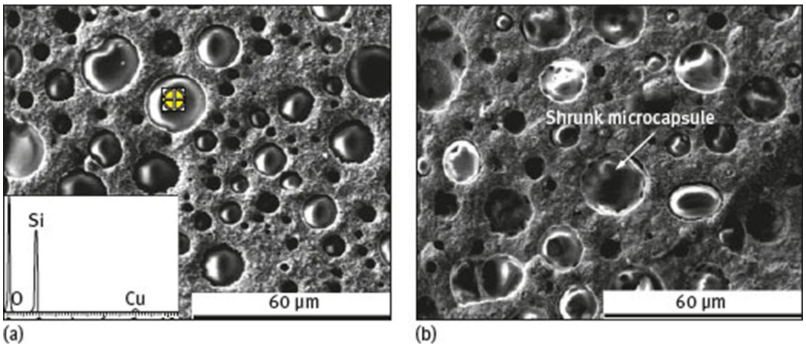

Figure 31: Scanning electron microscope (SEM) images of (a) fresh prepared Cu/liquid microcapsule composite coating and (b) composite stored in air for 30 days at 25 °C (reprinted from [75] with permission from Elsevier).

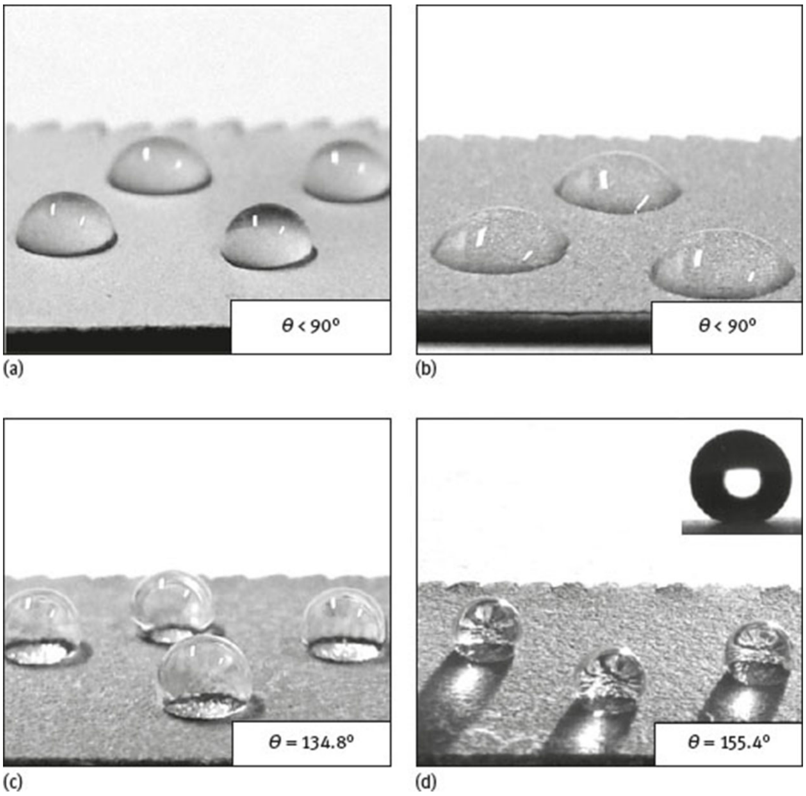

Figure 32: Contact angle of water droplet on (a) pure copper surface, (b) copper composite surface, (c) composite stored in air for 7 days, (d) composite stored in air for 15 days (reprinted from [76] with permission from Elsevier).

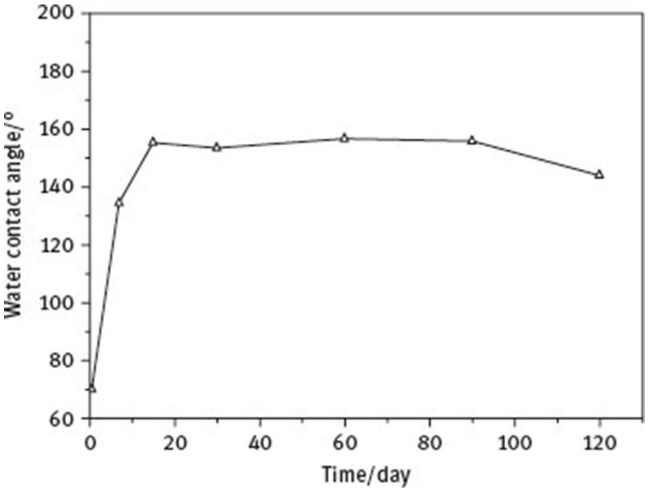

Figure 33: Contact angle plot related to the stability of the hydrophobic protective layer (reprinted from [76] with permission from Elsevier).

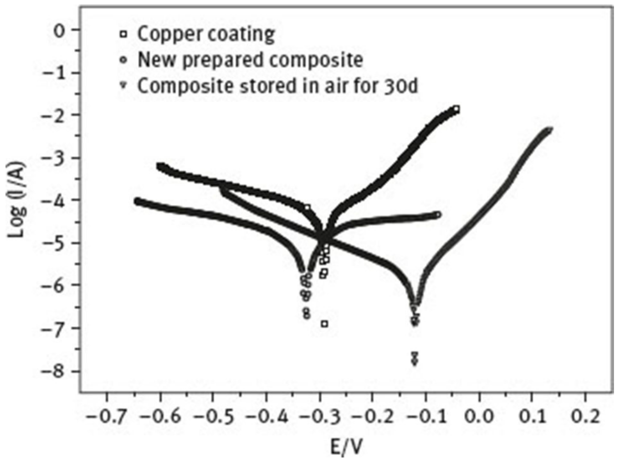

Figure 34: Polarization curves of coating composite and copper coating (reprinted from [75] with permission from Elsevier).

Whatever the metal or the type of microcapsules used, the only requirement for the co-deposition of the microcapsules is that the shell must be thick enough to withstand the forces generated during the application. They must be resistant to the chemicals agent of the plating bath and temperature. Moreover, by controlling the condition of plating, e.g. current applied, capsule size, composition of the plating bath, plating time and concentration of the microcapsules [67, 77], it is possible to tailor the amount of embedded microcapsules on the metal surface, thus tailoring the properties of the composite. Large microcapsules (>10 µm) are more likely to break during the process and are not easy to co-deposit with metal ions in the plating bath [77, 130]. Furthermore, it was found that composite coatings embedded with smaller microcapsules (2–8 µm) displayed better corrosion resistance compared with larger ones. In fact, large cracked embedded microcapsules act like superficial defects, compromising the stability of the coating with adverse effects from a corrosion resistance standpoint (Figure 35) [130]. Moreover, it was found that different liquid-containing microcapsules have different deposition times under the same current density applied, suggesting a direct correlation between the current applied, the co-deposition time and type of microcapsules. As the microcapsules are chargeless particles, Zhu suggested that they may acquire the positive charge by chelation of their hydroxyl group and oxygen of the microcapsule shell (methyl cellulose) with copper ions (Cu^{2+}) and be forced to move towards the cathode by the electric field force and eventually co-deposited on the metal surface Figure 36 [77, 130].

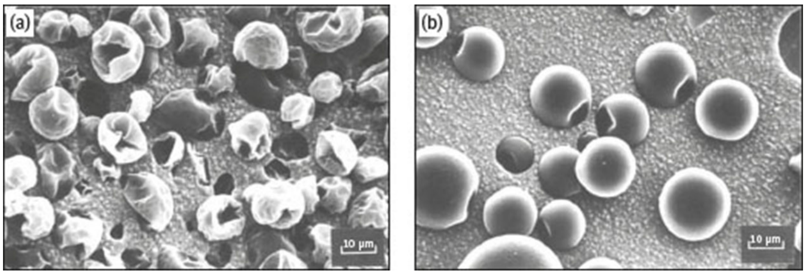

Figure 35: (a) Cracked microcapsules embedded on the metallic surface, (b) large microcapsules partially embedded on the metal surface (reprinted from [66] with permission from Elsevier).

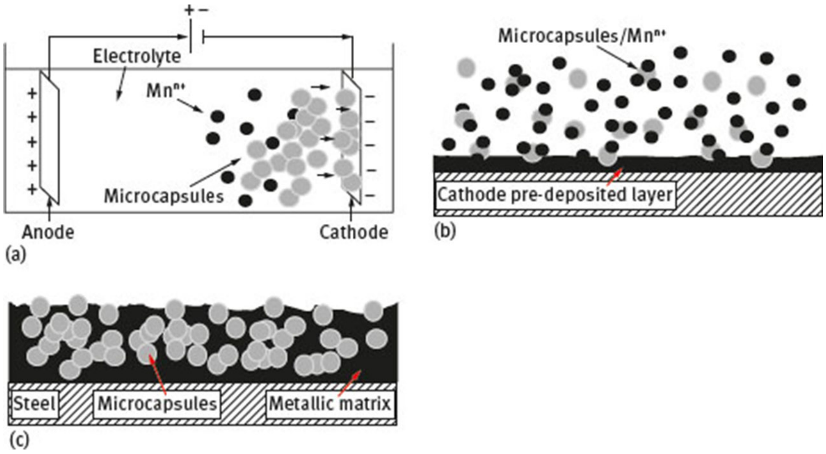

Figure 36: (a) Codeposition of liquid-containing microcapsules on the metallic matrix, (b) ions/microcapsules move towards the cathode, (c) final composite coating.

6 Drawbacks

Whatever the type of microcapsule used, in order to perform their function properly a series of requirements must be fulfilled:

- remains intact during the application and storage;
- raptures readily when needed;
- does not compromise the properties of the coating, e.g. mechanical and adhesion;
- loads with sufficient amount of agent;
- ensures good compatibility with the polymeric matrix.

As during the application of the coasting the microcapsules have to withstand high compression forces, special attention must be paid to the mechanical stability of the microcapsules. If the wall of the microcapsules is not strong enough (thin wall), they may break during the application; conversely, microcapsules with thicker walls do not break easily, preventing the release of the healing agent. Furthermore, they must be stable enough to remain intact for many years in the coating.

Adhesion of the coating is another controversial issue that is far from simple. The microcapsules themselves should not provide any additional adhesive properties to the coating. Nevertheless, it was found that microcapsules negatively affect the adhesion between the metal and the coating. Microcapsules in contact with the metal surface act as interfacial defects, generating low adhesion spots, lowering the adhesion of the coating towards the substrata, defects that increase by increasing the concentration and the size of the microcapsules [83, 85, 90, 131].

Boura and co-workers, in their study of the optimization of process parameters of the urea–formaldehyde microcapsules, found out that the adhesion strength of the coating was strongly affected by the size and concentration of the microcapsules [90]. This was controversial because other authors [61, 62] claimed that the dispersion of the microcapsules into the coating did not affect the adhesion properties of the coating if the size was optimized within the range 0.2–20 μm). Figure 37 shows the adhesion strength as a function of the concentration of the microcapsules, also taking into account the size of the microcapsules. It is seems that increasing the concentration of the microcapsules leads to a decrease in the adhesion of the coating. Moreover, at the same concentration, smaller microcapsules display higher adhesion strengths. The amount of agent stored in the microcapsule also plays an important part. In order for the microcapsules to function properly, they must be loaded with enough amount healant. Lower amounts of healant means insufficient material available, either to entirely fill the damage in the case of the self-healing system or to be released in the polymeric matrix in the case of the corrosion inhibitors [132]. However, on one hand, increasing the size of the microcapsules allows an increase of the amount of healant agent, on the other hand, as was discussed above, larger microcapsules lead to a decrease of the adhesion performance of the coating. The amount of healing agent can also be incremented by increasing the concentration of the microcapsules themselves, but as the size, the adhesion strength of the coating also decreases.

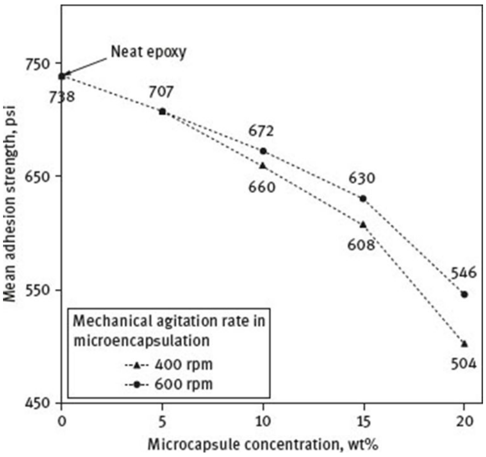

Figure 37: Adhesion strength of neat epoxy coating and coating with embedded microcapsules obtained at different agitation rates (reprinted from [89] with permission from Elsevier).

Kumar et al. also studied the effect of microcapsules from an adhesion standpoint. In this work [83], they compared the adhesion strength of coatings obtained by applying the microcapsules using two different techniques. In the first one, the classic method, the coating was prepared by mixing the microcapsules directly with the primer and then applying it onto the metal (Figure 38). In the second technique, a layer of microcapsules mixed with the primer was sprayed on top of a first layer of primer, previously applied, and then a second lining layer of primer was applied on top (sandwich) (Figure 39). The findings showed that the adhesion strength of the coatings prepared by sandwiching the microcapsules between two lining layers was remarkable higher than those prepared with first method. The authors suggested that the presence of the first lining layer of primer prevents the contact between the microcapsules and the metal surface, thereby leaving the primer free to adhere to the metal.

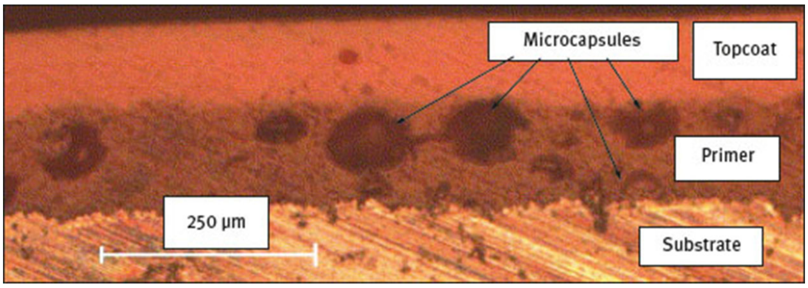

Figure 38: Optical micrograph of cross section of coating prepared by mixing the microcapsule directly with the primer (reprinted from [83] with permission from Elsevier).

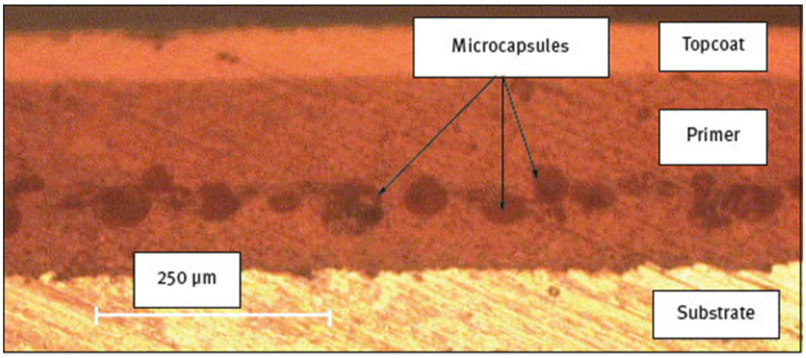

Figure 39: Optical micrograph of a cross section of coating prepared by sandwiching a layer of microcapsules between two layers of primer (reprinted from [83] with permission from Elsevier).

Furthermore, as microcapsules are pigments, there is a limit to the amount of pigment that can be added (critical pigment volume concentration [CPVC]) to the coating. CPVC is a physical transition point at which the properties of an organic coating can change significantly at or near this point [24, 36, 38, 39]. When this value is exceeded, the appearance and behavior of the paint change significantly. Therefore, the addition of the microcapsules into the coating system can have a significant influence, not only on the adhesion but also on the mechanical properties of the coating [81, 133]. Tripathi et al. [134] studied the mechanical properties of epoxy resin matrix incorporated within microcapsules comprised of urea-formaldehyde and melamine-formaldehyde. According to the authors, both tensile strength, modulus, and impact resistance of the matrix was found to decrease with an increasing amount of microcapsule in the formulation. Blaiszik et al. [135] discovered that only a slight change in modulus was found from the control resin with low concentrations of microcapsules incorporated and a size of 1.5 μm. However, Rzeszutko et al. [136] noted a proportional decrease with the concentration with microcapsules of 180 μm. Nevertheless, all agreed that a significant improvement of the toughness of the final product was observed. As Toughness is defined as the ability to absorb energy and undergo extensive plastic deformation without rupturing [137]. Tougher coatings can withstand the impact of tools. The compatibility and the adhesion of the microcapsules with the polymeric matrix is also a crucial aspect that can determine the final quality of the coating and which coating scientists have to consider. Microcapsules should be matched to the coating matrix. A judicious choice of the chemistry of the microcapsules can remarkable increase this compatibility, leading to the formation of uniform and homogeneous continuous film. Tatya and co-workers [131] found out that by using microcapsule of polyurea dispersed in a polyurethane matrix, as the two materials shared similar chemistry, the adhesion of the microcapsules with the matrix was improved. FTIR analysis showed that chemical bonds were formed by the isocyanate group of the polyurethane matrix and the amine groups present on the wall of the microcapsules. Suryanarayana et al. [84] discovered that the surface of the microcapsules themselves could affect the compatibility between the two parts. It was observed that rough microcapsules enhanced the adhesion of the microcapsules with the matrix, allowing the formation of strong bonds with the coating. Furthermore, it was observed that a good adhesion helped breaking the microcapsules when stressed.

The use of a *one-step* self-healing approach, i.e. a self-healing system comprised of only healing agent that does not require the use of catalyst, e.g. linseed oil, tung oil, etc., seems an effective viable way of overcoming the above drawbacks. The presence of a second phase decreases the likelihood of having both phases present at the same time and in the required ratio at the region of the scratch; hindering the restoration of the barrier properties of the coating itself and reducing the concentration of the microcapsules into the system. Figure 19 and Figure 22 depict the corrosion results obtained after exposing the specimens in an aggressive media by using different *one-step* self-healing approaches, i.e. tung oil [85] and POTS [89], respectively. The difference is mainly due to the type of action by which the healant repairs the damage, i.e. the first tends to reduce the growth of the damage by filling it with new material released from the microcapsule (Figure 17), while in the second the damage is isolated by the formation of a passive layer on the metal surface rather than repair. Both figures clearly display no sign of undercutting corrosion, indicating the effectiveness of the healing system used. However, based on the final use of the coating, the choice of correct methodology makes a difference. In fact, even though the second method showed a significant increase of the anticorrosion property of the healed coating, from an aesthetic stand point it is not suitable in a field where the decorative aspect is important, i.e. the automotive industry, on jewelry, etc.

As we can see, all those requirements are strictly connected to each other and can improve or degrade the quality of the coating, and they have to be takes into account in order to develop self-healing coatings through microcapsules with outstanding anticorrosion properties. These adverse effects are leading coating scientists to focus their attention on the development of coatings comprised of pH-sensitive inorganic nanocontainers as intelligent controlled release corrosion inhibitors [63–65, 93, 116–118, 138–140]. The use of smaller capsule will enhance this probability, ensuring higher homogeneous dispersion of the nanocontainers within the coating matrix [141]. Due to their high lateral surfaces, particles are able to delivery significant amount of either healing agents or corrosion inhibitors. In addition, due to their nanoscale size it is possible to distribute them uniformly in the matrix.

7 Conclusion

This work is intended to provide the reader with an appreciation of the complexities of this problem and some possible solutions. Some selected recent contributions are reported here and critically assessed.

Acknowledgment

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