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Advanced Multifunctional Corrosion Protective Coating Systems for Light-Weight Aircraft Alloys— Actual Trends and Challenges

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Additional information is available at the end of the chapter

Abstract

The present chapter is devoted to the recent trends in the field of the advanced corrosion protective layers elaboration. The chapter begins with brief classification of the standard aluminum alloys, remarking their importance for the transport sector, as well as the basic corrosion forms, typical for these alloys. It continues with the basic requirements regarding the elaboration of durable and reliable coating systems and the factors of detrimental effect during the service life time. The concept for passive and active corrosion protection capabilities is remarked as well. After description of the need for multi-layered coating systems elaboration, the function of each layer is described beginning from (i) UV light–absorbing exterior layers, (ii) self-repairing reinforced intermediate barrier layers, and (iii) cerium oxide primer layers (CeOPL). The importance and the basic approaches for metallic alloy preliminary treatment are remarked, as well. Finally, the basic concepts and the function of each layer in advanced multilayered coating system are summarized in a special section. The chapter finishes with brief conceptual description of two advanced versatile technological synthesis methods, which enable elaboration of organic/inorganic hybrid polymers and reinforcing nanoparticles.

Keywords: aircraft alloys, corrosion protection, cerium conversion coatings, technological aspects, hybrid and nanocomposite materials, corrosion inhibitors, multifunctionality

1. Aluminum alloys as basic constructional material for the aircraft and transport industry

Aluminum (Al) is a lightweight relatively easily treatable metal that possesses an aptitude for passivation by formation of a natural oxide layer. Nevertheless, the pure Al is inapplicable in the industrial practice, since it does not present satisfying mechanical properties. The Al-based and

magnesium (Mg)-based materials used for construction of various transport devices and vehicles must correspond to industrial standards, to construct transport equipment with reliable and predictable properties and performance. Recently, besides in the aircraft industry [1–3], the aluminum alloys have found continuously increasing applications for car body panels [4] and even in the modern shipbuilding [5, 6]. Besides, it is a common practice to apply multilayered coating systems for corrosion protection of metallic details, assemblies, and entire vehicle constrictions [7] (**Figure 1**).

According to the worldwide nomenclature, the Al alloys are denominated as "AA" with four digit numbers that reveal their chemical compositions as follows: AA1XXX—almost pure Al; AA2XXX with 1.9%–6.8% of copper (Cu); AA3XXX with 0.3%–1.5% of manganese; AA4XXX with silicon (Si) addition between 3.6% and 13.5%, AA5XXX with Mg content between 0.5% and 5.5%; AA6XXX prepared by both Mg 0.4%–1.5% and Si 0.2%–1.7%; AA7XXX with zinc (1%–8.2%); and finally, AA8XXX with other additives [14]. The rest three digits reveal the lower content elements and the acceptable contaminant concentrations. The compositions of the most widely used Al–Cu alloys, according to ISO 3522-2007, are summarized in **Table 1** [14].

The aluminum alloys are ranked second following the steels for industrial and household applications. Their mechanical properties—strength, stiffness, and durability—combined with their low weight and relatively low price make them preferable constructive materials. For instance, about 70% of all metal details in the nowadays airplanes are composed of aluminum alloys [3]. Irrespective of their excellent mechanical properties, these alloys exhibit a serious disadvantage—they are susceptible to corrosion. It is attributed to the additive components (Cu, Fe, Mn, Mg, Si, and so forth), which form intermetallics of a various composition dispersed throughout the aluminum matrix during the alloys hot rolling. In aggressive media, such as chloride ions containing ones, these inclusions become centers of initiation and further proliferation of localized corrosion [15].

Figure 1. Various kinds of vehicles composed by aluminum alloys. (a) Airbus A380 [8], (b) Boeing 747 [9], (c) Antonov 225 [10], (d, e) aluminum car bodies [11], (f) aluminum ship type Littoral Combat Ships [12], (g) aluminum sport boat [13].

Designation	Si%	Cu%	Mn%	Mg%	Ni%	Ti%	Others%
AA2011	0.4 max	5.0–6.0	—	—	—	—	Pb–0.4, Bi–0.4
AA2014	0.5–1.2	3.9–5.0	0.4–1.2	0.2–0.8	—	0.15 max	—
AA2017	0.2–0.8	3.5–4.5	0.4–1.0	0.4–0.8	—	0.15 max	—
AA2018	0.9 max	3.5–4.5	—	0.4–0.9	1.7–2.3	—	—
AA2024	0.5 max	3.8–4.9	0.3–0.9	1.2–1.8	—	0.15 max	—
AA2025	0.5–1.2	3.9–5.0	0.4–1.2	—	—	0.15 max	—
AA2036	0.5 max	2.2–3.0	0.1–0.4	0.3–0.6	—	0.15 max	—
AA2117	0.8 max	2.2–3.0	0.2–0.5	—	—	—	—
AA2124	0.2 max	3.8–4.9	0.3–0.9	1.2–1.8	—	0.15 max	—
AA2218	0.9 max	3.5–4.5	—	1.2–1.9	1.7–2.3	—	—
AA2219	0.2 max	5.6–6.8	0.2–0.4	—	—	0.02–0.10	V–0.10 Zr–0.18
AA2319	0.2 max	5.6–6.8	0.2–0.4	—	—	0.10–0.20	V–0.10 Zr–0.18

Table 1. Nominal standard compositions of copper-containing aluminum alloys.

2. Corrosion processes nature and impact

According to the exact definition, the corrosion, according to IUPAC, is a physical-chemical interaction between a metal and its environment, which results in changes in the properties of the metal and which may often lead to impairment of the function of the metal, the environment, or the technical system of which these form a part [16].

Nowadays, the term "corrosion of the materials" comprises a large variety of detrimental processes which lead to lose of material integrity and mechanical properties of the corresponding details. Thus, recently, concepts for "corrosion of the plastics," formulated by Hojo et al. [17], as "degradation of polymeric materials with chemical reaction in which the molecular chains is cut" or "glass materials corrosion" [18], described as "fast and structure-dependent proton/cation(s) exchange and associated volume contraction which mechanically ruin the parts." In addition, the term "corrosion" already includes "microbially induced corrosion (MIC)" [19–21] caused by the metabolism of various acidogenic microorganisms or alcaligenes. The anaerobic microorganisms, such as iron-reducing bacteria (IRB) and sulfate reduction bacteria (SRB), also cause considerable corrosion damages [19]. The former reduces the insoluble ferric corrosion products to the soluble ferrous ones, whereas the latter reduces sulfate to sulfide compounds, contributing for additional cathodic activity enhancement. In general terms, all the corrosion processes result in partial or complete destruction of the metallic details.

Particularly, the metal corrosion processes possess electrochemical nature, and their appearance, rate, and impact are strongly dependent on the metal part features (i.e., structure and composition) and the environmental conditions (i.e., temperatures, pH, oxidant concentrations, and so forth).

Davis [22] has summarized all the basic corrosion impact forms, classifying them in uniform and localized corrosion phenomena (**Figure 2**).
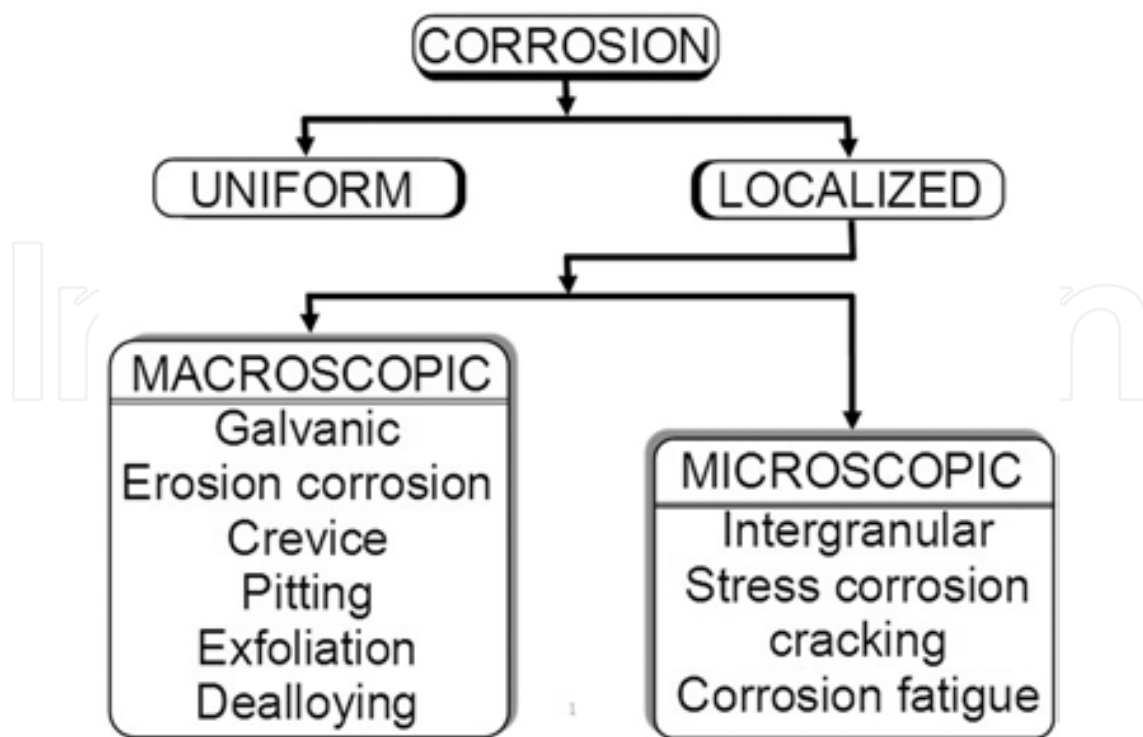
Figure 2. Basic types of corrosion phenomena, according to Davis [22].

Finally, it is worth to remark that the corrosion process can alter its form pitting to intergranular [23]. The occurrence of especially cyclic mechanical loading enhances the corrosion impact, resulting in complete assembly or equipment failure. In general terms, the corrosion processes, related to the industrial alloys, usually begins as galvanic corrosion on the alloys' surface and continue subsequently as complete selective dissolution of the more active composing metals. Afterward, the complete dissolution of these alloy's components, resulting in pitting corrosion, continues in depth on the grain boundaries inside the metallic alloy, converting to intergranular corrosion. This already severe form of corrosion can lead to large domains exfoliation, due to thermal expansion of the heaped corrosion products and the entrapped moisture freezing. All these localized corrosion forms decrease the efficient cross-section of the metallic details, composing whatever assembly or construction. Finally, all these processes together lead to complete constructional failure, being sometimes even potential danger for the human life. One of the most famous cases is the accident with flight no. 243 at 1988 [24] (**Figure 3**).

After this accident, all the worldwide aircraft industry has accepted regular inspections, and the exploitation lifetime of the used commercial airplanes has been strongly restricted, in terms of maximal permitted flight hours, before decommission.

Thus, from all statements mentioned above, it can be considered that the term "corrosion" relays to whatever physical, chemical, or biological process which causes gradual geometrical shape altering and mechanical properties deterioration of given solid state object of industrial origin, due to interactions with its surrounding environment.

To prevent all these phenomena, the metallic surfaces should be insulated from the surrounding environment by coating. However, it should be mentioned that even the protective coatings

suffer destructive ageing processes and consequently should be created advanced coating systems with extended durability and capabilities for active protection even after any damage of their integrity.

Figure 3. Photography of the flight accident happened at 28th of April 1988 due to corrosion fatigue [24].

3. Protective coatings and layers: basic requirements

The efficient corrosion protection is only achievable when dense, uniform, and adherent layers are deposited. These protective layers should serve as efficient barriers against corrosive species ingress toward the protected metallic surface. However, these protective layers suffer the surrounding environment impact, as well. Consequently, the protective layers are susceptible to deterioration until barrier layer failure. Such failure can appear due to various reasons, like:

- Mechanical impact—caused by scratching, friction, and so forth

- Thermal expansion coefficient noncompliance—between the metallic surface and the protective layer itself.

- Chemical impact—when organic solvents or strong oxidants occur in the surrounding environment.

- Sunlight radiation—The UV spectrum of the sunlight radiation causes polymer chain disruption by direct scission or by photoinduced oxidation with the presence of oxidants [25].

Undoubtedly, the real exploitation conditions usually include combinations of the above mentioned detrimental factors. Thus, the coating systems should form durable adhesive barrier layers to execute efficiently their function of passive corrosion protection. Hence, in the industrial practice, the deposition of multilayered coating systems is commonly accepted practice (**Figure 4**). This
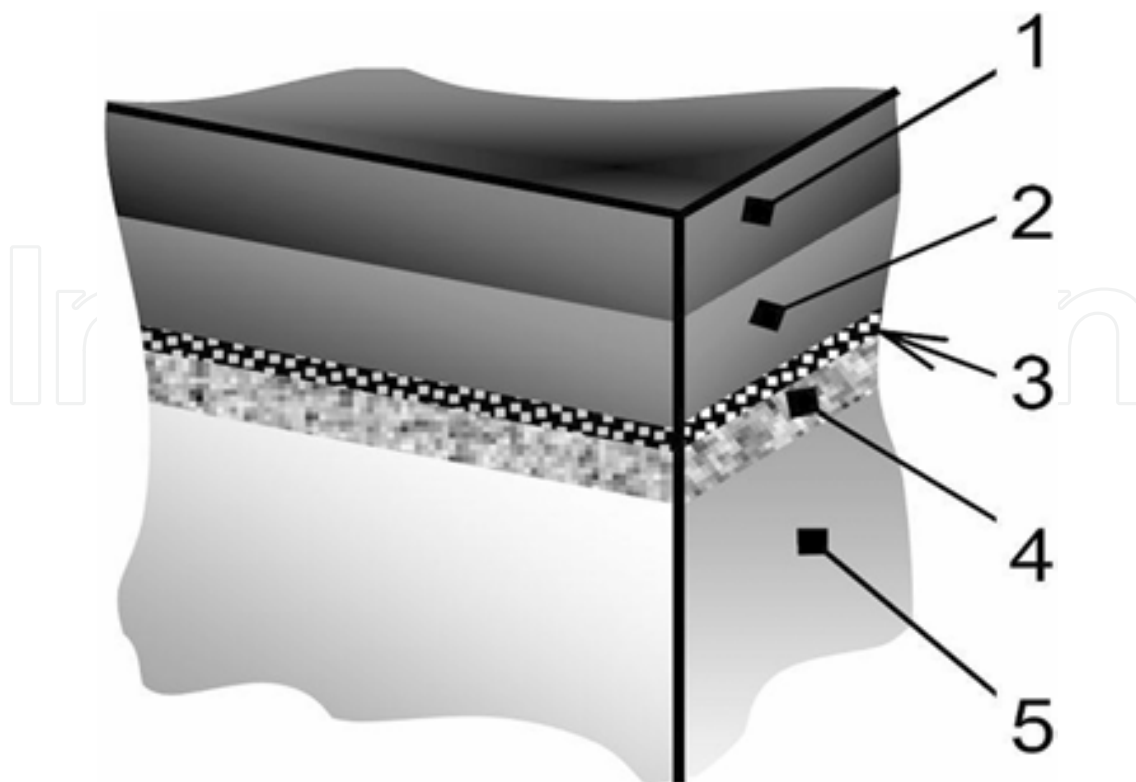
Figure 4. Schematic presentation of multilayer coating system according [7]. (1, 2) finishing double layer of polyurethane, (3) intermediate adhesive layer; (4) primer hybrid coating; (5) metal substrate.

approach enables deposition of advanced barrier coatings, where each composing layer has its own function.

However, recently new requirements arisen, related to further extension of the corrosion protective capabilities after barrier layer integrity disruption. Consequently, nowadays, coating systems should be capable for active corrosion protection, after damaging of their integrity. There are three basic roads to achieve active corrosion protective abilities:

•   Incorporation of corrosion inhibitors

•   Encapsulation of polymerizable compounds

•   Introduction of hydrophobic compounds

•   Addition of UV absorbers

According to the application of the coating system, other more specific requirements should appear. Montemor [26] proposes more complete classification of the beneficial properties and the respective requirements, related to the coating system application (**Figure 5**).

Other actual aspects related to the elaboration of advanced corrosion protective layers are rather related to the technological approaches used for their synthesis and deposition and the respective coating ingredients. In other words, every new coating system elaboration should comply the environmental restrictions, related to the use of volatile organic compounds (VOCs), [27, 28] and toxic metals, such as Pb, Cr, As, and so forth [29, 30].
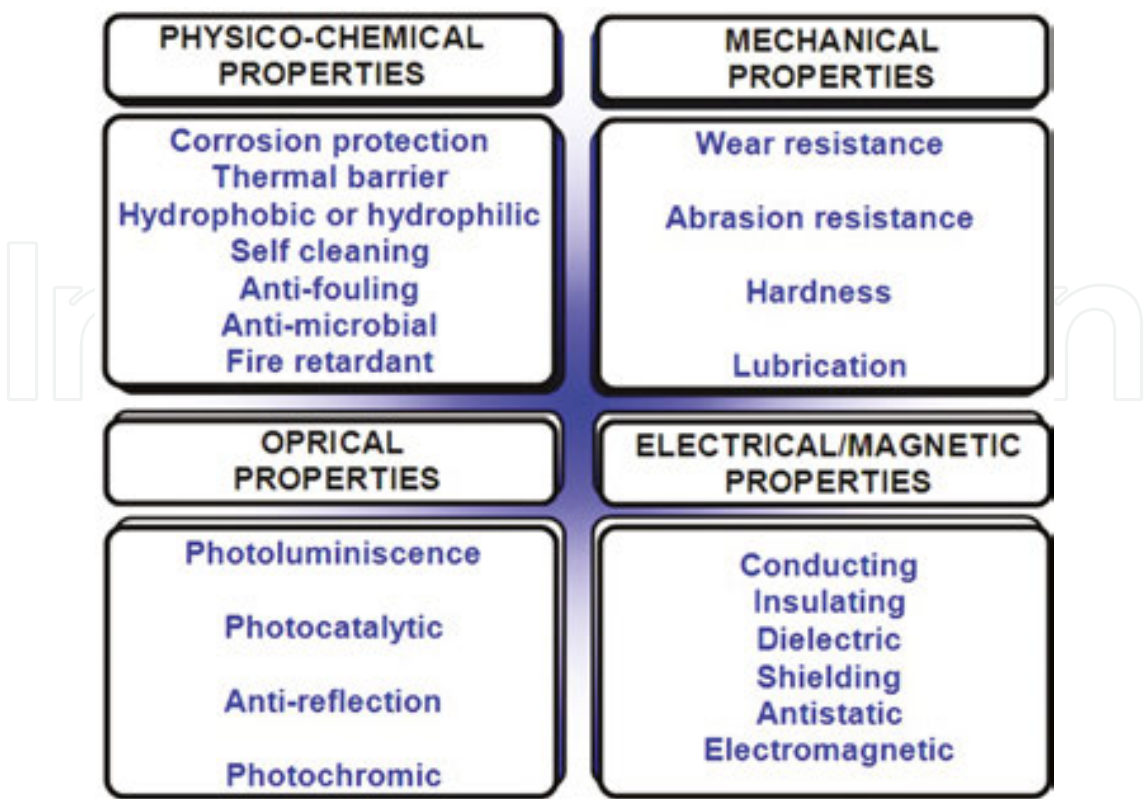
Figure 5. Overview of surface properties that can be developed or enhanced through functionalization by organic, inorganic or hybrid coatings, according to Montemor [26].

This considerable variety of requirements, related to the elaboration of durable and reliable, environmentally compliant coating systems with active corrosion protective capability impose the need for multilayered systems, where each layer has its own function. Thus, the coatings have at least exterior films, intermediate layers, and coating primers. Hence, the large number of requirements can be distributed to each one of the coating layers to obtain advanced multilayered coating system.

4. Exterior protective coatings and layers: basic requirements

The main function of the exterior layers is to protect the coating intermediate and primer layers against the impact of the surrounding environment. These exterior layers should possess mechanical strength against abrasion with high-speed solid particles, like dust or ice fogs, which spoil the fuselage metallic surface with the same speed as of the flight (i.e., up to 850–900 km/h). Other properties necessary for extension of the coating service lifetime are UV light absorption ability and hydrophobicity. The former property can be rendered by addition of UV absorbers into the external layers' composition. In this sense, Guillet [25] proposes several bi-phenyl, carbonyl-based compounds (**Table 2**).

Because the direct inclusion of these compounds to polymeric chain matrix is related to considerable difficulties, their preliminary incorporation in porous nanoparticles looks more appropriate approach. In this sense, ZnO, TiO$_2$, and titanates-based porous nanoparticles are

much appropriated, since these oxides possess photochemical properties, as well. Besides, the photosensitizing of TiO_2 particles is well-known method used for other applications such as photocatalysis [31], UV-spectrum photosensors [32, 33], elaboration of alternative energy sources [34, 35], and so forth.

Nevertheless, the approach of involvement of TiO_2 with incorporated photoabsorbers should be applied very attentively because the TiO_2 particles possess photodecomposition activity [36–39], and the organic UV light absorbers can terminate the polymerization processes of the basic coating layer matrix synthesis. Consequently, the elaboration of such coating compositions by addition of TiO_2 particles loaded by photoabsorbers should be combined by systematic comparative investigations with long-term UV-illumination, to detect whatever incompatibility effects on the basic polymer matrix. On the other hand, the successful introduction of preliminary impregnated titania nanoparticles into the basic polymer matrix converts the final coating as a composite material, where the TiO_2 particles serve as reinforcing phase, enhancing the mechanical strength, whereas the organic UV absorbers protect the polymer matrix against photochemical degradation. On the other hand, since ZrO_2 occupies the second place of the Mohs hardness scale after the diamond. That is why, zirconia-based composite protective coatings are already proposed for epoxide [40] and hybrid [41] polymer matrix.

Another aspect for barrier properties enhancement and service lifetime extension is to render hydrophobicity of the coating surface. Undoubtedly, one of the most efficient manners to avoid any corrosion phenomena is to render hydrophobic properties to the metallic surface. The surface hydrophobicity remarkably decreases the contact area with water condense. Another,
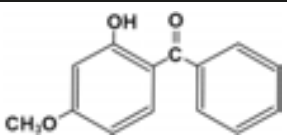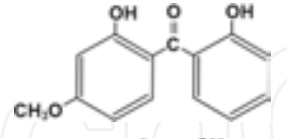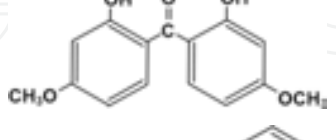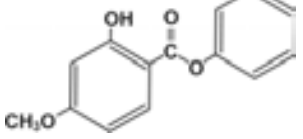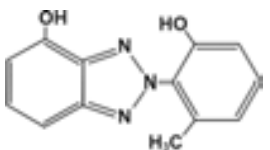
Name	Structural formula	Wavelength of maximal absorbance	Specific absorptivity
2-Hydroxy-4-methoxy benzophenone		326 nm	42.4
2,2′-Dihydroxy-4-methoxybenzophenone		327 nm	41.2
2,2′-Dihydroxy-4,4′-dimethoxybenzophenone		343 nm	50.2
Phenyl salicylate		310 nm	23.6
2-(2′-Hydroxy-5′-methylphenyl)-benzophenone		340 nm	73.0

Table 2. UV light–absorbing compounds proposed by Guillet [25].

much more important benefit is that the water drops have low cohesion to the metallic surface and can be leached from it by the spoiling air streams during flight. The hydrophobic surfaces do not allow water film formation on the metallic surface, preventing continuous contact between the metallic surface and any corrosive electrolyte.

The actual trends for hydrophobic and super-hydrophobic coating layers development are based on the formation of highly textured cerium oxide primers with micro and nanoflower [42], Gecko footprint [43] morphologies. This approach enables to avoid also the snow and ice heaping on the wings, which was the suspected reason for the aircraft crash at 7th of February 1958 in Munich, which was appeared to be a great disaster for the "Manchester United" football team during large years [44].

Nowadays, the de-icing procedures accepted as a common practice for the winter time exploitation in the commercial aircraft services appears the main reason for inconveniences, often related to schedule delays. In addition, these operations increase the economical spends, related to the needs for deicing solutions, staff, and equipment. In this sense, the hybrid polyfluorinated hybrid coatings [45] appear to be rather attractive alternative, since these coating materials combine the hydrophobicity with the beneficial features of the hybrid materials, discussed in the previous sections.

An interesting approach appears to be the proposed one by Arellanes-Lozada et al. [46]. This author's work-team proposes poly(1-vinyl-3-alkyl-imidazolium hexafluorophosphate, as corrosion inhibitor for aluminum corrosion in acidic media. This polymer seems really interesting, since it is able to be used as an alternative hydrophobic coating system, because it combines the beneficial effects of the presence of phosphate groups, long aliphatic chains, and hydrophobic fluorine moieties (**Figure 6**).
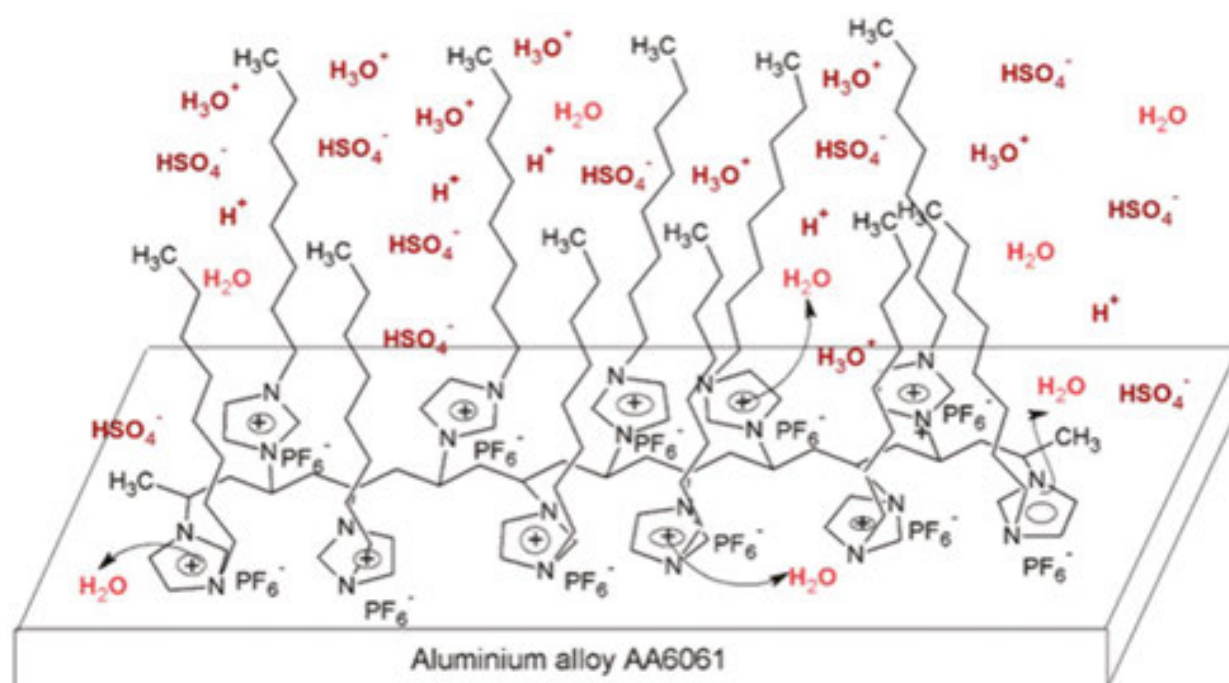

Figure 6. Schematic model of the corrosion protective action of poly(1-vinyl-3-alkyl-imidazolium Hexafluorophosphate toward AA 6061, proposed in [46].

Finally, it is important to mention that the exterior finishing coating layers should possess good adhesion to the intermediate layers. This indispensable property can be achieved easily when the basic polymer matrix is based on the same ingredients. Thus, some recent trends for development of the basic matrix of the exterior layers are described in the next paragraph.

5. Intermediate coating layers: barrier properties and self-reparation abilities

The polymer matrixes can possess organic nature, like polyepoxides, polyurethanes, polymethylmethacrilates, and so forth, or to have inorganic composition, being in form of glasses (i.e. silicates). Recently, various intermediate classes of materials have been introduced in the industrial practice. Hence, the use of organically modified inorganic polymers or hybrid materials opens entire new directions for advanced polymer matrix development. Haas and Rose [47] have done a versatile classification, including namely these intermediate classes of materials (**Figure 7**).
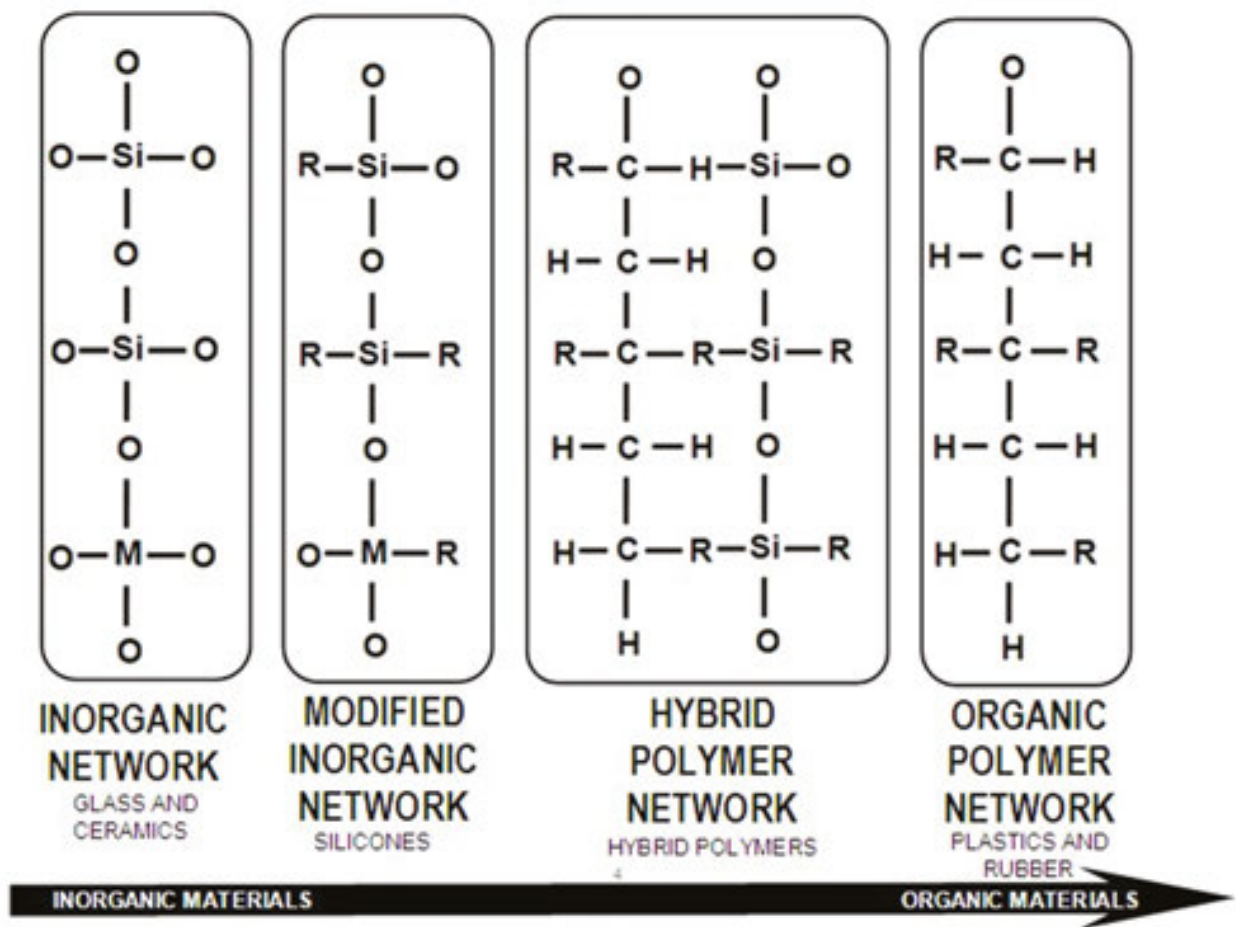

Figure 7. Classification of the basic types of polymer materials, according to Haas and Rose [47].

These intermediate groups of materials enable specific combination of the beneficial features of both the organic and inorganic composing moieties as follows [48, 49]:

- Organic part: (i) improved adhesion to the finishing organic paint layers; (ii) elasticity for compensation of the higher dilation coefficient, possessed by the metallic substrate; and (iii) hydrophobicity.

- Inorganic part: (i) improved adhesion to the coating primer layers; (ii) thermal resistivity; and (iii) mechanical strength.

In this sense, Frignani and coauthors have done [50] comparative assessment of primer coatings, obtained from alkoxides with different aliphatic chains, as follows: c n-propyl
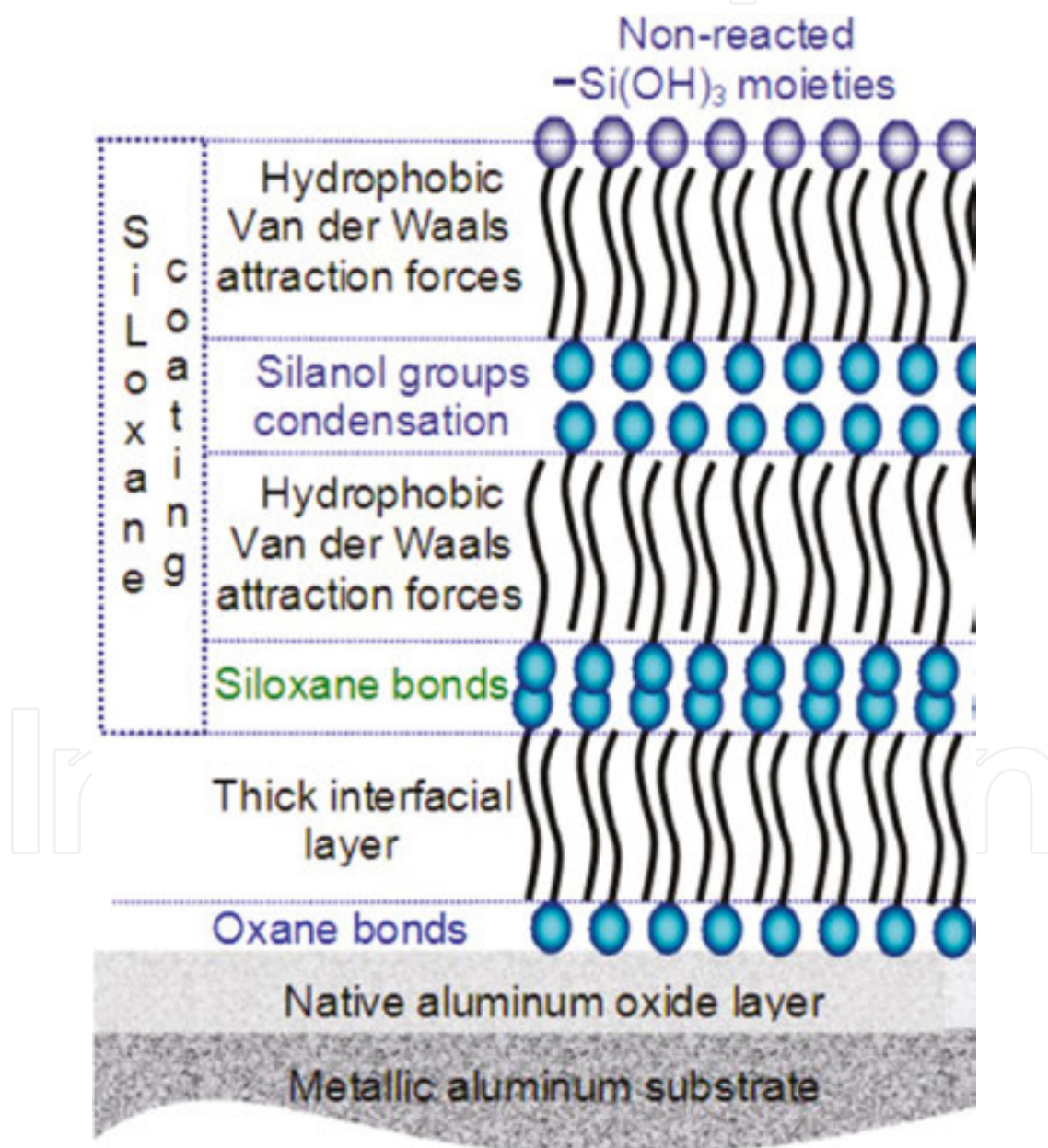

Figure 8. Schematic view of self-assembled barrier protective film on aluminum surface according to Frignani et al. [50].

trimethoxysilane-C_3H_7-Si-$(OCH_3)_3$;   n-octyl   trimetoxisilane-C_8H_{17}-Si-$(OCH_3)_3$;   n-octadecyl trimethoxysilane-$C_{18}H_{37}$-Si-$(OCH_3)_3$ and bis-trioximethyl-silyl-ethane – $(CH_3O)_3$-Si-C_2H_7-Si-$(OCH_3)_3$. As conclusion, the authors have established that the larger aliphatic chains enhance the obtaining of thicker layers. The aptitude for self-healing provided by the hydrophobic intermolecular attraction (**Figure 8**), with simultaneous repulsion of entrapped water drops appear additional beneficial properties

These layers reveal aptitude for self-assembling, and this kind of hybrid materials is also known as (SAM—self-assembled monolayers). They have significantly lower number and size of defects in their structures and thus enable more efficient protection via formation of dense barrier layers [51, 52].

Another strategy is to encapsulate polymerizable substances. In this case, polymerizable compounds are enclosed inside polymer or glass capsules to polymerase when are exposed to air, by mixing each other or by toughing ingredients of the basic matrix. Following this concept, several authors [53, 54] have characterized an epoxy resin loaded by urea-formaldehyde submicrometer-sized capsules, filled with dicyclopentadiene as an active healing agent. Recently, three review works have been done over the variety of possible self-healing organic coatings [55–57] (**Table 3**).

The protective properties of the intermediate layers can be further improved, by addition of ceramic micro-sized and nanosized particles as reinforcing phase. In this sense, CeO_2 [58, 59] and titanium dioxide (TiO_2) [60, 61] have been recently obtained by precipitation from colloidal systems. Both these oxides possess significant mechanical and thermal strength and can be successfully used as reinforcing phase of advanced nanocomposite coating systems with

No	Self-reparation mechanism	Examples for self-reparation agents
1.	Molecular interdiffusion	Poly(methyl methacrylate) (PMMA) and PMMA–poly(methoxyethyl acrylate) (PMEA) copolymers
2.	Photo-induced self-healing	1,1,1-Tris-(cinnamoyloxymethyl) ethane (TCE) with urethane dimethacrylate (UDME), triethyleneglycol dimethylacrylate (TEGDMA)–based monomers
3.	Recombination of chain ends	Reactions such as polycarbonate (PC), polybutylene terephthalate (PBT), polyetherketone (PEK), and PEEK, polyphenylene ether (PPE)
4.	Reversible bond formation	Organosiloxanes, ionomers
5.	Living polymer approach	Living ring-opening metathesis polymerization (ROMP)
6.	Self-healing by nanoparticles	Described above
7.	Hollow fiber approach	Described above
8.	Microencapsulation approach	Diglycidyl ether of bisphenol-A (DGEBA), nadic methyl anhydride (NMA), benzyl dimethylamine (BDMA)

Table 3. Possible self-healing mechanism and active reparation agents according to Wu et al. [55].

extended durability. In addition, when these particles are preliminary filled by corrosion inhibitors, the final nanocomposite coatings obtain additional capability for active corrosion protection by gradual inhibitor release in the damaged zones, as it is already proposed by Zheludkevich et al. [48, 62] (**Figure 9**).

A promising alternative to the use of ceramic nanoparticles as inhibitor containers reinforcing the basic polymer matrix is the involvement of carbon nanoparticles (CNP) [63, 64]. Especially, the hollow carbon nanotubes (CNT) allow to be filled by inhibitors via intercalation. Indeed, the remarkable adsorption capability of the carbon-based materials was demonstrated by Lavrova [65] and Jumayeva et al. [66].

Various corrosion inhibitors are recently tested to substitute the already banned Cr(VI) compounds. Hence, the corrosion inhibition capability of benzotriazole and tolyltriazole [67–70] was examined, evincing the possibility for the use of these compounds as corrosion inhibitors. The inhibition mechanism of these compounds is based on film formation via adsorption on the metallic surface or by precipitation of derivative complex compounds. In this sense, the UV light absorbers, proposed by Guillet [25] (**Table 2**), should also possess potential corrosion inhibitive effect, protecting simultaneously both the coating polymer matrix against UV radiation, metallic surface against corrosion.

Alternatively, Cotting and Aoki [71] have proposed to encapsulate cerium-based corrosion inhibitor inside polystyrene capsules before their inclusion in an epoxide matrix. Indeed, the lanthanides have also shown high inhibition efficiency, due to their aptitude to form insoluble
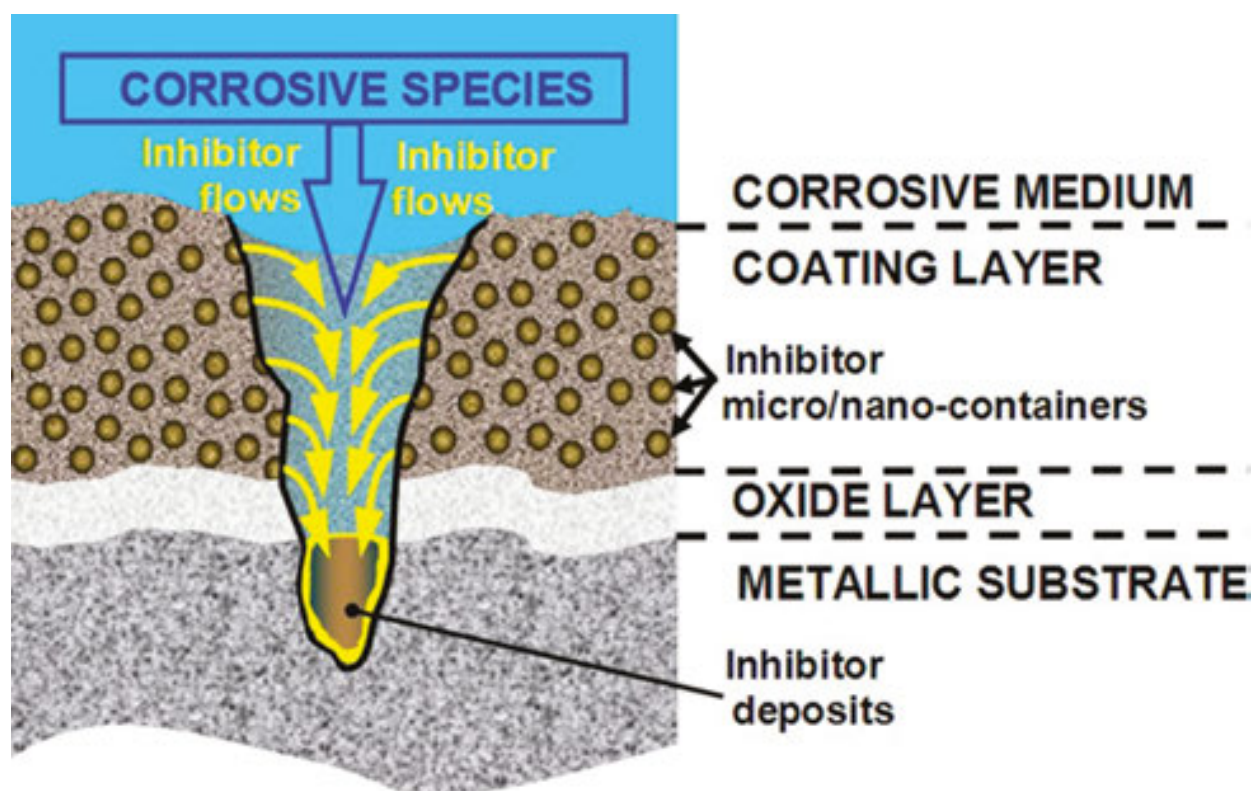

Figure 9. Schematic view of self-healing effect by inhibitor gradual release from reinforcing nanoparticles.

hydroxides with the free OH⁻ ions in the corrosive medium. The compounds of these elements are particularly efficient for corrosion prevention of Al corrosion, since this metal and its alloys are very susceptible to corrosion even in weakly alkaline media. Among the lanthanides, the cerium compounds have shown the highest inhibition efficiency [72]. In this sense, various comparative investigations have been performed, to determine the influence of Ce(III) or Ce (IV) compounds [73–75], the optimal Ce-inhibitor concentration [73, 75, 76], as well as the impact of the anionic moiety of the respective Ce-salt [76]. As general results of these research activities, it was evinced that the Ce(III) compounds are much more efficient inhibitors for AA2024-T3, whereas the Ce(IV) ones can even enhance the corrosion attack at higher concentrations. Furthermore, for each Ce(III) compound, an optimal concentration threshold exists, depending on the alloy to be protected, the corrosive medium properties, and so forth. Thus, at higher concentrations, the Ce-compounds enhance the corrosion instead to inhibit it. Here, the term "catalyst" is not appropriate, because the Ce-compounds also suffer chemical conversions, being activators of the corrosion processes. As was already mentioned above, the Ce-compounds and the organic inhibitors follow different mechanisms of inhibition. Besides the former decelerate the cathodic reactions, affecting predominantly the cathodic zones, whereas the latter form protective films on the entire metallic surface. Consequently, a question has appeared about whether a synergistic effect could occur between these distinguishable kinds of inhibitors. Hence, recently, the potential synergism between both kinds of inhibitors was examined by various authors on Al/Cu couples [77], AA5052 alloy [78], and even carbon steel [79]. Finally, the Ce-compounds have shown capabilities to form uniform adherent primer layers at defined conditions.

6. Cerium oxide primer layers deposition: basic concepts and requirements

The basic function of the primer coating layers (i.e., the coating primers) is to improve the adhesion between the native Al-oxide layer of the metallic substrate and the upper (i.e., intermediate and finishing) layers, commented in the previous sections. Some authors even report for self-healing properties, possessed by these films [80].

Undoubtedly, among the basic advantages of this group of coatings is the possibility to deposit them by physical [81, 82], electrochemical [83–87], or chemical methods [88–94]. Regardless the method applied for cerium oxide primer layer (CeOPL) deposition, the respective technological regime includes three basic stages: (i) preliminary treatment of the metallic substrate, (ii) the CeOPL deposition itself, and (iii) final sealing of the already deposited CeOPL film [94, 95]. In this sense, a large field of possible combinations among the conditions for execution of each technological procedure exists.

As was mentioned in the previous sections, the inhibitor effect of the cerium compounds is based on the precipitation of $Ce(OH)_3$ and/or $Ce(OH)_4$, predominantly on the cathodic areas of the Al alloys (composed by nobler metals), due to the cathodic reduction of the dissolved oxygen. However, the real mechanism is much more complicated and includes participation of intermediate peroxo-complexes [93, 94].

Scholes et al. [93] have made a simplified scheme (**Figure 10**) of the processes proceeding during the CeOPL deposition, after addition of H_2O_2 as deposition activator.

The deposition of uniform, dense, and adherent CeOPL films instead of obtaining of discrete Ce precipitates appears a great challenge namely because of the complicated chemical mechanism. Besides the influence of the Ce-compound type and concentration, and, of course, the H_2O_2 activator content, the deposition mechanism and rate can be driven by regulation of various factors, like pH, temperature, occurrence of additives, and so forth. In this sense, the beneficial effect of various additives has been evinced, like black cuprous oxide "smut" [94], Al^{3+}, and Cl^- ions [96], pH-buffers [90, 97], and so forth. The recent work of Jiang et al. [98] has proposed combined Ce-V conversion layers for protection of magnesium alloys, discovering entire new direction for elaboration of combined conversion coatings. Finally, it should be mentioned that the metallic surface roughness and composition are of key importance for the quality and performance of the CeOPL, predetermining its adherence, structure, and density. The metallic surface characteristics can be easily modified by suitable preliminary surface treatment.
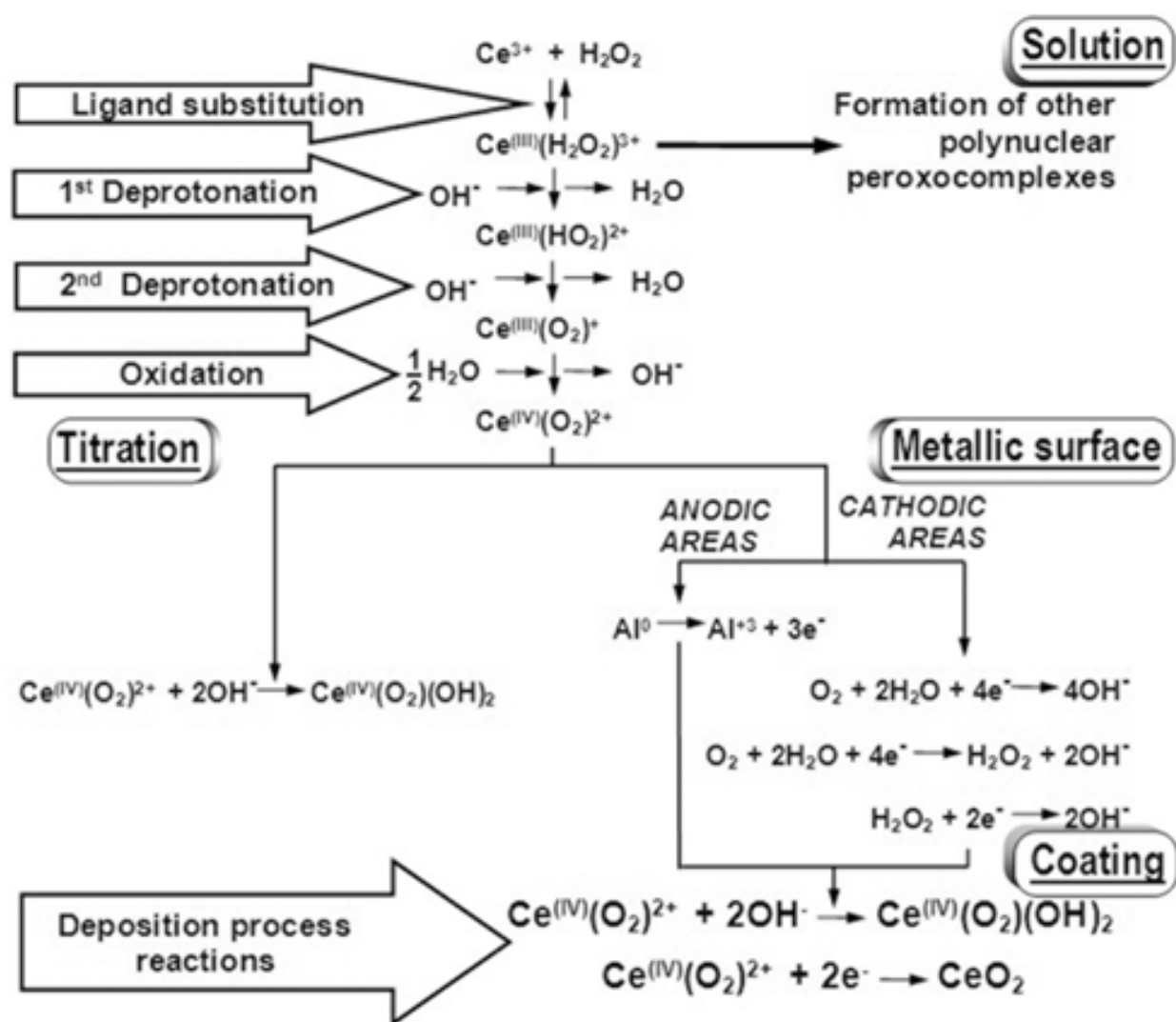

Figure 10. Schematic summarizing of the proposed mechanism of the cerium oxide layer deposition by Scholes [93].

7. Preliminary treatment procedures: basic concepts

The purpose of the preliminary treatment procedure is to modify the metallic substrate surface to be suitable for deposition of uniform and adherent primer layers. The impact of the preliminary surface treatment procedures comprises both the metallic surface roughness (by mechanical grinding in laboratory's conditions, or sand blasting in industrial scale) and the superficial chemical composition (by selective dissolution of the intermetallic inclusions, or affecting the surface oxide layer [92]).

The commonly accepted preliminary treatment procedures include four basic steps:

- Degreasing—by organic solvents, for removal of the temporal anticorrosion protective layer, deposited by the corresponding Al-producer, for protection during the alloy storage and transportation before its use for production of Al-details and tools.

- Mechanical grinding—This procedure is being performed by emery papers in laboratory's conditions and sand blasting, in real industrial scale. The basic purpose of this procedure is to smooth the metallic surface and to remove the thicker oxide layer, formed during the finishing metallurgical thermal posttreatment. Of course, immediately after this procedure, a new oxide layer is being formed on the bare metallic surface (even underwater film) because the exceptional passivation aptitude of this metal.

- Alkaline etching—This procedure results in dissolution of the surface aluminum layer, penetrating through the thin oxide layer, due to its defective structure and nonuniform composition. Usually, this film consists of boehmite γ-AlO(OH) domains with about 5 nm of thickness [99]. Even the corundum Al_2O_3 fraction has strongly defective surface, due to the incompleteness of the superficial crystalline lattice cells. That is why, the surface oxide layer cannot protect the underlying metal against the aggressive OH^- attack.

In addition, the surface oxide layers of the highly doped Al alloys are always interrupted by the intermetallic inclusions on the alloy's surface.

- Acidic desmutting—The purpose of this procedure is to remove the black smut of the oxides of the intermetallic inclusions (like Cu_2O, CuO, MnO_2, and so forth). Usually, this process is being performed by dissolution in diluted HNO_3.

Each one of these operations should be performed very attentively to obtain desirable surface conditioning. Besides, the optimal technological prescription for given aluminum alloy is not always appropriate for other alloys.

In this aspect, a comparative systematical investigation [100] was recently performed to evaluate the impact of each one of the above mentioned procedures. The authors have compared four groups of AA2024-T3 plates:

- Group G1: degreasing with an equal ratio of ethanol/ether mixture at room temperature for 10 minutes subjected to continuous stirring and subsequent abundant washing with distilled water;
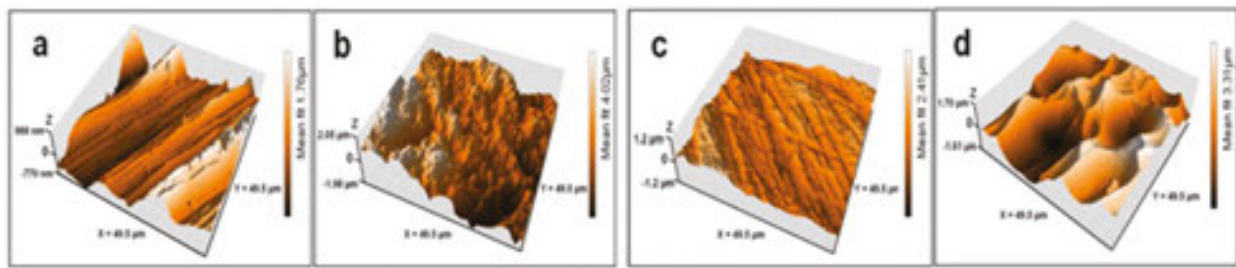
Figure 11. AFM images of samples underwent different approaches of superficial treatment; (a) degreasing (G1), (b) grinding (G2), (c) grinding and etching with a weak alkaline solution (G3) and (d) grinding and etching with a strong alkaline solution at high temperature (G4).

- Group G2: consecutive grinding with finer graded emery papers of 200, 360, 500 and 800 grit, followed by degreasing procedure with the same conditions as G1;

- Group G3: grinding as for G2 group, followed by etching with weak alkaline solution of (0.18 M) Na_3PO_4 and (0.19 M) Na_2CO_3 for 10 minutes at 30°C and subsequent abundant washing with distilled water;

- Group G4: grinding as for G2, followed by etching with a strong alkaline solution of (1.0 M) NaOH, (0.18 M) Na_3PO_4, and (0.19 M) Na_2CO_3 for 3 minutes at 60°C, followed by abundant washing with distilled water, desmutting in (6.0 M) HNO_3 solution for 2 minutes at room temperature and a final copious washing with distilled water.

As main conclusion, the authors have established that the highest rate of reproducibility belongs to the mechanically polished (G2) and the softly etched (G3) groups, whereas the only degreased (G1) and the hard etched (G4) samples are more distinguishable among themselves. Besides, the different preliminary treatment procedures have rather distinguishable impacts on the resulting morphology (**Figure 11**).

The surface morphology of given Al alloy after any preliminary surface treatment procedure depends on both its chemical composition and the thermal treatment regime, applied for its metallurgical production. Thus, although the same chemical composition, the obtained alloys could possess completely different mechanical properties, predetermined by the finishing metallurgical thermal treatment. Indeed, in another comparative investigation, involving CeOPL
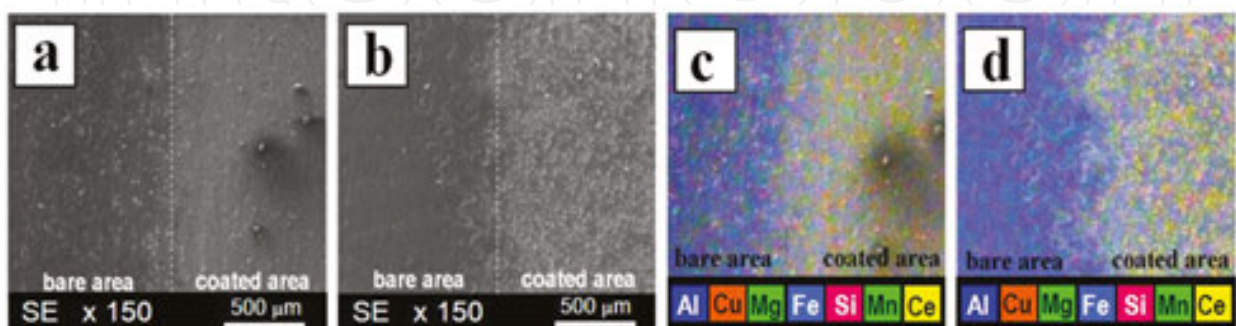

Figure 12. SEM (a, b) and EDX (c, d) images of the boundary between the bare and the coated areas of AA2024–T3 (a, c) and D16 AM (b, d) [100].

deposition at the same regime on AA2024-T3, and its Russian analogue—D16 AM tempered clad alloy [101], it was established that the CeOPL is much more uniform and fine grained in the former case, whereas in the latter case, the film is less uniform, because of the tempered shielding layers (**Figure 12**).

8. Conceptual summary

Following all the statements and the concepts, described in the present chapter, it can be inferred that a continuous need exists for elaboration of reinforced multilayered durable coating systems capable to provide active corrosion protection even after already appeared mechanical damages. Namely, the providing of durable and reliable corrosion protection enables extension of the service life time of the engineering construction and equipment and particularly—transport vehicles and aircraft. Thus, the reliable corrosion protection is the right way to save economical spends related to the shortening of the service life time before decommission of the used transport and especially aircraft equipment. In this sense, the UV light–protected, hydrophobic-reinforced self-reparable coating systems form reliable barrier against access of corrosive species to the constructive element metallic surfaces.

In this sense, the recent trends related to the elaboration of durable and reliable corrosion protective systems include several basic directions:

- Introduction of UV-radiation absorbers—to extend the service lifetime of the external coating layers polymeric matrixes.

- Involvement of reinforcing phases—to enhance the mechanical strength of the coating exterior finishes and the intermediate interlayers. This phase can serve even for UV-absorbent and/or corrosion inhibitor carriers.

- Use of hydrophobic and super hydrophobic finishes—to repel the water drops, preventing water film formation. Besides the hydrophobic intermolecular attraction forces among the coating ingredients enable additional repulsion of the already penetrated humidity in the coating bulk, achieving active corrosion protection.

- Encapsulation of active polymerizable agents—to achieve self-healing effect via coating self-recuperation.

- Addition of environmentally friendly synergistic corrosion inhibitor mixtures—to protect the metal surface even after coating damage.

- Deposition of reliable environmentally friendly coating primers—to substitute the widely used but already banned chromium conversion coatings (CCC).

As a result, advanced, environmentally compliant multilayered systems are under elaboration. Such system is well illustrated by Figueira et al. [102] (**Figure 13**).
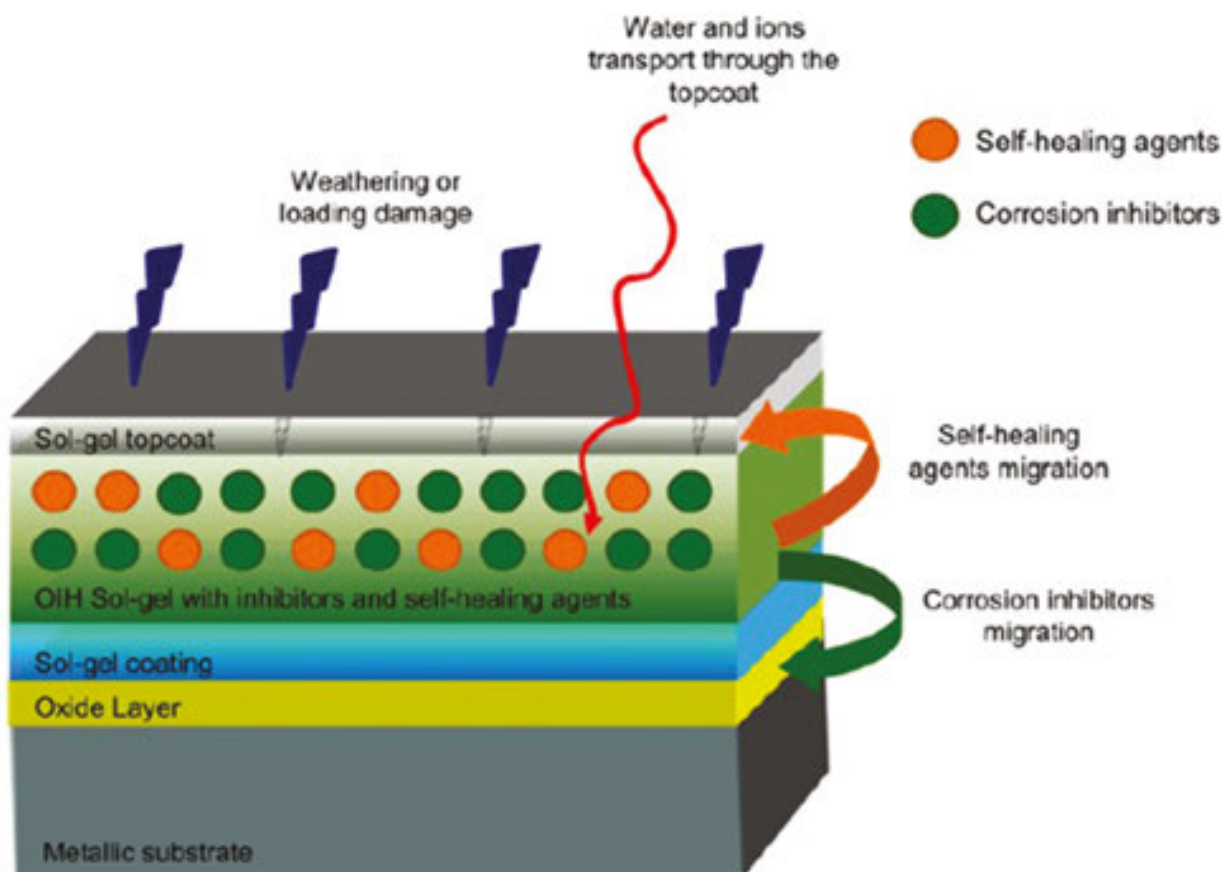
Figure 13. Schematic view of advanced multilayered coating system capable for active corrosion protection, according to Figueira et al. [102].

9. Advanced technological approaches

Besides the VOC-emission removal, the rest general trend in the technological aspect regarding the elaboration of advanced corrosion protective coating systems is to decrease the number of the intermediate technological states and the related energetic and material spends.

9.1. Sol-gel road

The literature analysis shows that recently the sol-gel approach enlarges its application, being more attractive for ease synthesis of hybrid polymer matrixes, able to combine the benefits of the organic and inorganic moieties (discussed above). As a result, a miscellaneous organic/inorganic polymer matrix is being obtained, as is illustrated by Wang and Bierwagen [103] (**Figure 14**).

The sol-gel method, with hybrid precursors, like the proposed by Frignani and coauthors [50], is based on hydrolysis of the metal alkoxides, with coincident polymerization of the hydrolyzed radicals. By this manner, the initial precursor mixture (sol) gradually converts to gel.
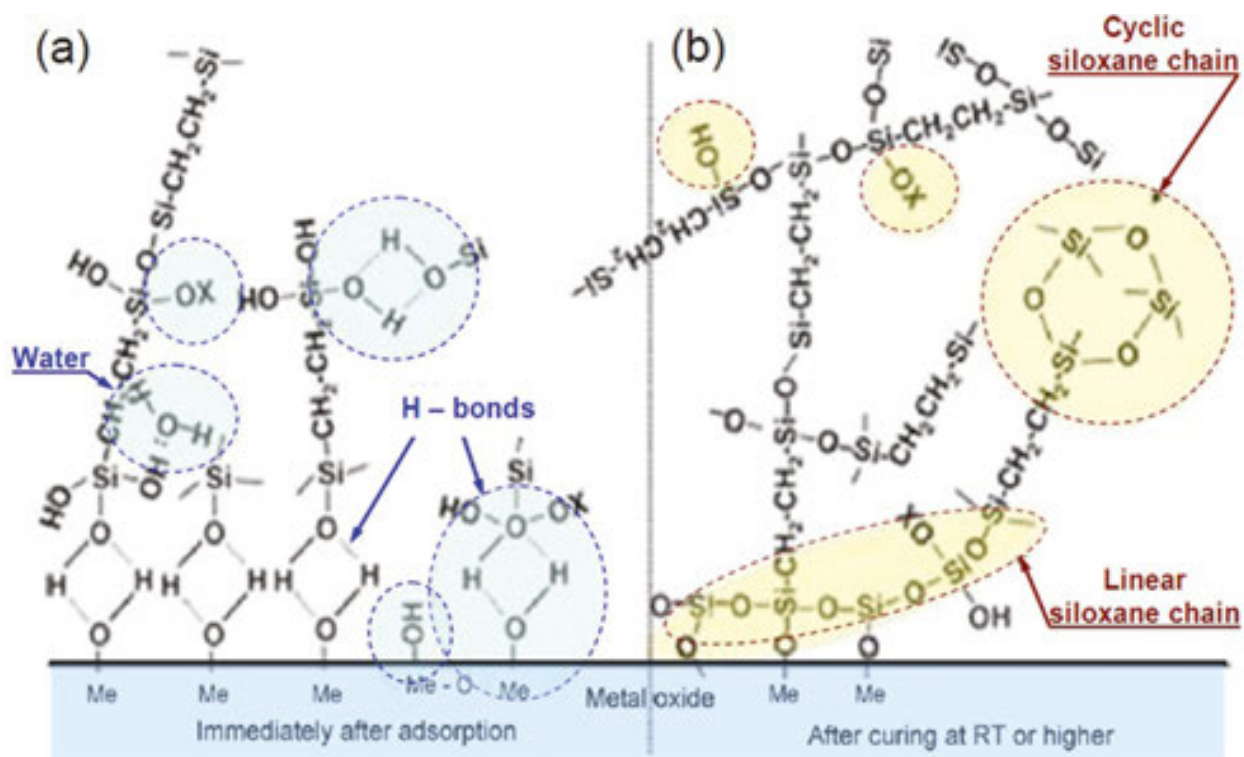
Figure 14. Simplified schematic of bonding mechanism between silane molecules and metal surface hydroxide layer (a) before condensation: hydrogen-bonded interface; (b) after condensation: covalent-bonded interface [103].

After deposition and posterior appropriated thermal treatment, the already deposited gel film converts to solid state protective coating layer.

According to Kozhukharov [104], there are seven basic important conditions, which have to be driven, to obtain desirable gel product (i.e., dense, uniform film):

- Chemical composition of the liquid medium

- Chemical composition of the precursors (alkoxides)

- Molar factor (ratio between the alcohol as medium and the alkoxides as precursors)

- pH of the medium

- Presence of additives

- Temperature

- Pressure and chemical composition of the gaseous medium over the gelling system during the drying (annealing) process

The basic technological stages of the sol-gel synthesis process are illustrated in **Figure 15**.

As was mentioned in the present chapter, the basic manner for further improvement of the sol-gel–derived hybrid polymer matrices is to add micro-/or nanosized solid state fine dispersed phase directly into the sol-gel liquid system at intensive stirring, to obtain equally distribution. Among the most efficient methods for production nanoparticle production is the so-called
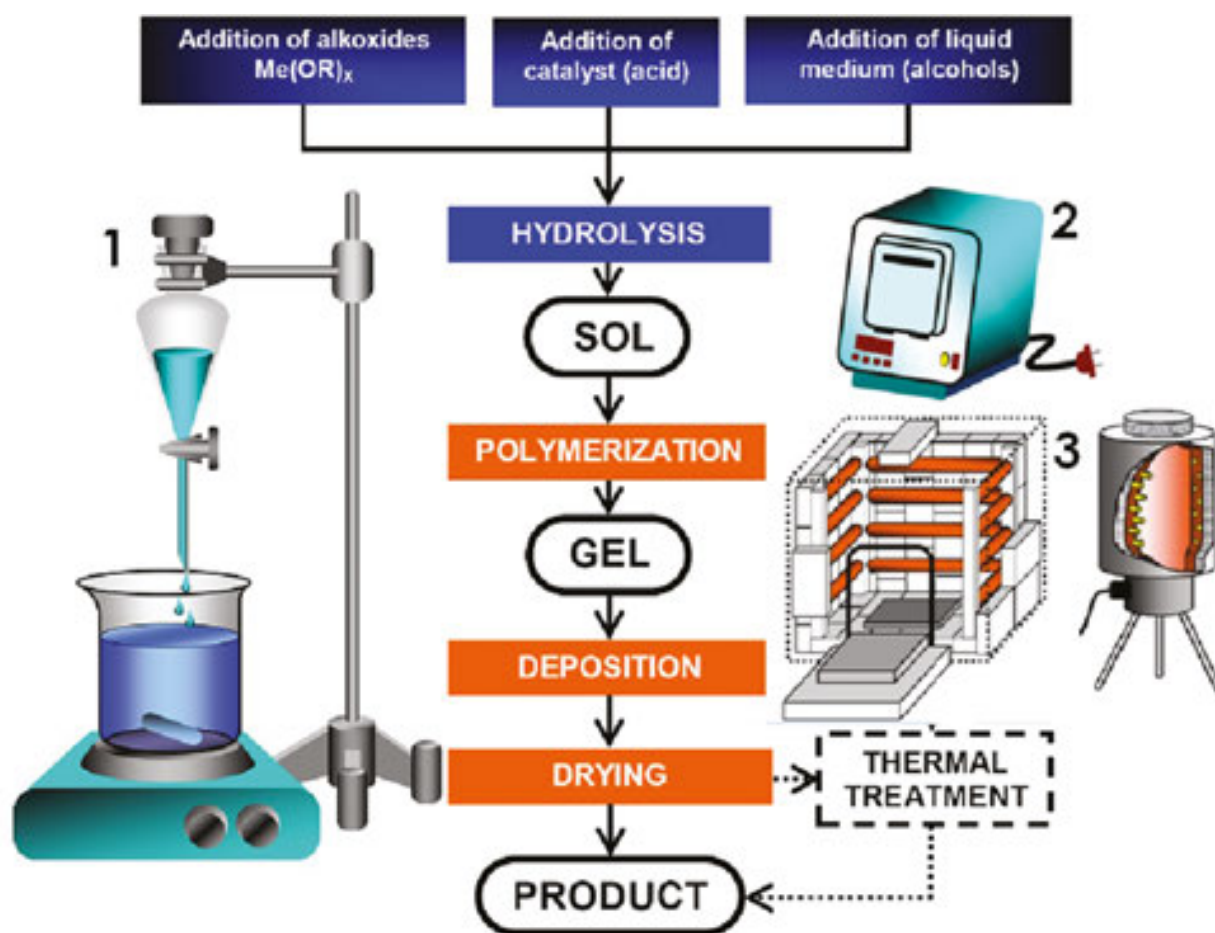
Figure 15. Schematic presentation of the basic stages of the sol-gel synthesis process [104]: (1) initial gel formation, (2) gel drying, (3) finishing high temperature treatment.

spray pyrolysis synthesis (SPS). Besides, thin ceramic protective films able to work at very high temperatures can be produced by so-called spray pyrolysis deposition (SPD). This method is applicable for protective layer deposition for turbine blades in jet turbines, compressors, and so forth

9.2. Spray pyrolysis

According to [105], when a liquid drop of solution is already sprayed, it undergoes several processes in the high temperature space, until its conversion to a solid particle. These processes are illustrated in **Figure 16** and described, in brief, below.

Initially, each drop suffers heating, and evaporation of the solvent (1), until it achieves the stage A. It could be described as a liquid particle, represented by saturated solution, surrounded by vapors of the solvent. Afterward, due to the evaporation, an additive solid shell forms (2), leading to intermediated three phases system (B). It is represented by vapors, solid porous shell, and still liquid core. That process passes simultaneously with initiation of chemical conversion of the precursors to the desired product. During this stage, an additive interaction between components of the vapors and the solid shell are possible, as well. After completion of the evaporation,
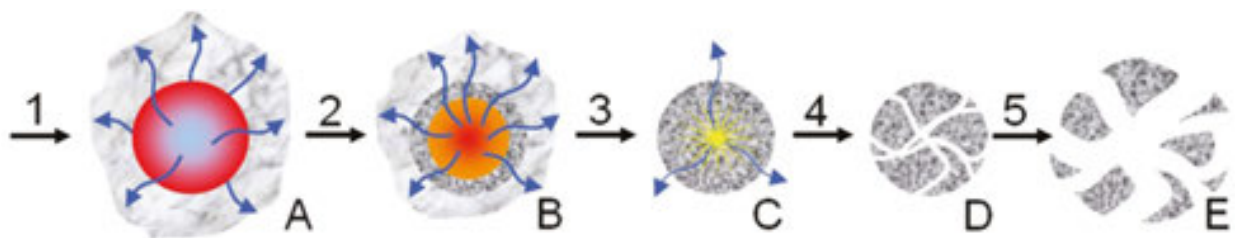
Figure 16. Thermal processes related to SPS [105].

because of expense of the entire liquid, a spherical solid particle of the product appears (C). The process could be finished until this stage. That approach is also known as "one drop–one particle." It enables production of powder materials with one fraction size of particles. If these particles are submitted to further calcinations, then they could split up to form even smaller particles (E). That approach permits production of ultra dispersive nanoparticles. The transition from stage C to E passes through intermediate stage D. This stage could be reached because of appearance of cracks and ruptures (4). Their appearance is consequence of mechanical tensions, due to difference of the temperatures, and the volume expansions between the core and the surface of the respective particle. Another reason for the crumbling of the particles is that the processes described above could pass accompanied by polymorphic transitions in the solid phase.

Among the basic advantages of this method is that it enables large scale production of fine dispersion solid particles by use of rather simple equipment [106].
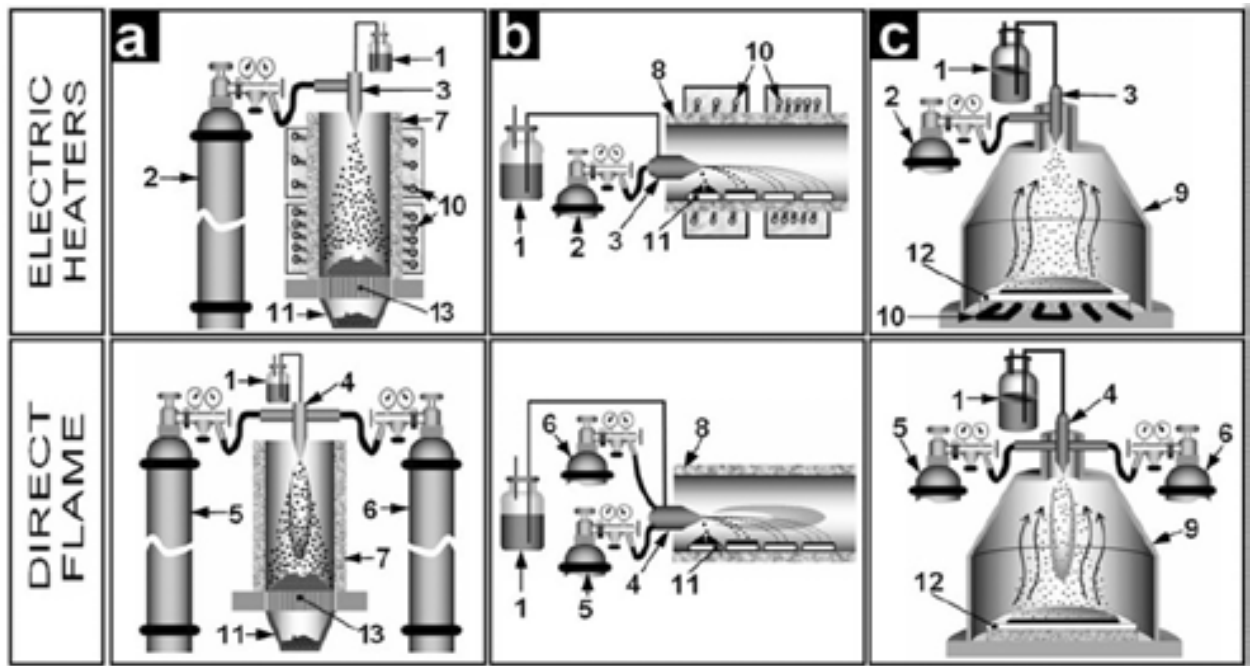
Figure 17. Basic constructions of spray pyrolysis installations [106, 107] a- vertical chambers; b- horizontal chambers; c- chambers for film deposition; 1- vessel for precursor solution; 2- gas bottle for carrier gas; 3- spray nozzle; 4- spray burner; 5- gas bottle for combustible; 6- gas bottle for oxidizer; 7- vertical chamber; 8- horizontal chamber; 9- chamber for spray deposition; 10- electric heaters; 11- powder collectors; 12- substrates for film deposition; 13- filters.

In general, all the possible modifications of the spray pyrolysis installations are consisted on several basic operation units, which function is assisted by additional devices. The main equipment components for synthesis via spray pyrolysis method are: 1—spraying nozzle, 2—High temperature work space (i.e., furnace), 3—product collector for the fine dispersed powder-like products or film deposition substrate. To insure the regular function of these basic operation units, additional units are necessary, such as: initial precursor solution containers, nozzle feeding pumps, carrier gas compressors, thermal energy sources, powder fraction separators, and so forth. The basic types of SPS/SPD installations are illustrated in **Figure 17** [107].

Of course, the spray drops and the respective obtained particles size formation are almost entirely predetermined by the nozzle construction. There are specially designed nebulizers and atomizers, which enable nanosized drops formation. Alternatively, nozzle-less spray pyrolysis equipment is also proposed in the literature [108].

10. General conclusions

Aluminum (Al) is a lightweight, relatively easily treatable metal that possesses an aptitude for passivation by formation of a natural oxide layer. Nevertheless, the pure Al is inapplicable in the industrial practice, since it does not present satisfying mechanical properties. Irrespective of their excellent mechanical properties, these alloys are very susceptible to corrosion, due to occurrence of alloying phases, which become centers of initiation and further proliferation of localized corrosion

Nowadays, the term "corrosion of the materials" comprises a large variety of detrimental processes which lead to lose of material integrity and mechanical properties of the corresponding details. In addition, the term "corrosion," already includes "microbially induced corrosion (MIC)". Particularly, the metal corrosion processes possess electrochemical nature, and their appearance, rate and impact are strongly dependent on the metal part features (i.e. structure and composition) and the environmental conditions (i.e. temperatures, pH, oxidant concentrations, and so forth).

Thus, the term corrosion relays to whatever physical, chemical or biological process which causes gradual geometrical shape altering and mechanical properties deterioration of given solid state object of industrial origin, due to interactions with its surrounding environment.

To prevent all these phenomena, the metallic surfaces should be insulated from the surrounding environment by coating. However, it should be mentioned that even the protective coatings suffer destructive ageing processes and consequently, should be created advanced coating systems with extended durability and capabilities for active protection even after any damage of their integrity.

Other actual aspects, related to the elaboration of advanced corrosion protective layers, are rather related to the technological approaches used for their synthesis and deposition and the respective coating ingredients. In other words, every new coating system elaboration should comply the environmental restrictions, related to the use of volatile organic compounds (VOCs), and toxic metals, such as Pb, Cr, As, and so forth.

This considerable variety of requirements, related to the elaboration of durable and reliable, environmentally compliant coating systems with active corrosion protective capability imposes the need for multilayered systems, where each layer has its own function. The main function of the exterior layers is to protect the coating underlayers against the impact of the surrounding environment, like UV light absorption ability and hydrophobicity. The intermediate coating layers should possess extended barrier properties and self-repairing ability. The actual trend in this sense is to use hybrid matrix-based polymeric materials, able to combine the benefits of the organic and inorganic materials. Besides, this approach enables to deposit self-assembled mono-layers (SAM), composed by siloxanes with large aliphatic chains. They have significantly lower number and size of defects in their structures, and thus enable more efficient protection via formation of dense barrier layers. Another strategy is to encapsulate polymerizable substances. In this case, polymerizable compounds are enclosed inside polymer or glass capsules to poly-merase when are exposed to air, by mixing each other or by toughing ingredients of the basic matrix. A promising alternative to the use of ceramic nanoparticles as inhibitor containers reinforcing the basic polymer matrix is the involvement of carbon nanoparticles (CNP). Espe-cially, the hollow carbon nanotubes (CNTs) allow to be filled by inhibitors via intercalation.

The basic function of the primer coating layers (i.e., the coating primers) is to improve the adhesion between the native Al-oxide layer of the metallic substrate and the upper (i.e., intermediate and finishing) layers, commented in the previous sections. Some authors even report for self-healing properties, possessed by these films. Undoubtedly, among the basic advantages of this group of coatings is the possibility to deposit them by physical, electro-chemical, or chemical methods. Regardless the method applied for cerium oxide primer layer (CeOPL) deposition, the respective technological regime includes three basic stages: (i) prelim-inary treatment of the metallic substrate, (ii) the CeOPL deposition itself, and (iii) final sealing of the already deposited CeOPL film.

The purpose of the preliminary treatment procedure is to modify the metallic substrate surface, to be suitable for deposition of uniform and adherent primer layers. The impact of the prelimi-nary surface treatment procedures comprises both the metallic surface roughness (by mechanical grinding in laboratory's conditions, or sand blasting in industrial scale) and the superficial chemical composition (by selective dissolution of the intermetallic inclusions or affecting the surface oxide layer). The commonly accepted preliminary treatment procedures include four basic steps: degreasing, mechanical grinding, alkaline etching, and acidic desmutting.

Finally, it should be remarked that among the various technological approaches, the sol-gel route and the spray-based techniques have shown to provide the synthesis of various nanosized materials and thin layer deposition.

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