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Corrosion issues in joining lightweight materials: A review of the latest achievements

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Abstract:
Multimaterials assemblies and, in particular, assemblies made of lightweight components are of utmost relevance in many technical applications. These assemblies include multimetal, metal-polymer, metal-adhesive, and metal-composites combinations, among others. Presently, the transportation sector is looking for lighter materials that allow for reducing fuel consumption and the environmental footprint. Aluminum and magnesium alloys, as well as composites and polymers, are considered strategic for such purposes, and their joining in metal-metal or hybrid assemblies has been explored to develop lightweight components. These multimaterial assemblies are often exposed to aggressive environments in which moisture and aggressive species are present. Under these conditions corrosion phenomena are a major source of material failures. Depending on the nature of the metals and nonmetals and of the joining process, the mechanism and extent of corrosion can vary significantly. Thus, it is essential to understand the impact of corrosion in joined materials and to know which counter-measures can be adopted to mitigate corrosion events in the system of concern.
This chapter aims at reviewing the latest results of studies focused in corrosion issues in the joining of lightweight materials. It describes the most common corrosion phenomena observed in joined materials, and it emphasizes corrosion issues in assemblies that combine different metals and that combine metals with nonmetals. Moreover, it overviews the state-of-the-art in corrosion protection strategies that can be applied and, finally, it overlooks the future trends.

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1 Introduction

Joining is a technological process, which places together different materials to form a single unit. The goal is to create a product displaying properties and performance unattainable in the individual materials. Joining technology is based in three main processes: mechanical joining that makes use of mechanical forces, adhesive bonding that is based on chemical forces, and welding, resulting from physical forces.

Mechanical joining relies on mechanical forces to join distinct materials. Normally this process does not involve chemical reactions or atomic interactions. Adhesive bonding makes use of foreign materials which promote the bonding between the distinct materials that need to be put in place. This additional material is the adhesive. Welding makes use of a combination of heat and, when required, pressure and can be classified as fusion or nonfusion type.

Joining of dissimilar materials is of extreme relevance in many applications. The process requires suitable matches concerning the chemical, physical, and mechanical properties between the materials placed together. When these properties do not have a closer match, the process can be completed by using joining agents such as adhesives or rubbers. In all the joining routines an interface is formed and its presence creates areas susceptible to corrosion.

Ideally, the joining processes should not affect the mechanical properties of the materials involved and should not create physical discontinuities, chemical modifications, or microstructural changes in the materials being joined. Regrettably, despite many advances, the reality is that the joining methods do adversely affect the local properties of the materials. When metallic materials are concerned, these changes may affect the electrochemical activity of the metals and, in the presence of moisture and aggressive agents, corrosion activity becomes a major problem. Various corrosion phenomena can be observed, depending upon the nature of the joined materials and of the joint, composition of the environment and presence of mechanical stresses.

Presently, two of the most important lightweight metals are aluminum alloys and magnesium alloys. The electrochemical behavior of these materials is very distinct, as is its corrosion susceptibility. Research on cor-

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rosion issues in joining lightweight materials has been evolving very fast, and the most recent trends are overviewed in this chapter.

2 General aspects of corrosion in joints

Aluminum and magnesium alloys present a very favorable weight-to-strength ratio which allows decreasing the weight of the components. Joined assemblies may include different aluminum alloys, different magnesium alloys, steel combined with magnesium alloys, steel combined with aluminum alloys, and composites combined either with aluminum alloys or magnesium alloys. Since both magnesium and aluminum alloys are very susceptible to corrosion, it is important to characterize the possible corrosion mechanisms that may arise when these materials are considered. Some of the most relevant features related to the corrosion processes commonly found in aluminum and magnesium alloys are summarized below.

The corrosion activity of magnesium alloys is governed by some well-known key steps: (i) magnesium (or its alloys) are typically covered by a protective surface oxide/hydroxide; (ii) In the presence of oxygen and moisture, the oxide film is not protective enough, magnesium dissolves, and the process is accompanied by intense hydrogen release; (iii) magnesium is characterized by a negative free-corrosion potential, and even more negative pitting potential in aggressive solutions such as NaCl, making it very susceptible to localized corrosion attack. The high reactivity of magnesium and the low protectiveness of the oxide layer are responsible for the low resistance to localized corrosion attack. The lateral and in-depth spread of the corrosion process leads to undermining and falling off of parts of the attacked material. In Mg alloys, the local differences in composition and microstructure also promote local galvanic corrosion cells which spread, leading to identical phenomena. Addition of some alloying elements such as aluminum, zirconium, or rare-earths can improve the corrosion resistance of magnesium alloys. Depending on the composition and microstructure of the magnesium alloys, the corrosion processes can be slowed down and some particularities may arise in what concerns the corrosion-governing mechanisms.

Aluminum and its alloys are characterized by the presence of a stable and highly protective thin oxide film that keeps the material in a passive state in many environments. However, this oxide film always presents some defects and flaws which create fragile areas that can be attacked in the presence of aggressive ions (e.g. chlorides). The local dissolution of the protective aluminum layer originates a pitting attack. The diameter and the depth of the pitting depends on the alloy composition, the local pH, and presence of aggressive species. Aluminum and its alloys are very susceptible to pitting corrosion in near neutral pH, which is found in many environments. The pitting process is typically characterized by two stages: (1) pitting onset, which involves adsorption and attack of the oxide layer by chloride ions. Eventually during this stage the oxide may repassivate and the pitting process does not enters the second stage; (2) pit growth, characterized by intense aluminum (or alloying elements) dissolution and precipitation of corrosion products such as $Al(OH)_3$,

In Al alloys, the presence of alloying elements (such as Mg, Mn, Cu, Fe, Si, Li, ...) induces the formation of a multiplicity of intermetallic particles, of distinct composition, and different electrochemical behavior, compared to the pure Al matrix. The presence of redox-active intermetallic creates preferential sites for localized corrosion onset. In general, corrosion of Al and Al alloys is a localized process. Other forms of corrosion in aluminum alloys include transgranular dissolution (the corrosion affects the various metallurgical features, and it is not selective), intergranular corrosion (the corrosion propagates in preferential paths), stress-induced corrosion, galvanic corrosion, and exfoliation corrosion.

The corrosion processes which may occur in the individual Mg and Al alloys depend on several variables, and are extremely complex. Therefore, its joining is a challenge with regard to corrosion issues. In addition to the specificities of each single material there is need to consider the joining area that may be considered as a "new" material, bringing additional peculiarities and eventually new forms of corrosion.

The joining of two metals or a metal and a composite is characterized by the presence of a joint that places together the two individual parts. When two dissimilar metals are placed into contact there is formation of a galvanic cell. In the presence of aggressive electrolytes, galvanic cells induce dissolution of the less noble metal (or phase) in the assembly. This form of corrosion is known as galvanic corrosion. On the other hand some joining process creates local changes, including modification of microstructures and formation of new phases that may form microgalvanic corrosion cells at the microstructural level.

The presence of stress (even if residual) on and around the joint may, additionally provoke stress corrosion cracking phenomena. This form of corrosion requires the presence of stress, a corrosive media, and a corrosion-susceptible microstructure. Corrosion normally starts at the points of stress concentration, leading to nucleation of cracks. When the cracks develop, there is formation of an anodic tip, and the corrosion process propagates by branching. The presence of stress in high strength materials may promote hydrogen embrittlement and hydrogen-induced cracking.

Joints and welded areas are quite susceptible to pitting corrosion. Pitting corrosion always starts in defects or “weak points” arising from microstructural features existing in a passive layer. The pit works like an anode, and it is supported by a larger cathodic area. The corrosion process inside the pitting is accompanied by strong acidification, and in the presence of chloride ions an autocatalytic process may develop, resulting in catastrophic failure of the material.

Crevice corrosion is also a phenomenon which can be observed in joined parts. The joining process may create defects, microfissures, or occluded zones that can result in the formation of crevices in which localized concentration cells are formed. Due to fast consumption of oxygen, the crevice becomes anodic and the surrounding metal cathodic. The process may involve strong acidifications, and the effect can be catastrophic in the presence of aggressive ions such as chlorides.

The differences in the chemical composition of the metals in the joined assembly can also be sensitive to high temperature-induced corrosion. The different chemical compositions across the interfaces and the microstructural changes can result in selective oxidation when the assembly is exposed to a high-temperature environment. Thus, the interfacial zone is very susceptible to high-temperature corrosion phenomena.

Corrosion effects on joints can be minimized by cleaning the surfaces to be joined, applying the proper materials (fillers and adhesives), and by applying suitable pre-and post-joining treatments. Galvanic corrosion effects can be minimized by selecting appropriate fasteners and materials which are chemically and electrochemically compatible. It can also be prevented by adjusting the weld metal in such a way that it can provide cathodic protection of the base metal which is more susceptible to galvanic dissolution. Corrosion prevention can also be achieved by applying coatings or surface finishers.

3 Corrosion in lightweight metallic joints

The transportation industry, mainly the automotive industry and aeronautics, is one of the most dynamic sectors with regard to envisaging of new lightweight material assemblies. The main target is to decrease the vehicle weight, reducing fuel consumption and CO_2 emission, while optimizing the vehicle design and its overall performance. Presently, steel, aluminum, magnesium, and composites are the most often considered materials for these targets. These materials require a variety of joining technologies, which have been evolving and optimized. However, corrosion phenomena are still a major concern, and intense research activity has been carried out in this specific field.

3.1 Steel and lightweight metals

N. Le Bozec at al. [1] studied the corrosion behavior of various automotive joined assemblies using standard corrosion tests, such as the N-VDA test. The conventional steel materials tested included various carbon steel grades, hot dip galvanized steel, and electrogalvanized steel. Lightweight materials tested were the magnesium alloy AM 50 and various aluminum alloys. The joining techniques included adhesive joining with epoxy, clinching, spot welding, laser welding, and arc welding. The loss of mechanical properties was correlated to the extent of corrosion degradation. It was demonstrated that the depth of attack was greatly increased during exposure to the VDA test. The joint strength was evaluated, and it was found that clinching did not affect this parameter. On the other hand, adhesives showed increased loss of strength during the VDA test. The adhesives failed because of corrosion propagation at the interface metal-adhesive and the subsequently generated stresses. It was demonstrated that the assemblies made of steel and zinc-coated steel presented improved mechanical properties. In another work [2], the same authors demonstrated that the corrosion in joined materials, particularly in adhesive-bonded interfaces, was potentiated by the simultaneously application of fatigue loading during samples exposure to the cyclic tests. It was also observed that weld-bonded and spot-welded samples did not evidence failure during the combined fatigue-corrosion tests.

Automotive grade galvanized steel and the aluminum alloy 6016 were joined by the laser keyhole welding technique. The microstructure of the joints formed in the process was investigated in detail. The results showed the presence of a dendritic eutectic structure and the presence of equi-axis crystals at the centre of the welded area. The results also revealed an interfacial layer formed with galvanized steel, with thicknesses ranging from 1.5 to 13 μm [3]. This layer was composed of three distinct phases which were characterized by different mechanical properties.

The corrosion behavior of laser-beam joined steel and aluminum was investigated in salt spray tests. Hot dip galvanized steel and AA6016 were joined in the presence of two different fillers [4]. The results showed that the fusion zone was the one most susceptible to corrosion, and that the extent of corrosion damage was also dependent upon the cathodic response of the surrounding metal, namely steel. The welding process produced a Zn-rich runout area (Figure 1(a)), which revealed itself to be the one most susceptible to corrosion. The Zn-Al microstructure in the run presented an anodic behavior and therefore was the first one to dissolve. The corrosion processes induced internal tensions and formation of cracks which affected the durability of the assembly (Figure 1(b)).

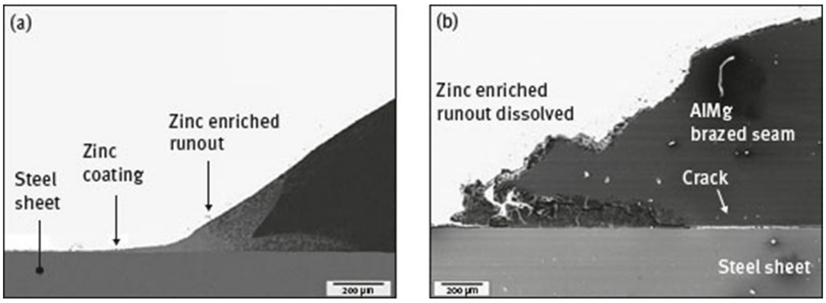

Figure 1: Cross sections obtained by SEM on the aluminum based filler (AlMg6Mn) material joint: (a) Before corrosion test and (b) after 192 h in salt spray r. The zinc-enriched run out dissolves first forming a crevice between brazed seam and steel sheet. From [4]

Galvanized steel and aluminum are dissimilar materials, and their welding can be performed in different ways. Laser welding is a very promising method in many industrial applications. However, when these materials are joined, there are some risks, such as the formation of pores and of brittle intermetallics. Zinc possesses a boiling point much lower than that of aluminum and, consequently, iron and zinc vaporization may occur. The quality of the welded materials and the corrosion susceptibility depends upon the laser-processing parameters. This effect was investigated by H.-C. Chen et al. [5], who found that the corrosion resistance of the joined parts was improved when argon gas was used as shielding gas. However, the shear strength was improved by using N_2 gas. Laser joining of Al-plated steel and aluminum were investigated recently [6]. Different parameters such as the laser intensity and the addition of fillers were considered. The results showed that the addition of carbon and tungsten to the steel could reduce the formation of intermetallic particles.

Adhesive bonding has several advantages, and this technique is often used in the preparation of assemblies for automotive applications. Moreover, it can be easily applied over coated metals. When applied over coated metals, the properties of the coating affect the bond strength and must also be considered. Studies were performed using various coated samples. The results of lap-shear and butt-joint tests showed that failures were more prone to occur at the interface metal coating and inside the coating. The work demonstrated that softened adhesives were able to reduce peak stresses [7].

3.2 Lightweight metals

Mg and Al alloys are among the most strategic alloys for developing lighter materials for the automotive and aeronautic sectors.

Riveting, i.e. self-piercing riveting, is a plastic-joining process that can be applied to join thin metallic sheets. It does not require drilling and is a cold process. However, one of the major limitations to its widespread use in automotive and aeronautics has been the risk of localized corrosion damage. The cold forming processes may induce local stresses, which potentiate stress corrosion cracking. Other surface heterogeneities may result in the formation of micro-occluded areas and consequently crevice corrosion. AA 6082 was joined by this process, and its susceptibility to corrosion was investigated by L. Calabrese et al. [8]. The relation between the geometry, the mechanical resistance, and the corrosion behavior was evaluated. The riveting process induced local stress that increased the probability of crack formation and the corrosion susceptibility. The local corrosion activity was associated with crevice corrosion and pitting corrosion, and decreased the performance of the joined parts and the resistance of the assembly during the pull-off tests.

The corrosion behavior of welded Mg parts (Mg alloy AZ61A) has been carried out using various techniques such as friction stir welding (FSW). Given the high susceptibility of Mg alloys to chloride-induced corrosion, the effect of pH, chloride concentration, and immersion time was investigated in detail by A. Dhanapal et al. [9]. The results showed that the corrosion rates decreased in alkaline pH conditions and increased in more neutral/acidic pH ranges in the presence of chloride ions. The formation of a hydroxide layer over the welded joints created a resistive pathway that slowed down corrosion damage over time.

The FSW process results in the formation of different zones that present different susceptibility to corrosion. These zones are: (i) the base metal; (ii) the weld nugget; (iii) the heat-affected region; (iv) thermo- and mechanically-affected areas. The corrosion susceptibility of stir welded joints on AlMgSiCu alloys (6xxx series) as well as the microstructure and microhardness were investigated in detail by P. Dong et al. [10]. The work demonstrated that there was a correlation between microstructure and intergranular corrosion susceptibility. The fine precipitates resulted in higher hardness, and the coarser precipitates increased softening. Coarsening of the intergranular precipitates decreased the susceptibility to intergranular corrosion, but seemed to promote pitting corrosion in the zones affected by heating. The formation of micro-galvanic cells occurred at the grain boundaries of the precipitates, which displayed either a more active or a more noble character, compared to the aluminum matrix. The corrosion resistance was increased in the areas showing more homogeneous microstructure [10].

The way corrosion develops in the different zones formed in the FSW process was investigated by several authors, producing some controversial statements.The nugget zones and the heat-affected zones have been identified as the most susceptible to corrosion onset [11]. However, other work carried out on FSW AA7108 proposed that the thermomechanically affected zone was more susceptible to corrosion development [12]. The corrosion process was associated with intergranular dissolution due to the nonuniform distribution of $MgZn_2$ intermetallics across the affected zone.

The corrosion behavior of FSW welded joints was investigated in various alloys such as 2219-T87 plates. The thermomechanically affected zone revealed the presence of Al_2Cu intermetallics, and it was found that the welded areas exhibited identical environmentally-assisted cracking corrosion susceptibility. Moreover, the work reported that the joints seemed to be more resistant to corrosion then the unaffected zones. The effect was attributed to the coarsening of the Al_2Cu precipitates [13]. On the other hand, polarization curves and electrochemical impedance measurements obtained on FSW joint in AA 2024 panels revealed identical pitting tendency of the heat-affected zone and thermomechanically affected zones.

J. Kang el al. [14] also investigated the pitting susceptibility of FSW-joined AA2024-T3. The corrosion susceptibility was associated with the presence of Al-Cu-Fe-Mn-Si and Al-Cu-Mg intermetallic particles. The particles induced the dissolution of the adjacent aluminum matrix. The zones more susceptible to corrosion were the S-Phase (Al-Cu-Mg). The corrosion activity was influenced by the parameters used in the FSW process. For example it was demonstrated that the nugget zone was more susceptible to anodic dissolution under low rotation speeds, whereas the heat-affect zone became more susceptible to corrosion at higher speeds. The propagation of intergranular attack occurred at the grain boundaries as result of their sensitization. The nugget worked as cathode and enhanced cathodic reactivity that protected this area from corrosion [15].

The susceptibility to intergranular corrosion of the welded areas in AA2024 was investigated by Bousquet et al. [16]. The corrosion process was investigated in the various zones formed after FSW. Thus, in the bare alloy, corrosion of some grain boundaries was observed, and the corrosion process (mainly pitting corrosion) was attributed to the preferential dissolution of Cu-containing precipitates. On the heat-affected zones, the pitting corrosion activity was similar to that observed in the bare material. This was explained under consideration that the composition, size, distribution and density of the intermetallics were quite similar to those observed on the base alloy. However, when immersed in aggressive solutions, the potential gradients across the heat-treated zone induced galvanic dissolution, with the weld behaving anodically and the bare metal cathodically. Closer to the thermomechanical affected zone, the processes changed. Pitting attack in the coarser intermetallics was observed, but the intergranular corrosion attack became more pronounced with time. The most sensitive area was the one in the transition zone, between both affected zones. It was more susceptible to both pitting attack and intergranular corrosion [16].

The corrosion resistance of FSW in AA7449-T7951 joints could be improved by laser melting. Such effect was reported by Padovani et al. [17]. Without the laser treatment, the heat-affected zone revealed several pits, about 100 µm deep. The treatment with the laser created a homogeneous layer, which dissolved the intermetallic particles within a solid solution. The corrosion damage at the nugget area was not significantly affected by the laser treatment; however in the heat-affected zones, the pits formed were not as deep as the ones observed in the untreated zone. The corrosion potential breakdown was assessed by d.c. potentiodynamic polarization using the micro capillary cell. The findings showed that the laser treatment practically did not affect that electrochemical parameter. The laser-treated zone exhibited lower open circuit potential values, which seemed responsible for some sacrificial cathodic protection, concentrating the corrosion in the laser affected zone, and hindering its propagation to the unaffected areas (Figure 2). Corrosion propagation caused partial delamination of the treated zone, an effect that could be a serious drawback with regard to the laser melting treatment of welded zones.

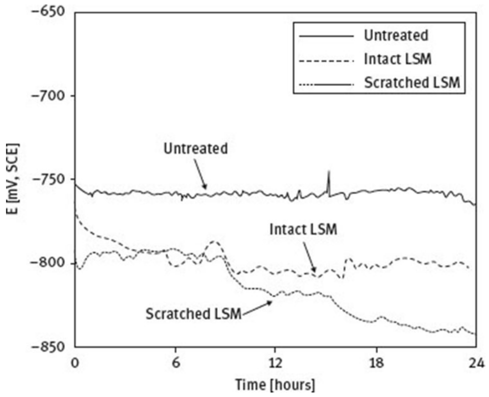

Figure 2: Open circuit potential evolution of untreated, intact laser-treated and scratched laser-treated parent material specimens measured during immersion in 0.1 M NaCl. From [17].

Various surface treatments such as laser and shot peening were performed on FSW 7075 alloys to increase the resistance against stress corrosion cracking susceptibility. It is known that the weld zones are subjected to different stresses, which are more intense in the nugget zone, as demonstrated elsewhere [18]. The welded samples were immersed in 3.5 % NaCl solutions for 2 months. The peened samples did not reveal pitting corrosion or intergranular corrosion attack. The unpenned surfaces showed severe pitting attack, but this form of corrosion was avoided in the laser treated surface. For the tested period the effect of stress corrosion cracking was not evident.

Microstructure, impurities, presence of residual stress, formation of intermetallics, and corrosion onset are factors that determine the lifetime of joined components. These issues were investigated in FSW joints formed on the Al-Zn-Mg alloys used in aeronautic applications [19]. In the Al-Zn-Mg alloy the thermomechanically affected zone was richer in Fe and Si, containing intermetallics that are more cathodic then the surrounding Al matrix. This potential difference, which attained 400 mV, induced microgalvanic corrosion activity. Thus, the localized corrosion process propagated as intergranular corrosion, resulting in intergranular cracking. However, in the Al-Zn-Mg-0.10Sc-0.10Zr alloy, there was formation of secondary $Al_3Sc_xZr_{1-x}$ particles that promoted the formation of more protective layers, decreasing the anodic dissolution and therefore increasing the corrosion resistance of this alloy.

A correlation between the microstructure and the corrosion onset susceptibility on Al-Cu joints was recently reported [20]. The study revealed that the microstructure near the interface showed the presence of $CuAl_2$ intermetallic particles and the α-Al phase. In the transition zone it was possible to postulate the presence of a solid solution composed of Cu-Al-Zn. The Volta potential of the surface was studied by atomic force microscopy (AFM) coupled to scanning Kelvin probe force measurements (SKPFM). The measurements showed that the initiation of the corrosion processes (pitting) occurred on areas showing the largest differences in Volta potential. These are, for example, the interface of Cu particles and Al-rich phases. Some evidence of pitting was also found inside the Al-rich phase (in the vicinity of the intermetallic particles). On the other hand, the presence of both Al and Zn in the interfacial region could promote the formation of protective products in the transition zones, delaying the corrosion propagation at initial stages.

The galvanic corrosion effects on polished FSW joints formed on AZ31 Mg alloys and AA2024 were investigated by C. Liu et al. [21]. Water-based polishing routes created surfaces that were more prone to galvanic corrosion attack compared to water-free polishing solutions. The corrosion onset was mainly located on the AZ31 region adjacent to the AA2024, where the area anode to cathode was lower. The accumulation of porous corrosion products, mainly magnesium hydroxides, led a decrease of the mechanical properties. No relevant corrosion was observed on the base alloys.

3.3 Coatings to minimize corrosion in multimetal assemblies

The corrosion resistance of welded parts can be improved by the presence of coatings. A micro-arc oxidation coating was deposited over AA7075, and its corrosion resistance was assessed by electrochemical techniques. The results revealed that the presence of a Na_2SiO_3 coating could considerably improve the corrosion resistance of the welded parts [22].

A protective ceramic coating was produced by plasma electrolytic oxidation (PEO) on the friction stir welded joints of the magnesium alloy AZ31 B. This coating was composed of an inner protective layer and an outer porous layer. It was demonstrated that the morphology of the PEO coating was not affected by the microstructure of the welded Mg alloy. The corrosion behavior was studied by means of electrochemical impedance spectroscopy and d.c. polarization on samples exposed to 3.5 wt.% NaCl. The results demonstrated that the heat-affected zone was more prone to corrosion, whereas the stir zone with a finer grain structure was more resistant. Overall, the presence of the PEO coating could protect the stir welded alloy AZ31 B [23]. The effect of grain size on identical alloys was investigated by J.R. Kish et al. by combining different electrochemical techniques, including localized electrochemical techniques. d.c. Potentiodynamic studies revealed identical anodic kinetics and some differences in the cathodic kinetics. The extent and kinetics of filiform corrosion was affected by the grain size. Thus, the initiation of the filament occurred in the coarser-grained areas. On the other hand, the grain size did not affect the kinetics of corrosion propagation from the bare metal (coarser grains) across the stir zones, where the grain was more refined [24].

Thermal sprayed coatings can also offer protection of joined aluminum and magnesium plates in a salt spray corrosion test. However failure was still observed after some time of exposure in the salt spray test [25].

Cold spraying could be used to deposit protective coatings over the FSW joints in AA alloys as proposed by Li et al. [26] The pure Al coating with thicknesses between 90 and 100 μm was adherent to the joined surfaces, free of cracks, and showed only little evidence of some outer pores. The presence of the coating contributed for increased hardness and offered corrosion protection of the joined surfaces. Samples without coating evidenced serious exfoliation and pitting corrosion, especially in the thermomechanically affected zone. The pits grew and deepened with time and became interconnected, leading to intergranular corrosion paths that finally resulted in exfoliation of the material. However this process was absent on the coated samples. Although corrosion was also observed in the Al coating, the process was not severe. Thus, in the coated samples, corrosion started in the interfaces of the deposited particles. Then corrosion caused a decrease of the coating thickness, but the joints were protected. It can be inferred that, if properly designed and applied, coatings may significantly delay the corrosion attack in joints.

4 Corrosion in metal-nonmetal joints

The advantages of using metallic and nonmetallic materials, combining properties unattainable by using any of the single materials, can be achieved by joining dissimilar materials in a hybrid assembly. These hybrid combinations are foreseen for applications requiring the decrease of the weight of the components and, presently, are used in a wide array of technical applications as structural components. The durability of these structures is very much impacted by the durability of the interfaces within the hybrid assembly. The challenge of placing together distinct materials like metals, ceramics, composites, plastics, and polymers that display different chemical, physical, and mechanical properties has not been solved yet, and many solutions are being proposed. Corrosion is once more a major source of failure.

Fiber-reinforced composites (FRP), because of their stiffness, decreased weight mechanical properties, and corrosion resistance, are used in several engineering applications. The joint between metals and FRPs is sensitive to failure, and the main causes of failure that have been identified include corrosion, delamination and/or de-bonding, tensile failure, crack development, and bearing. Since most of the reinforced composites contain carbon fibers and other conductive fillers, when in contact with the metal there is an increased tendency for galvanic corrosion. The process can be accelerated by the presence of moisture and oxygen and aggressive species such as chloride ions. Due to themore noble character, normally the composite works as a cathode where oxygen reduction takes place. On the other hand, the metallic side acts as an anode, and the metal dissolves. The mitigation of these detrimental events requires profound development of new joining materials, such as adhesives and rubbers, and improvement of the mechanical properties, adhesion behavior, and strategies to increase the corrosion resistance of the composites and metals.

E. Sarlin et al. [27] investigated the adhesion performance of rubber joined stainless steel parts and glass fiber reinforced composites. This assembly aimed at combining the good mechanical properties and the high corrosion resistance of steel with the flexibility and good adhesion of rubber and decreased weight of the composite part. Transmission electron microscopy experiments showed that close and high quality contact was obtained in the joined parts. Although neither corrosion issues nor parts durability were assessed, the use of rubbers demonstrated increased adhesion in the bonded surfaces. It was also shown that none of the rubbers used was degraded. The resistance against environmental ageing effects (hot, hot/moisture, andmoisture) was also investigated by FTIR and TGA in the same type of materials [28]. After exposure to the testing environments, samples showed good adhesion, and the performance of the material suggested that the behavior was independent of the surface treatment of the steel prior to joining. This route suggests that corrosion impact can be minimized.

Nanotechnology and nanomaterials have been contributing to advances in the materials properties, and this has been considered to improve the corrosion resistance of joined parts. For example conductive carbon fillers, such as carbon nanotubes, present good conductivity, thermal and electronic properties in addition to increased mechanical resistance and have been explored as additives to the epoxy matrix of the composites. Even in small amounts, the addition of carbon nanotubes to the matrix may have an important benefit on several properties. Carbon nanotubes also possess an increased interfacial surface area that enhances the mechanical behavior of the composite or of adhesives used in joints. Therefore there is an increased interest in understanding the corrosion behavior of joints when carbon nanotubes are used as fillers. Concerning corrosion related processes the following issues have been addressed: (i) Does the addition of carbon nanotubes to FRPs increase the susceptibility to galvanic corrosion between the modified composite and the metallic alloy? (ii) Does the presence of carbon nanotubes delay the ingress of aggressive electrolyte to corrosion-susceptible areas? (iii) Do carbon nanotubes contribute to enhanced adhesion and reduction of delamination effects in adhesive joints? Various studies have addressed these issues. For example, R. Ireland et al. [29] demonstrated that the addition of conductive fillers to the composite material promoted the formation of galvanic cells when the composite was placed into contact with the metallic part. Adhesives modified with carbon nanotubes were applied on the AA 2024 and the galvanic corrosion effects were studied in detail [30]. The work demonstrated that the presence of carbon could retard (and in some cases inhibit) electrolyte uptake through the interface. The effect was explained, under consideration that the presence of nanotubes limited microcracking and water bonding. The extent of the galvanic coupling effect was dependent upon the percolation threshold of nanotubes in the modified epoxy-based matrix. It was also found that the addition of nanotubes to the adhesive decreased the corrosion current densities and also slightly nobler potential values. One of the most important effects of the presence of nanotubes was related to adhesion enhancement; however, the effect was more pronounced when the alloy was previously anodized [30].

The addition of carbon nanotubes to metallic composites such as Mg-based composites has been reported as a possible strategy to improve mechanical properties of the material. However, in this case, the carbon filler was nobler then the magnesium alloy, and galvanic corrosion susceptibility was increased. This can be minimized by adding Al to the Mg-nanotubes composite. In this case the resulting composite (nan-otubes containing alloy) should present increased corrosion resistance. This effect was observed for AZ61 composites modified with carbon nanotubes [31]. It was possible to prepare a material in which the aluminum atoms, in solid solution, coated the carbon nanoparticles. This preferential distribution resulted in a decrease of the galvanic coupling effect, thus reducing the corrosion susceptibility of the Mg matrix, and retarding the corrosion effects of this material compared to magnesium composites.

The galvanic corrosion effects between the AA7075 and glass fiber reinforced composites (GFRP) obtained from an epoxy matrix modified with carbon nanotubes were investigated in samples exposed to different environments characterized by high humidity and/or the presence of NaCl. The two materials were placed into direct contact and the ratio composite to aluminum alloy was also investigated. Electrochemical measurements confirmed that the presence of carbon nanotubes increased the galvanic corrosion effects. The galvanic corrosion mechanism was investigated in detail in galvanic couples made of a carbon fiber reinforced epoxy matrix and *two different aluminum alloys (AA 7075 and AA1050)*. The corrosion mechanism was detailed in the presence of NaCl solutions with and without adding copper sulphates [32]. The corrosion processes was examined by d.c. potentiodynamic polarization. The results revealed very interesting findings: (i) the cathodic current was mainly originated in exposed fibers; (ii) the presence of copper led to a significant increase of the cathodic current density due to Cu precipitation over the exposed fibers; (iii) the galvanic current density was higher for the AA1050 compared with the AA7075. This behavior was justified by the presence of an increased density of cathodic areas in the AA7075 compared with tree AA1050.

The galvanic corrosion of rivet joints in a CFRP-aluminum alloy (Aw 6060) joint was examined in the presence of chloride ions by M. Mandel et al. [33, 34]. The corrosion studies were carried out by exposing the material to a 5 % NaCl solution and revealed that anodic activity occurred in the metallic side, in direct contact with the GFRP. Potentiodynamic polarization measurements showed the presence of a passive and a transpassive region. The pitting potential was determined as well as the critical potential difference for pitting corrosion that was approximately 100 mV. The electrochemical studies were combined by numerical simulations in which various aspects such as joint geometry were considered. The results showed that the zone sensitive to pitting attack was extended for 1.35 cm over the aluminum alloy. The pitting density decreased as the distance from the joint was increased. A cyclic VDA test [34] allowed identification of three stages of pitting corrosion development: in the first stage the pitting process was initiated at the aluminum alloy, being characterized by little pit volume change; in the second stage there was a significant pit growth; in the last stage the pitting growth was inhibited by the accumulation of corrosion products.

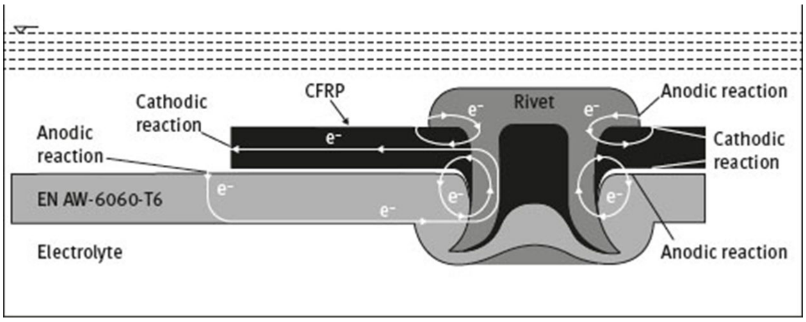

Figure 3: Schematic view of a section in which the corrosion susceptible areas are marked. This is a rivet joint between an aluminum alloy (EN AW-6060-T8) and the GFRP component. Adapted from [33].

4.1 Coatings to minimize corrosion in hybrid assemblies

Despite the relevance of new coatings for protection of joints for metallic and non-metallic materials, there are still very few works focusing on this specific issue. The galvanic effects between the GFRP and the metallic parts can be reduced by the use of corrosion inhibitors and/or coatings. This protective route was recently proposed in [35]. This work investigated the cooperative behavior of two different corrosion inhibitors: cerium nitrate, a well-known cathodic inhibitor, and benzotriazole known as an anodic/film-forming inhibitor. Both inhibitors were stored in ion exchange clays: layered double hydroxides (LDHs) and bentonites. LDHs are anion exchangers, being able to deliver an interleaved ion while capturing chlorides and hydroxyl ions; ben-tonites are cation exchangers and capture metallic ions. The modified pigments were added into an epoxy coating that was used to protect the GFRP-AA 2024 assembly. The coating was artificially damaged, and the corrosion inhibition processes was monitored using the scanning vibrating electrode technique (SVET). The results showed the cooperative inhibition mechanism of cerium ions, released from the bentonites and BTA released from the LDH particles. The bentonites were able to exchange the entrapped cerium cations with Al or Cu cations formed during the anodic dissolution of the S-phase present in the AA2024. The released cerium ions reacted with the hydroxyl ions formed during the cathodic reaction, leading to the deposition of an insoluble layer of cerium hydroxides that blocked the cathodic sites formed on the galvanic couple. This layer inhibited the cathodic reaction of oxygen reduction, and the overall corrosion process was hindered. On the other hand, BTA was released by exchanging with chlorides (thus, chlorides were trapped, while the inhibitor was released) and/or hydroxyl ions, forming an adsorbed layer on the surface of the aluminum alloy [35]. The corrosion protection effect of coatings modified with ion exchange pigments loaded with cooperative inhibitors was demonstrated for the first time, thus delivering a concept that can be used to protect several metallic couples either on hybrid joints or in multimetal joints.

Plasma electrolytic oxidation (PEO) coatings were investigated as possible routes for the protection of galvanic couples and Ti and Al alloys [36]. The results demonstrated that the galvanic effects were substantially reduced when the PEO coating was deposited over the Al alloy. The beneficial effect was not so evidenced for Ti alloys, because both the uncoated and coated Ti alloys revealed increased resistance against galvanic corrosion.

Similarly to what has been observed for metal-metal joints, the presence of coatings in metal-nonmetallic assemblies can be envisaged as a route to minimize the corrosion susceptibility.

5 Future trends

Presently, the search for lightweight structures, characterized by improved mechanical properties, is one of the top priorities in many industries, such as the automotive and aeronautical industries. Metal-metal assemblies and the joining of metals with very distinct properties such as steel and Al alloys or Mg and aluminum alloys are critical and will evolve in the near future. These materials, because of their electrochemical behavior, are very susceptible to multiple corrosion problems. On the other hand, the joining technologies also create interfaces that are very susceptible to the onset of corrosion and that create all the conditions for the onset of galvanic corrosion. For example, friction stir welding (FSW) creates zones with different levels of stress and microstructures that increase the probability of corrosion-related problems. Thus, post treatments, coatings, andothersurface treatments become critical for minimizing the problem.

The use of laser joining able to produce stable interfaces, including chemical (or ionic) bonding between nonmetallic and metallic components is another promising route to tailor interfaces with improved behavior.

The possibility of tailoring the properties of the joined materials by optimizing various laser welding parameters contributes to the overcoming of corrosion-related issues in laser-joined parts.

Glue bonding is another form of joining that is considered, because it can be used to join any kind of materials, especially very dissimilar ones. It allows for the reduction of local corrosion effects, but there are still several disadvantages, such as fast ageing, mechanical strength, and reduced stiffness.

Hybrid assemblies, joining metallic alloys and nonmetal composites, present a real challenge. When they are directly jointed, there is an increased risk of galvanic corrosion failure. Therefore, it is essential to design transition zones that can minimize the corrosion susceptibility while ensuring mechanical integrity and strong adhesion. Different transition zones must be studied. These include rubbers, polymers, adhesives, and coatings. Moreover, there is a need of material manipulation at the nanoscale level to minimize microcracking and microgalvanic effects. In this area the controlled addition of fillers, such as carbon nanotubes, and metallic or composite laminates, may play a critical role.

New adhesives, including adhesives modified with corrosion inhibitors either freely dispersed or encapsulated, for symmetric and dissymmetric joined materials can be a solution to overcome some localized corrosion effects. The introduction of nanofillers in these additives, targeted to increase mechanical properties, adhesion, and corrosion resistance are a step forward in advanced joining strategies. Certainly these advanced interfaces can place together many distinct materials, combining the best properties of the individual materials in a composite component.

Delamination and galvanic corrosion effects are major issues to be overcome in order to deliver new materials with improved properties for critical components in many sectors. For these purposes coatings and corrosion inhibitors are strategic routes. However, very little is known in this field, and new advances are urgent. Such new protection strategies will pave the way for a widespread use of these materials and for its reliability in structurally high-risk components. These will certainly be explored in the future.

There is undoubtedly a need for new multimetal combinations, either symmetric or dissymmetric. However, in parallel, the joining technologies must be optimized to overcome the multiple gaps related to corrosion performance. It is clear that all these advances need a concerted interdisciplinary effort by material science, chemistry, nanomaterials, and engineering to find more advanced solutions which can minimize the impact of corrosion in joined materials, while contributing for increased reliability of joined materials and its widespread application.

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