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Corrosion and Protection of Aluminum Alloys in Seawater

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Abstract

The paper deals with pitting and uniform corrosion and effectiveness of cathodic protection in reducing these corrosion forms. In stagnant waters or presence of low flow rates, pitting may occur. However, pitting corrosion, driven by the Fe-rich cathodic intermetallic compounds, is often of superficial nature. The pits tend to passivate as a result of etching or passivation of the intermetallics with time. Cathodic protection is an effective way of preventing pitting. It also requires low current densities since the cathodic area, defined by the Fe-rich intermetallics, is small in contrast to steel, which is uniformly accessible to the cathodic reaction. Although thermodynamic calculations suggest possible instability of the oxide in slightly alkaline solutions, such as seawater, protective nature of the oxide in practice is attributed to the presence of alloying elements such as Mg and Mn. Thus, the passivity of both the aluminum matrix alloy (the anode) and the intermetallics (cathodes) have to be considered in evaluating the corrosion and protection of aluminum alloys. With increasing flow rate, the possibility of pitting corrosion reduces with increase in the rate of uniform corrosion, which is controlled by the flow dependent chemical dissolution of the oxide. Cathodic protection does not stop this phenomenon, and coatings have to be used.

Key Words: Aluminum, corrosion, cathodic protection, seawater, hydrodynamics

Introduction

Use of aluminum alloys in seawater is of continuous interest because of the need for light-weight structural materials. As long as galvanic contact with more noble metals is avoided, most structural alloys, such as those in the AA1000 (commercially pure), 3000 (AlMn), 5000 (AlMg) and 6000 (AlMgSi) series, are resistant to corrosion in sea water, especially the so-called seawater resistant alloys in the 5000 series [1]. The high strength alloys in the 2000 (AlCu) and 7000 (AlZnMg) are normally not recommended for use in seawater.

In support of the foregoing, aluminum boats constructed from 5000-series alloys were already in use in 1930's with recorded lifetimes exceeding 40 years. Since then, areas of application have increased significantly. The largest use still involves marine vehicles of all types. Other applications include outboard motors, propellers, masts, ladders, floating bridges, desalting equipment, buoys *etc*.

Under stagnant and low flow-rate conditions, uniform corrosion rate lies below 1 µm/y. Crevice corrosion is normally not a problem for aluminum alloys. However, it is observed in joints, and it is basically a design problem like galvanic corrosion. Alloys in the 5000-series become susceptible to intergranular corrosion if the Mg content exceeds 4.5 %. The 6000-series may also become susceptible to intergranular corrosion if the Si/Mg ratio exceeds the

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stoichiometric ratio for the intermetallic compound Mg_2Si, especially if Cu is also present, even if in small amounts. Thus, proper design and material selection can prevent these corrosion forms. Pitting, flow-dependent corrosion and erosion corrosion are the basic corrosion problems for aluminum alloys in seawater. The purpose of the paper is, therefore, to review the danger and mechanisms of these corrosion types and possible protection methods, especially cathodic protection.

Fundamental Aspects of Corrosion

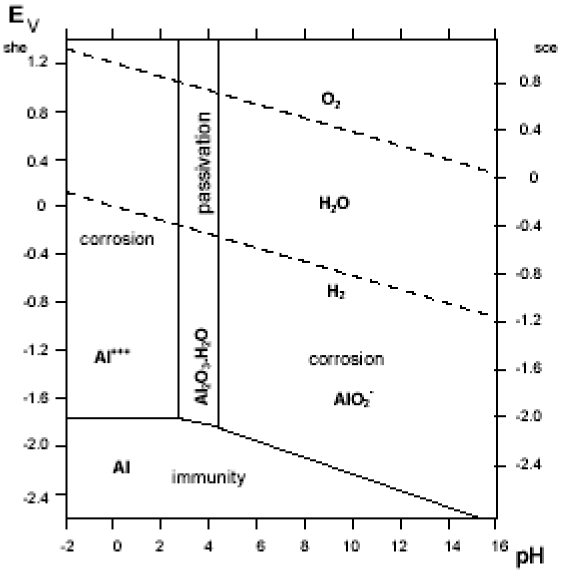

Figure 1. Pourbaix diagram for aluminum [2].

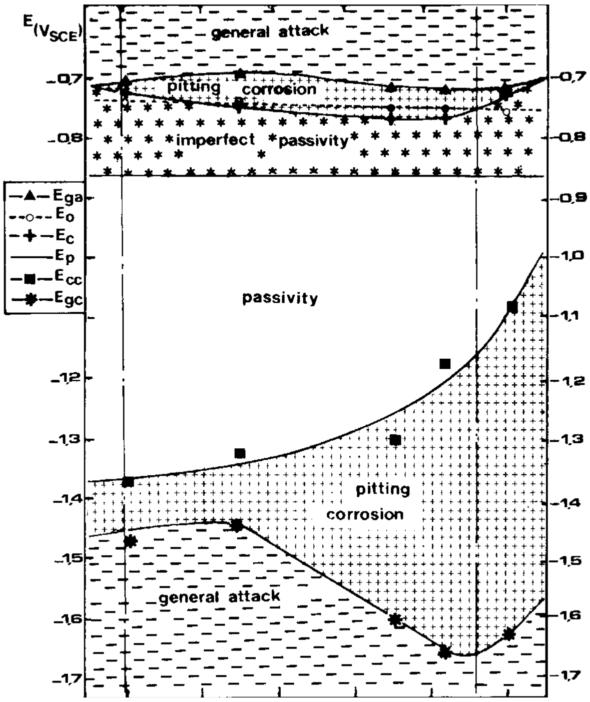

Figure 2. Experimental potential-pH diagram for alloy 5086 in chloride solution [3].

Starting with the thermodynamic aspects, the Pourbaix diagram for aluminum, published recently for type of oxide (bayerite), which is realistic for seawater [2], is shown in figure 1. It may look unfavorable for applications of the metal in seawater at pH 8.2. Therefore, the passivity of the metal in slightly alkaline environments like seawater is ensured by use of alloying elements such as Mg and Mn, which have small but adequate solid solution solubility in aluminum. The point is demonstrated for the practical Pourbaix diagram of Gimenez *et al.* [3] for seawater resistant alloy 5086 (nominal composition in wt% 0.1 Si, 0.3 Fe, 0.4 Mn, 4.3 Mg, 0.1 Cr) reproduced in figure 2. The diagram is based on experimental corrosion data obtained in chloride solutions rather than thermodynamic calculations. Probably due to the presence of the passivating alloying elements Mn and especially Mg, whose oxide becomes increasingly passive with increasing pH, the range of passivity of the oxide forming on the alloy becomes significantly larger than that obtained by thermodynamic calculation. These solid-solution alloying elements become enriched in the oxide in exposure to seawater as a result of selective dissolution of the more active aluminum component and, thereby, render the oxide more passive against seawater.

It is not always realized that, in contrast to steel, the localized corrosion of aluminum is primarily determined by the properties, size, and distribution of intermetallic compounds and secondarily by the properties of the solid-solution matrix alloy discussed above, unless

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copper is present. Pit initiation on multiphase commercial alloys occurs invariably at weak spots on the oxide around the intermetallic particles [4,5]. The weakness results firstly from the presence of a flaw in the oxide at the particle-matrix interface. Secondly since the stable oxides on these materials are largely insulators against electronic conduction, the reduction reaction required for the corrosion process can only occur on the type of intermetallic particles which are electrochemically nobler than the matrix.

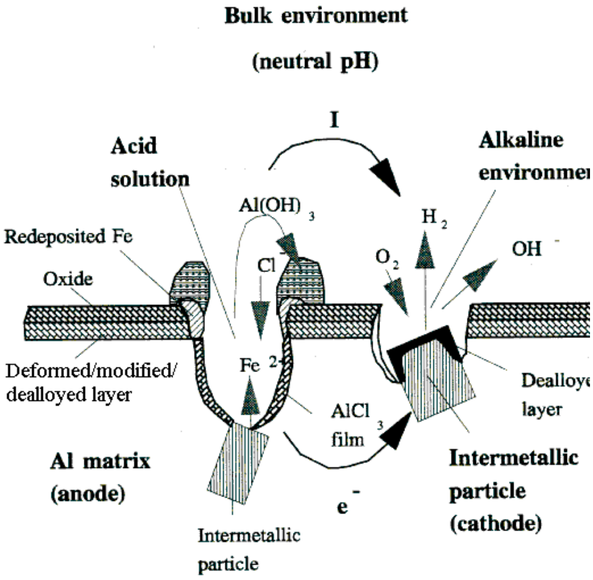

Figure 3. Schematic illustration of localized corrosion on aluminum alloys.

The events which occur during stable localized attack, *e.g.*, pitting, are summarized in figure 3, illustrating the development of localized environments in the pit (acid) and adjacent to the cathodic site (alkaline), resulting from metal hydrolysis and reduction processes, respectively. High pH developing adjacent to the cathodic site causes etching of aluminum matrix around the particle as a result of destabilization of the amphoteric aluminum oxide. At the same time, this local alkalinization alters the chemistry and structure of the intermetallics on aluminum. The particles with more noble components become essentially enriched at the surface as a result of the selective dissolution of the aluminum component. It has also been shown for aluminum that the Fe^{2+} produced in the pit by the corrosion of iron-rich intermetallics redeposit in or at the immediate vicinity of the pit, thereby increasing the cathodic area fueling the corrosion process [6]. Selective dissolution of the aluminum from the matrix alloy and the resulting enrichment of a more active, passive or noble component may also have beneficial or deleterious effect on the corrosion process. For example, while enrichment of the surface with magnesium may be beneficial against pitting of aluminum in the manner discussed above, enrichment of copper is known to have the opposite effect.

Nearly all aluminum alloys exposed to an aqueous solution, whether chloride is present or not, are likely to exhibit micropitting in the form of crevicing around the intermetallic particles as a result of the microgalvanic coupling between the noble, Fe-containing intermetallic particles and the surrounding more active solid solution aluminum matrix, as described above and shown in figure 4 [7]. This gives only superficial attack, so called cathodic etch pits, with pit size commensurate with the size of the intermetallic particles. This type of pitting corresponds to the pitting region depicted in figure 2 under the passive zone. Pits passivate after the intermetallic particles, visible in figure 4a, are undermined and removed from the surface as shown in figure 4b. The type of pit sketched in figure 3 with the acidified anolyte, which can propagate autocatalytically and cause material damage, does not initiate unless the surface of the metal can be polarized temporarily over the critical pitting potential, which is about $-0.75\ V_{SCE}$ in seawater [8]. The value varies somewhat depending on the composition of various alloying elements [9]. Once initiated, however, such pits can propagate at potentials appreciably lower than the pitting potential. This type of pitting is represented in figure 2 by the pitting zone above the zone of passivity.

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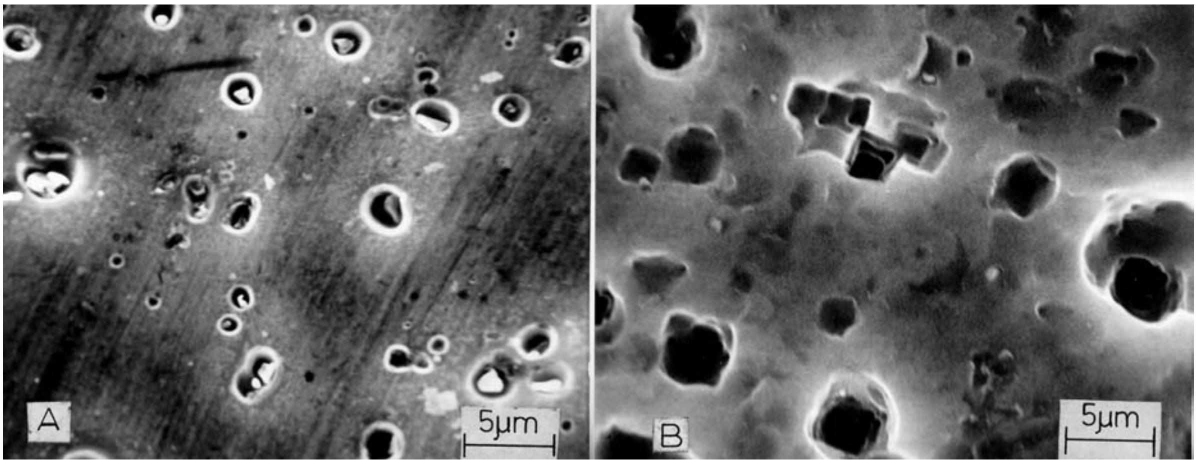

Figure 4. Initiation of micropits around Al_3Fe phases (A) and the passivated pits after the intermetallics are undermined (B) and removed from the surface of commercialy pure alloy 1050 in chloride solution [7].

Susceptibility to pitting and crevice corrosion may increase with chloride content, temperature [1] and pressure [10,11]. Added presence of heavy metal ions and dissolved CO_2 is not beneficial, since unexpected negative synergy of these species, together with Cl^-, dissolved oxygen and elevated temperature and pressure may cause high corrosion rates [12]. Dissolved H_2S is an effective corrosion inhibitor for aluminum alloys [13].

The microgalvanic coupling between the intermetallic phases and the solid solution aluminum matrix has long been recognized [14]. Corrosion potentials of different phases found in various aluminum alloys in chloride media have widely been mapped out and correlated with pitting corrosion susceptibility, as reviewed in reference 15. The information has been utilized in the development of corrosion resistant alloys over the years. However, the application of the data and the know-how about mechanisms of pitting summarized above to corrosion protection purposes is relatively little and recent.

Effect of Flow on Corrosion Rate and Morphology

Increasing flow rates in seawater reduces the possibility of pitting observed in stagnant environments and low flow rates. However, the rate of uniform corrosion increases [16]. It is not possible to specify a flow rate for this transition because it depends on the alloy and the hydrodynamic conditions. In laboratory testing by use of small samples, *e.g.*, the transition occurred above 8 cm/s for alloys Al99.5 and AlMgSi1, while the seawater resistant alloy AlMg3 did not suffer any significant pitting in the flow range tested, as shown in figure 5. The scatter in the data at low flow rates is due to pitting. With increasing flow rate the data can be correlated by a single straight line on a log-log plot, indicating that the mechanism of uniform corrosion is similar for all alloy types. The corrosion rate does not decrease with time in the uniform corrosion regime in contrast to the decreasing rates generally observed in the case of pitting. The uniform corrosion rate remains nearly constant as a function of time, and it is not affected by elevated pressures up to the test limit of 30 bar. The mechanism of this flow-dependent uniform corrosion will be discussed further below together with the effect of cathodic protection.

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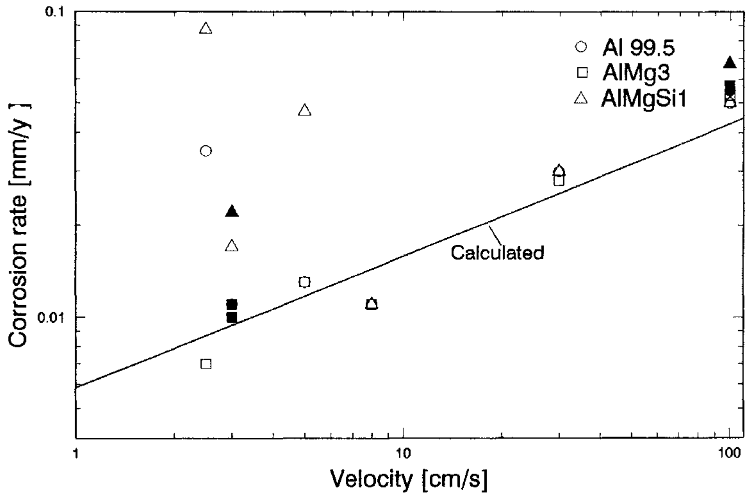

Figure 5. Corrosion rate of sheet specimens under open-circuit conditions (open) and cathodic protection at –1.0 V_{SCE} (bold) as a function of seawater flow rate. Specimen surfaces lie in the direction of flow. The data are based on weight loss measurments and an immersion period of two months. See reference 16 for experimental details. The line corresponds to the predicted uniform corrosion rate based on the mass.transfer considerations discussed in the text.

It should be emphasized that the transition velocity from pitting to uniform corrosion depends on the shear stress exerted by the flowing seawater on the aluminum surface. The shear stress exerted by the solution on small size specimens in the lab is high at low velocities. Similar shear stresses will be attained at significantly higher flow velocities past large aluminum structures. The scale up from laboratory to practice can be obtained in the usual manner by use of universal friction factor correlations for flow past a specified structure geometry [17].

Corrosion of aluminum alloys under exposure to one-phase flow, even under highly turbulent conditions, is a mass transfer controlled phenomenon, as will be discussed further. Cavitation, impingement, or multiphase flow is required for erosion corrosion to occur. Under such circumstances, aluminum alloys are susceptible to erosion corrosion. Several comprehensive experimental studies are available for corrosion of aluminum alloys in seawater at high flow rates [18-21]. Our analysis of the available data, although not shown here, indicated that the transition from localized to a more uniform etching type of corrosion, in which the cavitation and multiphase flow are apparently not present, is a result of the type of transition discussed above and not erosion corrosion in almost all cases. The transition often corresponds to laminar to turbulent transition in the experiments. It should be reiterated that this type of flow-dependent corrosion is a mass transfer limited phenomenon, whereas erosion corrosion involves mechanical removal of material from the surface in addition to chemical and electrochemical corrosion. A large amount of literature is available on erosion corrosion of aluminum alloys in multiphase flow. However, review of this subject is outside the present scope.

Cathodic Protection

Two important issues distinguish aluminum alloys from steel in terms of cathodic protection. Firstly, the oxide is amphoteric as seen in figure 1, *i.e.*, it is not stable in acid or alkaline environments. If the metal surface becomes alkaline during cathodic protection because of too high rate of the cathodic reaction, and the protective oxide may become destabilized. The transition between passivity and cathodic pitting in figure 2 can be used as a rough guideline for the negative limit of the potential applied during cathodic protection, although the limit actually also depends on the flow rate. Thus, protection is achieved by maintaining the passivity of the surface rather than bringing the potential close to or into the range of immunity, as is the case for steel. In principle, therefore, we are talking about anodic rather than cathodic protection. Moreover, it should suffice to maintain the potential sufficiently below the

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critical pitting potential, *e.g.*, at –0.85 V_{SCE}, to achieve the necessary protection. Cathodic (or more correctly anodic) protection is an effective way of preventing pitting corrosion of aluminum alloys [22].

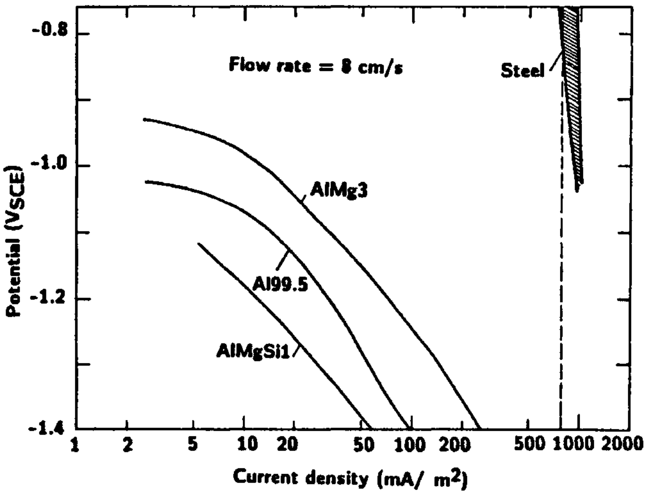

Figure 6. Cathodic polarizationcurves of freshly exposed aluminum and steel specimens at a flow rate of 8 cm/s. The dashed line is the calculated limiting current for oxygen reduction on steel [22].

The other issue is the need for very low current requirement relative to the cathodic protection of steel. This is related again to the fact that the cathodic process is restricted to the cathodic intermetallic sites, which constitute a small fraction of the total exposed area, while in contrast the entire exposed surface of a steel structure is uniformly accessible. Figure 6 shows cathodic polarization curves obtained on three aluminum alloys and carbon steel in flowing seawater [22]. These were obtained on small size (10 by 19 cm) plate specimens in an experimental flow channel at a linear flow rate of 8 cm/s, and the data were measured on freshly-exposed specimens before the onset of calcareous scale deposition. The cathodic current density measured on steel does not vary significantly with increasing cathodic potential because it is given by the limiting current for oxygen reduction on an uniformly accessible surface, which can be predicted by use of universal Nusselt number correlations for mass transfer. In contrast, the rate of cathodic reaction on the aluminum specimens is about an order of magnitude smaller, and it varies as a function of applied potential. Moreover, the current depends on the type of aluminum alloy. No flow dependence of the data for aluminum was detected [22]. The small current level and its alloy dependence indicate that the cathodic reaction is confined to microscale cathodic sites on the aluminum surface. The type and area of these cathodic intermetallic particles vary from one alloy to another. Because of their microscopic size, moreover, their mass-transfer properties are governed by the electrode size rather than by the stirring conditions in the bulk of the solution.

The current requirement for aluminum under cathodic protection in seawater is further reduced by an order of magnitude with time relative to the freshly exposed surface. The cause of this reduction is not only due to coverage of the cathodic particles by calcareous deposits, but more due to the detachment of the particles from the surface as a result of the cathodic etching phenomenon described above (see figures 3 and 4), as also sketched in figure 7. The current requirement may in fact become a few mA/m^2 positive [22] or oscillate around essentially zero current, thus the appropriateness of anodic rather than cathodic protection for aluminum.

The foregoing considerations of cathodic protection apply to low flow rates where pitting is the predominant corrosion mode. As uniform corrosion becomes dominating with increasing flow rate as discussed above, cathodic (or anodic) protection becomes ineffective [16]. In fact, cathodic protection may increase the corrosion rate rather than reducing it, as shown in figure 5 because the corrosion rate is controlled by the chemical dissolution of the oxide rather than

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by an electrochemical process. The dissolved oxide is replaced by anodic formation of new oxide at the metal-oxide interface.

In cases where the uniform corrosion under flow conditions is intolerable or erosion corrosion is possible, the most effective corrosion protection is to use corrosion resistant coatings. The technology of applying organic coatings on an aluminum surface is again quite different from the technology for steel. Since proper chemical cleaning and the use of a conversion coating are normally required, it is appropriate to use sheets or extrusions already coated at the plant in constructing aluminum marine structures. However, the subject of surface treatment of aluminum alloys is outside the scope of this paper, and the reader is referred to an authoritative treatise on the subject [23].

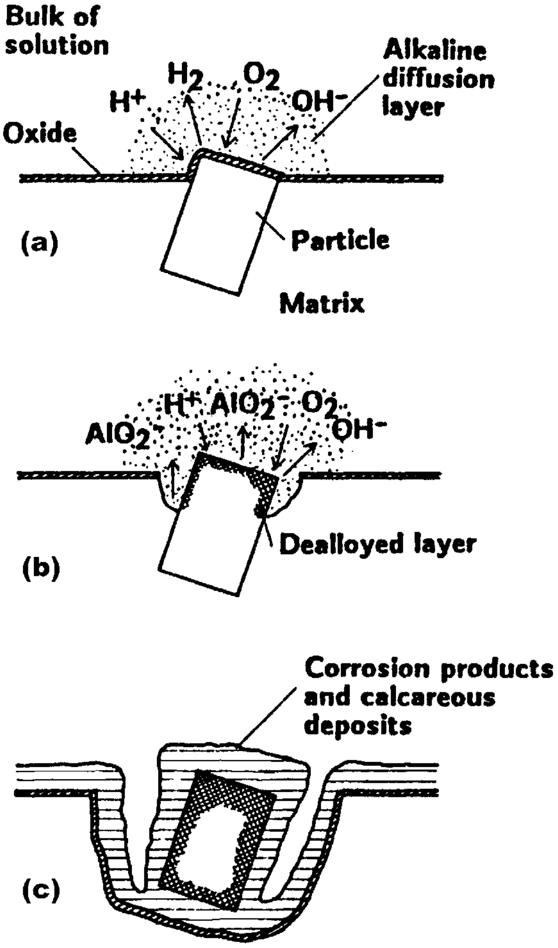

Figure 7. Schematic description of the mechanism of cathodic protection of aluminum alloys in seawater: (a) development of alkaline diffusion layer, (b) crevicing of the matrix around the particle and selective dissolution of the particle, (c) repassivation of the surface after detachment of particle[22].

Summary

As long as galvanic contact with more noble metals is avoided, most structural alloys, such as those in the AA1000 (commercially pure), 3000 (AlMn), 5000 (AlMg) and 6000 (AlMgSi) series, are resistant to corrosion in sea water, especially the so-called sea water resistant alloys in the 5000 series. In stagnant waters or presence of low flow rates, pitting may occur, with the possible exception of seawater resistant alloys. However, pitting corrosion, driven by the Fe-rich cathodic intermetallic compounds, is often of superficial nature. The pits tend to passivate as a result of etching or passivation of the intermetallics with time. Although thermodynamic calculations suggest possible instability of the oxide in slightly alkaline solutions, such as seawater, protective nature of the oxide in practice is attributed to the presence of alloying elements such as Mg and Mn. Thus, the passivity of both the aluminum matrix alloy (the anode) and the intermetallics (cathodes) have to be considered in evaluating the corrosion and protection of aluminum alloys. The presence of acid or alkaline pH, heavy metal ions such as Cu^{2+} and Hg^{2+}, dissolved CO_2, or high temperatures, in addition to the presence of Cl^-, may cause unexpectedly high corrosion rates, while H_2S acts as a corrosion inhibitor.

With increasing flow rate, the possibility of pitting corrosion reduces with increase in the rate of uniform corrosion, which is controlled by the flow dependent chemical dissolution of the

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oxide. In multiphase flow, aluminum alloys may become susceptible to erosion corrosion, and they should not be used without a coating.

Cathodic protection is an effective way of preventing pitting. It also requires low current densities since the cathodic area, defined by the Fe-rich intermetallics, is small in contrast to steel, which is uniformly accessible to the cathodic reaction. Application of too negative potentials will cause cathodic corrosion resulting from reduced passivity of the oxide with increasing pH at the surface. Cathodic protection does not stop uniform corrosion at high flow rates, and use of a coating may again be necessary
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