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The Role of Indium in the Activation of Aluminum Alloy Galvanic Anodes

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Abstract:

Despite six decades use of aluminum as a galvanic (sacrificial) anode, there remains a need for a better understanding of the underlying mechanisms for enhancing its efficient performance in cathodic protection systems. A few mechanisms have proposed for the role of indium in the activation of Al-Zn-In anodes and there appears to be no general agreement on whether this element plays its depassivating role by modifying the bulk microstructure of the anode, chemical composition of its surrounding electrolyte or directly through doping the structure of the passive oxide film. These mechanisms have been critically reviewed to achieve a more comprehensive understanding of the role of indium in such applications. Moreover, the novel solidification processing called Controlled Diffusion Solidification (CDS) has been introduced for being used efficiently to surmount the poor castability of the anode alloy without any need for addition of some elements with detrimental effect on anode's electrochemical properties.

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1. Introduction:

Aluminum, owing to its low density and high current capacity, has been used for many years as a galvanic anode in cathodic protection systems for offshore steel structures. However, the passive layer that readily forms on its surface can prevent the maximum current capacity form being provided and potentially reduce its usefulness as a cathodic protection anode [1], [2]. Aluminum and its alloys are generally passive unless they are made active by the chemical environments, mechanical action or a combination of the two [3].

This behavior of aluminum is greatly influenced by the formation of a compact oxide film, usually consisting of an anhydrous amorphous metal side layer and a crystalline hydrous electrolyte side layer [4], [5], as thin as a single monolayer or a thick strippable layer [6], which reduces the dissolution potential in chloride-containing solutions to around -730 mV (SCE). This is significantly different to the theoretical value, based on the thermodynamic electrode potential of aluminum of -2300 mV (SCE) [7].

Nevertheless, it has been shown that micro-alloying aluminum with trace amounts of one or more of elements such as indium, gallium, mercury, tin and others [8] and/or the addition of small amounts of appropriate salts of these elements to the electrolyte [9]–[11], can provide aluminum with its maximum current efficiency. These elements, when alloyed with aluminum at very low levels, act as activators for aluminum dissolution and make its dissolution more uniform (higher pit density) [12].

Considerable work was carried out in the 1960’s to identify reproducible and biocompatible alternatives for useable zinc-based sacrificial anodes, resulting in the development of Al-Zn-In based alloys [13], but the role of alloying elements, especially indium, in preventing aluminum from passivation still needs to be understood more thoroughly.

It is widely accepted that alloying aluminum with small quantities of certain elements changes the nature of the aluminum/aluminum oxide/chloride electrolyte system [14], [15]. But there is no general agreement on the role indium plays in influencing this change.

Several mechanism have been proposed so far for the activation of aluminum anodes by indium [16]–[18]. The majority of these mechanisms are unable to fully justify the active dissolution of anodes of this type [19] such that no sign of intergranular corrosion is detectable in their corrosion morphology. Almost without exception, opinion has been focused on the function of indium in introducing indium ions into the surrounding electrolyte which then redeposit back onto the anode surface causing local disruption of the oxide film [16], rather than impairing the oxide layer through inverse segregation [20] and thereby promoting pitting corrosion. As a result, a complete understanding of the role of indium in preventing or interfering with the renewal of the protective aluminum oxide has yet to be realized. The fact is that indium, as an alloying element with an activating function, may substantially change the nature of the oxide film formed on the alloy or cause it to not form at all [17].

The present mechanisms, despite their relative validity, are not necessarily appropriate for high efficiency Al-Zn-In anodes and there remains a need to further consider the role of indium in the modification of the passive layer and propose a suitable mechanism for the current available commercial anodes in which the contribution of mechanical loss in deterioration of electrochemical performance of the anode is minimized. According to Menezes et al. [21] "corrosion resistance in Al and Al alloys is intimately related to the characteristics of the oxide film, and changes in the corrosion behavior are often connected with the subtle chemical/electronic changes in the film."

If the oxide film dissolves, the metal corrodes uniformly and Lorking et al. [22], [23] has shown that corrosion is associated with the initial rate of solution of the anhydrous oxide (the metal side of the passive film). On the other hand, when the film is damaged under conditions that prevent normal self-repairing, localized corrosion ensues [24]. The plentiful supply of local micropits and their perpetual activation ensures the active dissolution of aluminum galvanic anodes.

Keeping in mind the importance of delivering indium to the optimum locations for maximum effectiveness, the purpose of the present review is to throw new light on the metallurgical and processing requirements that must be met to produce commercially viable anodes with high current efficiencies.

2. Literature Survey and Discussion

2.1. Microstructure of aluminum anodes

It is apparent that the surface of an anode that will be in contact with the electrolyte, owing to undergoing high rate of cooling is of chill solidification structure and the larger dendritic or columnar macrostructure occurs in inner portion of the anode prior to central equiaxed grains [13], [25]–[27]. The chill zone might be even wider as most of aluminum anode produced by metal mold casting [27], [28].

This variation in the macrostructure of the anode may lead to inducing uneven and unpredictable electrochemical properties, as it is well understood that the electrochemical properties of an anode is intimately related to its metallurgical structure [13], [25]. For example it is shown in case of the dissolution morphology that a tin-activated aluminum anode subjected to a long term test present an external layer with `metallic sponge' characteristics, followed by an intermediate zone with slight dissolution and a central one with pronounced pitting [26]. Also, It has been noted that anodes of larger grain size relatively provide better electrochemical performances [13], [25].

The microstructure in each macrostructural zone typically composed of primary grains or dendrites encompassed by nearly continuous networks of complex eutectic solids, second phase particles, intermetallic compounds, and inclusions [27], [29].

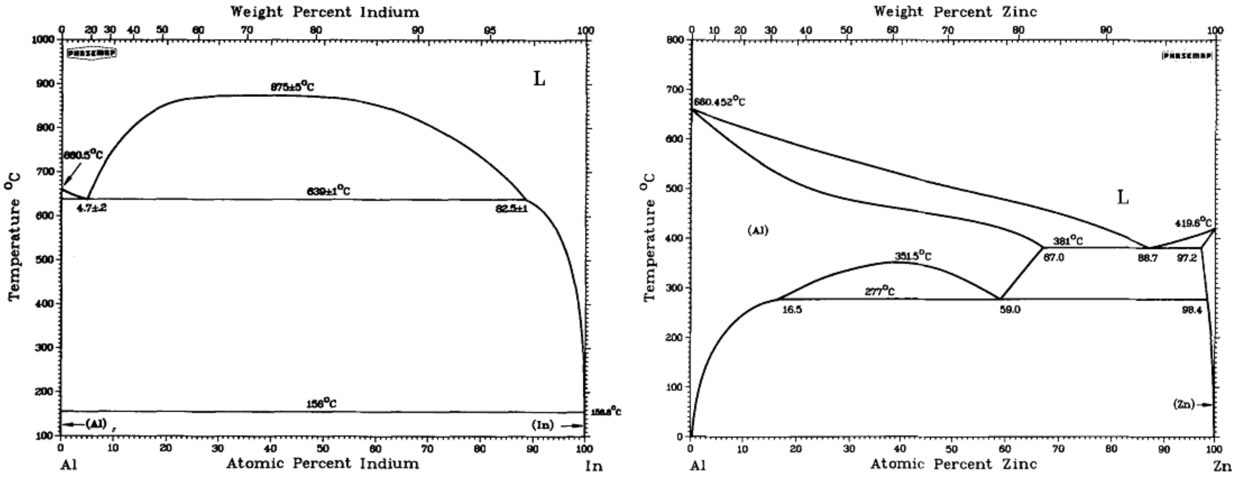
Concerning a specific anode alloy containing 5wt. % zinc and 0.02 wt. % indium, Reboul et al. [16] showed that zinc tended to be completely in solid solution and indium present partly out of solid solution in the form of pure precipitates.

With reference to the phase diagrams shown in Figure 1, it can be seen that the distribution coefficient of Al-Zn alloys with a typical content of zinc as present in Al-Zn-In anodes (3.5-6.5 wt.%) [30]–[32] is relatively small. Moreover, the solubility of Zn in Al increases up to 82 wt. % at the temperature of the eutectic reaction and to about 3-5 wt. % at room temperature [16]. Therefore by decreasing temperature the amount of zinc segregation is not much significant.

In the case of high cooling rates, such as may be experienced when casting in metal molds, one may expect to find approximately all the zinc content, at least in the chill zone, being in solid solution with the aluminum. All the excess indium content of the alloy over the solid solubility will be segregated in the intergranular regions which finally solidify by the eutectic reaction resulting in an intergranular eutectic microstructure. It should be remembered that the maximum solid solubility of indium in aluminum is very low (approx. 0.017wt. %) at room temperature [30].

The surface of anode therefore, consists of chill grains that are surrounded by an approximately zinc-free Al-In micro-constituent mixture and all the solidified alloy is pre-covered by the oxide film [33]. This film has generally been neglected with respect to the existing activation mechanism, while it is the first layer which requires to be overcome by the corrosive medium.

According to above discussion and Reboul's verification, while zinc is totally in a solid solution in aluminum, indium is present in two forms in the microstructure of the alloy, i.e. as a solute in the primary aluminum grains and as pure precipitates dispersed within the grains or segregated in the intergranular regions.



(a) (b)

Figure 1. Al-In (a) and Al-Zn (b) Binary Phase diagrams [34], [35]

Prior to reaching the temperature of the eutectic reaction, the In-rich liquid present in the intergranular regions, under the contraction forces applied by surrounding solid grains, is pushed toward the surface of anode.

It is noteworthy that the leakage of indium rich zones may or may not be able to cause disruption in the oxide film. If disruption does not occur, the segregated indium results in local bulging of the oxide film and thereby the structure of the oxide, especially at the location of these bulges, would be more open and more susceptible to diffusion by aggressive ions present in the surrounding electrolyte. In order for the activation of such an anode the following should occur: 1) local breakdown or weakening of the pre-existing passive layer and 2) inhibiting the renewal of the removed film.

2.2. Currently proposed activation mechanisms

It was proposed by Reboul et al. [16] that to activate aluminum by the usual alloying elements (Zn, In, Sn, or Hg), the following three-step mechanism occurs:

1. The simultaneous dissolution of aluminum along with the solute atoms present in solid solution with it introducing cations into the electrolyte and plating back of these cations onto the surface of the aluminum due to their nobility relative to aluminum.
2. Finally, and concurrent with the previous step, local separation of the oxide film.

This shifts the anode potential toward the potential of bare aluminum, which is significantly more active (−2.3 V SCE at pH 8).

Reboul and Delatte [36] showed experimentally that it was only Hg in solid solution that participates in depassivation of Al-Zn-Hg anodes. Reboul et al. [16] using the same experiments perused the activation mechanism of Al-Zn-In anodes by electrodeposition of indium on pure aluminum and subsequent heat treatment of some of these samples. They found that indium precipitates play no role in depassivation and it is only the indium in solid solution causing the potential to shift toward more negative values.

Subsequent to the researches by Reboul et al., Lin and Shih [37] conducted a research to study the effects of supersaturating indium in an aluminum solid solution by heat treatment. In spite of the rational expectance for the heat-treated and subsequently water-quenched specimens to exhibit the highest current capacity, due to the supersaturation of aluminum solid solution with indium upon quenching and consequently less self-corrosion, it was observed that the best performance is achievable by slow cooling of the annealed specimens in furnace. As a justification, the authors attributed this behavior to the development of quench-induced defects. But, the reason for lower performance of the quenched samples can possibly due to the elimination of the segregation layer covering all around of the anode's grains.

Despite the agreement with observations [38], there is some doubt in the absolute validity of the Reboul's mechanism as other noble elements relative to aluminum, like copper, iron and nickel, are unable to activate aluminum in this manner [17].

In Reboul's mechanism the modification role of indium is emphasized to be mostly within the aluminum beneath the passive film; to be in solid solution with it, and the surrounding electrolyte. No attention is paid to the importance of the passive film, especially in the first step, as a screen between these two media. Also, the reason why the pit remains active is not a consideration for this mechanism.

Venugopal et al. [20], pursue a solidification approach to suggest a depassivation mechanism for Al-Zn-In anodes. They identify that zinc and indium rich zones both have lower solidification temperatures than aluminum, are segregated from the dendritic primary aluminum and are responsible for weakening of the passive film and thereby for preferential dissolution of aluminum. As a result, by means of this pit nucleation, bare aluminum is exposed and again preferential dissolution occurs. They proposed also that with time this process results in surface enrichment of zinc and indium and finally, as a consequence of intergranular corrosion and mechanical loss of the anode due to detachment of grains or breaking of dendrites, the current capacity of the anode is deteriorated.

Similar to Reboul's mechanism, Venugopal does not explain the reason why the bare alloy was unable to repassivate after losing its passive layer.

Both local separation and pitting of the passive film may assist in non-uniformity of the corrosion morphology of the anode and promote the possibility of performance deterioration of the anodes through mechanical losses. In fact, none of these mechanisms, despite their relative validities, may be considered a mechanism for a high efficiency Al-Zn-In based anode. There remains a need to consider the role of indium in the modification of the protective character of the passive layer and propose a more appropriate mechanism for commercially available high quality anodes [19] in which the contribution of mechanical loss in the deterioration of the electrochemical performance of the anode is minimized.

2.3. Modification of aluminum passive film by activator elements

Aluminum oxide (Al_2O_3) is a wide-band gap semiconductor [39]. However, it is reported that the passive film formed on aluminum may contain some pockets with lower band-gap energies, (2.4-3.6 eV) [40]. Any inhomogeneity with the lower band gap would be responsible for making these pockets and thereby result in uneven electronic properties of the layer. As a result, passive films containing heterogeneities break down more readily in comparison to the film on pure aluminum [41]. If the alloying elements can incorporate themselves into the structure of the renewing layer, the renewed layer will contain some low band-gap pockets and will not therefore be as protective as a passive film free of any impurity atoms.

There is no general agreement on the structure of the passive layer on aluminum. The air-formed passive layer is an amorphous gelatinous (gel-like) alumina which, through an increase in the degree of humidity, can be transformed to pseudo-boehmite, then boehmite and finally bayerite in water [42], [43]. It can therefore be concluded that aluminum is usually protected by a double layer oxide film; an anhydrous amorphous oxide film on the metal substrate side of the film and a hydrated oxide film on the environment side of the film [4], [5], [44].

It is assumed in the proposed mechanisms that the inclusion of indium in the structure of the oxide layer, where possible, will have a negligible effect on the continuous activation of pits. Relatively little previous work has been carried out to investigate the capability of alloying activator elements to modify the corrosion resistance of the aluminum passive film [45]. Keir et al. [46], [47] reasoned that the poor affinity of tin oxide, relative to the oxide of other group IV elements, to form highly stable and high melting point compounds with aluminum oxide, is responsible for the efficacy of tin in increasing the ionic conductivity of the oxide layer and associated reduction in corrosion resistance of the film. They concluded that tin, with an oxidation number of 4, is positioned in the cation lattice of aluminum oxide, i.e. Sn^{4+} ions fill the existing vacant positions in the cation lattice and therefore additional cation vacancies are created and the ionic conductivity of the oxide film is increased.

There are a number of cation vacancies in the cation lattice of the layer structure such that an alien cation can potentially either occupy an already vacant position in it or replace an aluminum ion in a currently occupied position. Filling a vacant position will lead to the creation of additional cation vacancies, otherwise annihilation of pre-existing cation vacancies would occur, thereby increasing electronic conductivity. Comparing the AC resistivity of a passive film on pure aluminum and that formed on Al-Sn alloy in sodium chloride solution, it was found that the resistivity of the later is nearly two orders of magnitude lower than that of the former. It was suggested that this is related to enhancement in ionic conductivity caused by the creation of additional cation vacancies in the structure of the passive layer [46], [47].

The thermodynamic stability of indium ions at the corrosion potential (E_{Corr}) and ability of them to incorporate into the oxide layer during the redeposition process, resulted in Venugopal et al. [17] considering the role of indium, as a known activator, with a view to identifying whether this element follows a similar mechanism to that of tin in the activation of aluminum. They argued that it is possible for the trivalent indium ions to convert into bivalent and univalent ones, because the latter are more stable. These low valency ions, according to a point defect model [48], may position themselves into the cation lattice of the oxide film, converting it into a semiconductor film by lowering the excess electrons and creating additional anion vacancies. Chloride ions can replace these vacancies resulting in a decrease in anion vacancies and an increase in the cation ones. The pile up of these cation vacancies at the metal interface may be responsible for breaking the passive film [45].

However, the inclusion of tin or indium ions in the structure of the passive layer, which in turn provide passages or positions for easy diffusion of chloride ions into the structure, does not automatically lead to the breakdown of passivity. For depassivation to occur, Cl^- must pass the amorphous layer and reach the metal [49]. It is possible that these cations are able to incorporate themselves into the structure of the renewing passive film during the process of re-deposition and change the semiconducting properties of the aluminum oxide [17].

Being at the position of clearing the function of indium in active dissolution of Al/Zn/In based anodes which there are evidence of the interference of pitting during the first stages of their activation, there is a need to find mechanisms by which the oxide film loses its protective character.

2.4. Pitting of aluminum

The surface of aluminum with a low dissolution rate is vulnerable to pitting corrosion [49], [50]. The need to assist aluminum to resist pitting has led to the proposition of a number of mechanisms for the breakdown of the aluminum passive film based on chloride penetration, mechanical stresses, thinning, and the agglomeration of point defects [45]. Among them is a four step mechanism proposed by T.H. Nguyen et al. [24], [51] in which the following stages occur:

(i) The adsorption of the aggressive anion on the oxide film.

(ii) The chemical reaction of the adsorbed anion with the Al^{3+} in the oxide lattice $A1^{3+}$ (in $A1_2O_3.nH_2O$ lattice) + $C1^-$ → $A1(OH)_2C1$, or $A1^{3+}$ (in $A1_2O_3.nH_2O$ lattice) + $2C1^-$ →$Al(OH)_2C1_{2;}$

(iii) The thinning of the oxide film by dissolution; soluble species diffuse away from the surface resulting in a thinning of the protective oxide film, and

(iv) At sufficiently thinned sites aluminum reacts directly with the electrolyte; the direct attack of the exposed metal by the aggressive anion with the formation of transient complexes which rapidly undergo hydrolysis:

$A1^{3+} + 4C1^- \rightarrow A1Cl_4^-$ and

$A1Cl_4^- + 2H_2O \rightarrow Al(OH)_2C1 + 2H^+ + 3C1^-$

Reboul et al. [49] also proposed a similar ten-step process for pitting of aluminum alloys, in which the first five steps are responsible for forming the majority of micro-pits in the passive film, all of which may not remain active in the existing electrochemical condition. This is not the case for aluminum alloys, as some other passive metals in which once pits form on the surface propagate actively without repassivation [52]. Initiation of pits occurs on all aluminum alloys, including pure aluminum, in pitting corrosive media but active propagation of the pit depends on the specific aluminum alloy [49].

In fact, the propagation of pits ceases as soon as the soluble complex chloride layer is unable to renovate itself sufficiently quickly at the bottom of the pits. As a result the complex chloride layer dissolves and the passive oxide film readily forms and substitutes it on the surface. The dilution by bulk electrolyte of the solution in the pits to the pH range of oxide stability ($4<pH<9$) is responsible for suppressing the propagation of the pits [44]. The Pourbaix Diagram [53] for aluminum shows that the aluminum oxide film is stable in the near neutral 4 to 9 pH range only. It dissolves in acidic environments (pH < 4) to form Al^{3+} ions, and in alkaline environments (pH > 9) to form AlO_2^- [44], [54], [55].

2.5. Accumulation of activator atoms at the metal/renewing oxide interface

Solute elements present in aluminum alloys may be either more active than aluminum (e.g. lithium) or nobler than it (e.g. copper). The former elements readily oxidize and form a poorly protective layer at the outermost of the forming passive layer [44]. Upon renewal of the oxide film, the latter elements usually accumulate at the metal/oxide interface. As a result, providing the nobler alloying elements do not form large intermetallic compound with aluminum, the oxide film on aluminum alloys (with slight alloying additions) is almost pure alumina, similar to the film on unalloyed aluminum [44]. The intermetallic particles having sizes generally larger than 1 μm can effectively disturb the formation of a continuous oxide layer [44], [49]. According to this and the work done by Norris et al.[56], it can be possible for indium and zinc as two nobler elements relative to aluminum [54] which form no intermetallic compound with it (and also with each other) [34], [35], [57], to accumulate under the renewing oxide film.

Indium and zinc pass all the pre-requisites essential for the formation of a continuous oxide layer, as on pure aluminum. The accumulation of these elements at the interface of the metal and the renewing oxide layer may not be able to significantly reduce the corrosion resistance of the oxide layer but can certainly reduce the adherence between the oxide and substrate. The oxide film on Al-Zn-In alloys is therefore similar to that formed on pure aluminum with respect to continuity but differs in the level of adherence to the base metal.

2.6. The comprehensive mechanism for activation of aluminum by indium

The presence of indium in both aluminum solid solution and secondary phase is believed to be essential for ensuring the perpetual activation of Al-Zn-In alloys. Indium plays a multifunctional role in maintaining the depassivation of aluminum anodes, as described in the following sections.

2.6.1. Primary role of indium: introducing topographic changes in the passive film

The primary role of indium is responsible for the nucleation of multiple’ well distributed micropits on the as-cast surface of the anode or providing an easy to diffusion structure of the layer for chloride ions. As shown schematically in Figure 2, the precipitated or segregated indium is responsible for the primary role of this element in activation of aluminum i.e., inducing topographical changes such as bumps or bulges in the oxide film by being present just beneath the film. This results in a deformed and open structure passive film, especially at the locations of these bulges, making the film more vulnerable to diffusion by aggressive species and thereby causing the nucleation of micropits or reaching chlorine ions at the material beneath the layer, i.e. the onset of dissolution is established.

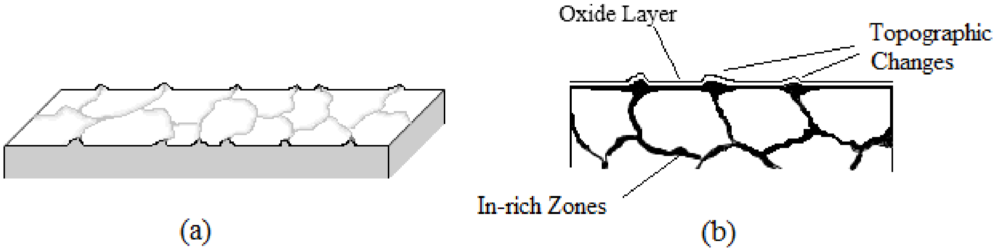


Figure 2. Scematic representaton of the deformed oxide layer (a) and topographic changes caused by segregation of In-rich zones at grain boundaries and metal/ oxide interface (b).

Mechanisms with emphasis on the breakage or rupture of the as-cast layer for the initiation of micropits are not fully acceptable as the bare aluminum recovers its tenacious oxide layer on its surface through exposure to air on the casting floor where no chloride ions are present to compete with oxygen. In fact, two cases are possible:

1) If oxygen present in the atmosphere at the ruptured sites does not reach the aluminum beneath the layer of In-rich zones, these zones will corrode preferentially in a galvanic manner resulting in intergranular corrosion and deterioration of the anode performance.
2) If oxygen is able to pass the segregated In-rich zones, then the aluminum beneath the zones passivate immediately and a freshly protective layer is formed on the bare aluminum. In fact, the segregated regions become ineffective and resemble contamination on the protective oxide layer that could also be corroded as the anode in a galvanic couple with the oxide cathode.

As stated earlier, the presence of the segregated coatings on the aluminum grains, while they may not interfere with the corrosion resistance of the oxide layer, reduce its adherence to the aluminum substrate. The deformed and unruptured oxide layer is therefore impaired by the chloride ions at the early stages during the activation process and as a result the uniform dissolution of the anode material is enabled.

Uniform dissolution or corrosion morphology of anode material is due to the occurrence of the following (either singly or in combination) on the as-cast oxide layer:

1) Nucleation of numerous well distributed micropits, all of which remain active during the dissolution process (a pitting approach), or,
2) Establishment of the onset of dissolution at the metal side of the oxide layer simultaneously by loss of adherence at the interface and direct attack of aggressive ions to material beneath the oxide layer.

Nevertheless, it is the primary role of indium that is responsible for early activation of anode and its subsequent uniform corrosion morphology. However, the active dissolution of anode after removing and/or passing through the as-cast layer is guaranteed by indium’s secondary role.

2.6.2. Secondary role of indium: Accumulation at the metal/renewing oxide film interface

It is reasonable to anticipate at this stage that a fresh passive layer will form and prevent further dissolution of the anode by repassivation of the nucleated pits. However, due to the accumulation of indium on its own or along with zinc at the interface between metal and the renewing oxide, the new film loses its protective character. This may either be by incorporation in the renewing oxide layer causing the creation of pockets with lower ionic resistance for aggressive anions or based on their chemical affinity to chloride ions, resulting in the direct reaction of the chloride ions with the aluminum under the oxide layer or changing the pH of the electrolyte over the oxide stability range.

The creation of low band gap pockets in the renewing film, as stated by Venugopal [17] may be achieved by incorporation of the indium ions present in electrolyte into the oxide during the redeposition process. The indium in solid solution with aluminum is responsible for providing indium beneath the renewing layer and indium ions in the electrolyte to incorporate into the structure of the renewing oxide film thereby making it more conductive to chlorine ions. The secondary role of indium is therefore composed of two sub-roles. Firstly, causing the renewing oxide to grow sluggishly as a result of shortage of aluminum atoms at the interface and secondly, reducing ionic resistivity of the renewing layer and making it more prone to diffusion by chloride ions.

The slow growth rate of the renewing oxide due to the reduced availability of aluminum atoms causes a much more thinner oxide layer to form whilst the strong affinity of the indium (as well as zinc) beneath the renewed thin oxide layer to chloride [58] cause the Cl^- ions to concentrate and change the pH of the electrolyte beyond the stability pH of oxide layer. This acidified and concentrated chloride solution therefore prevents repassivation [44]. In fact, the reactions responsible for the formation of chloride complexes is not suppressed resulting in active dissolution of anode.

In addition, the presence of the positively charged indium and zinc ions in the adjacent electrolyte [7], [9], [16], [59], [60], as a result of co-dissolution with the aluminum, may accelerate the process of attracting chloride ions from the bulk electrolyte to the renewing oxide layer.

The fact that the grains are enveloped within a thin continuous layer of segregation (In-rich zone) which is emphasized to be responsible for the primary role of indium may assist also in its secondary role by making a barrier against the diffusion of oxygen ions present in the adjacent electrolyte ready to deliver themselves at the renewing oxide film to support the repassivation process. The less ionic radius of chloride ion relative to that of oxygen ions [58] allow them to easily pass this barrier and thereby active dissolution of anode take places.

The secondary role of indium is thus to prevent repassivation of anode by sluggish growth of the renewal layer through depletion of the aluminum atoms beneath the layer and providing a selective barrier for relatively easy passage of chloride ions and more hard passage for oxygen ions.

2.7. Validity of the comprehensive mechanism

The range of indium in Al-Zn-In anodes is recommended to be within 0.015-0.04 wt.% [30]–[32] and there is evidence that the main limitation of indium levels below the lower limit is an anode for which the activation process may take long time [13], [30]. This may be due to the elimination of the primary role of indium for introducing disruption of the oxide film due to the presence of indium in solid solution with aluminum.

Setting the upper limit to around 0.04% is possibly to avoid self-corrosion [30] and to ensure the oxide film is not disrupted by indium precipitates or segregates. By providing an easier path for corrosive ions to reach the aluminum beneath the oxide layer, an as-cast disrupted oxide film encourages uneven corrosion of the anode which while enhancing the probability of premature failure of the anode during service, can reduce the current efficiency of an anode through the mechanical detachment of undercut regions. It may be envisaged that the indium precipitates responsible for the primary role, undercut and leave the surface of the anode during the first steps of dissolution.

The reported surface enrichment of the anode from indium may be attributed to the dealloying of aluminum where the electrolyte promotes preferential dissolution of aluminum atoms. As shown by Norris et al. [56], as a result of dealloying the chemical composition of the anode surface shifts to more indium-rich compositions. These undercut indium compounds can also mechanically detach from the anode and reduce the current efficiency of the anode through weight loss.

3. Controlled diffusion solidification (CDS) process

As is discussed in section 2.1., aluminum anodes possesses the characteristic macrostructure of cast ingots, i.e. a chill/columnar/central equiaxed macrostructure, and the coexistence of these zones with their unique electrochemical properties and corrosion morphologies makes anode performance unpredictable. The uniformity in the macrostructure of the anodes is usually obtained by adding grain refiners [61] whose more noble characteristics relative to aluminum may promote self-corrosion.

The alloy of the anode (aluminum rich Al-Zn alloy with trace amount of indium), can be problematic with respect to its castability and defects such as porosity, hot tear and surface cracks are hard to avoid with this alloy [62], [63], especially in case of more complex geometries such as bracelets [64]. These can be improved by the inclusion of well proven alloying elements such as silicon (to improve fluidity, hot tear resistance, and feeding characteristics [25], [65]), magnesium and iron (to improve hot-tear resistance and decreases the tendency for mold sticking [65], [66]).. However, each of these elements has a negative effect on the electrochemical properties of the anode.

Silicon is cathodic to aluminum and promotes the tendency to self-corrosion. Also, it is reported that its presence in the alloying composition may cause uneven corrosion morphology and a long-lasting activation process of the anode [67].

Magnesium can significantly shift the operating potential of the anode toward more negative values [67] and thus may cause the overprotection of the anode and through this the protected component may be prone to cracking by hydrogen embrittlement and stress corrosion cracking phenomena [68].

To overcome the poor castability, the minimum iron content of the alloy should be at more than the maximum allowed to be present in the alloying composition. In addition, it has been noted by some researchers that iron, if present up to a certain level, can assist the activation process of the anode [67]. At excessive levels iron, similar to silicon in being cathodic to aluminum [54], can lead to self-corrosion. As stated previously, the large intermetallic compounds formed in the presence of iron in alloying compositions

[65] may cause rupturing in the as-cast oxide layer resulting in an uneven, pitting corrosion morphology.

It is therefore beneficial to enhance the castability of the anode alloy by some manners other than through the addition of alloying elements.

If it is possible to optimize the positioning of the activator atoms so as to maximize their effectiveness in their primary and secondary roles, and also mitigate the problem of hot tearing accompanied with such alloys then it would be of significant technical and commercial benefit.

In the case of aluminum anode manufacturing one of the most commonly encountered problems is the crack susceptibility of the metal-mold cast Al-Zn based alloys [64]. According to the related standards, provided that these cracks cannot lead to the rejection of the anode they must be repaired by the manufacturers. Grinding, blasting and sometimes welding are used for repairing defective anodes [64]. All of these repair techniques may cause the anode activation to be impeded and result in an uneven corrosion morphology by removing the more active as-cast surface [30].

One way to overcome the poor castability may be to employ high cooling rates or rapid solidification to cast aluminum anodes. By enabling a planar solidification front, a higher cooling rate can avoid the dendritic growth [63] resulting in the production of low-defect anodes.

However, the higher cooling rates may also prevent the segregation of the activator element [69], [70] essential for the efficient dissolution of the anode. Also, when considering large anode sizes, it is both difficult and expensive to achieve sufficiently high cooling rates.

Semi-solid rheocasting processing routes can mitigate the problem of hot cracking in some cast alloys by enabling a non-dendritic morphology of the grains. Unfortunately, problems with producing sound castings plus the relatively high cost and lower productivity of the processes [62], [63], results in this method largely being disregarded for the fabrication of aluminum anodes.

Among the semi-solid processes available is a relatively novel method called controlled diffusion solidification (CDS) with a proven ability for producing sound casting of wrought aluminum alloys [71]–[74]. This processing technology is based on the concept of isothermal diffusion solidification which was employed for first time in the 1980’s by Langford et al. for rapid cycle production of steel [75]. CDS technology employs a combination of solute and thermal fields to enable non-dendritic morphology of the casting [63]. The work of D. Saha [76], K. Symeonidis [77] and A. Khalaf [78]–[80] have resulted in a sound basis for successful CDS processing.

In this process two precursor alloy melts with different thermal masses (temperature and mass), are mixed in such a way that the higher thermal mass melt is undercooled by the other [73]. Numerous nucleation of solid nuclei within the undercooled melt, uniform distribution of the nuclei throughout the melt by the forced convection resulting from the mixing process and diffusion of alloying elements toward the solidifying front leading to a negligible and diminishing chemical undercooling at the solid/ liquid interface, prevent instability of the interface and thereby ensure the globular morphology [76]–[80].

One of the major benefits of the CDS process is the reduced contraction of the alloy as a result of casting a semi-solid slurry containing 5% solid fraction instead of a melt [63]. This can potentially reduce casting defects such as porosity and cracks caused by the contractive forces. It should be noted that CDS does not have a negative effect on flowability of the melt and it is possible to cast the slurry by gravity casting. Alternative semi-solid processes with a high solid fraction (e.g. around 30%) can make it impossible to produce sound casting without pressure assistance [63].

The advantages of employing CDS processing to cast aluminum anodes can be summarized as follows:

1. Overcomes the poor castability of the anode alloy by changing the solidification regime rather than by adding elements that could be detrimental to the electrochemical properties.
2. Eliminates the need for adding grain refiners which are cathodic to the aluminum and may lead to self-corrosion. The overly-refined structure obtained by the addition of refining agents can also promote deterioration of the anode through mechanical losses.
3. Increases repeatability and predictability of the anodes as a result of a uniform micro and macrostructure, thereby reducing the risk of under or over protection.

4. With respect to the more controllable nature of CDS processing relative to conventional solidification processing, it is possible to control the presence of depassivator (indium) and modifier (zinc) elements in the microstructure. Using CDS, it is possible to ensure the presence of indium in its maximum solid solubility in the aluminum (the secondary role) and also, due to the relatively lower contraction of the alloy solidifying by this process, prevent the rupture of the as-cast oxide layer (the primary role), resulting in a more uniform corrosion morphology of the anode.

As expressed in previous sections, the microstructure of aluminum anodes obtainable by conventional solidification processing is composed of two phases, i.e. the aluminum primary phase and activator-rich intergranular or interdendritic secondary phase. The activator atoms exist in both the two phases, present in solid solution in the former (the amount is usually very low as the solid solubility of the elements in aluminum is very low) and as pure elements (in excess of its solid solubility in aluminum) in the latter.

As stated earlier, it is the presence of the activator atoms in solid solution with aluminum that ensures the perpetual activation of these anodes in chloride containing media, principally sea water. The intergranular activators are mostly responsible for activation of the as-cast surface of the anode and also assisting in disrupting the renewing oxide layer by a continuous covering of the anode’s grains.

In using the CDS process to cast aluminum anode, it is important to not compromise these activation functions in order to achieve defect free anodes. The parameters of the process, including the thermal-masses of the two precursors, should be controlled so that the electrochemical performance of the anode alloy is not adversely affected.

In the CDS process the higher thermal-mass alloy is undercooled by the lower thermal-mass alloy and to ensure the formation of a non-dendritic morphology it is essential to add activator at a level no more than its maximum solubility limit in aluminum. The presence of higher levels of activator risks segregation and thereby instability of the S/L interface as a result of constitutional undercooling.

If the activator is only present in the higher thermal-mass alloy there is a propensity for activator atoms to defuse toward the surrounding activator-free liquid, thus resulting in a shortage of the activator element at a level below the lower limit recommended for activation. There may also be no intergranular activators to activate the as-cast surface of the anode.

Based on the potential advantages of the CDS process, it appears attractive for the manufacturer of cast aluminum galvanic anodes, especially for those with shapes more sensitive to hot cracking such as bracelets.

4. Conclusion

From above discussion it can be concluded that to produce an anode with an even corrosion morphology (high efficiency), the following approaches can be considered:

1. Achieve nearly simultaneous nucleation of a large number of micropits at anode surface and provide conditions for perpetual activation of almost all the nucleated micropits.
2. Establish the onset of dissolution of anode at the metal side of the passive layer simultaneously caused by loss of adherence at the interface and direct attack of aggressive ions to material beneath the oxide layer.

It is concluded that using indium in alloying composition can fulfill the above requirements as follows. Indium has a multifunctional role in the activation of aluminum. The primary role of indium is the creation of topographical changes on the as-cast passive layer, including both the inner anhydrous and outer hydrous layers, as a result of indium segregation or precipitation. This is responsible for opening the structure of the oxide film, especially at these sites, which will be more vulnerable to diffusion by chloride ions and through this, the onset of activation of anode commences by near simultaneous nucleation of multiple well-distributed micropits.

The dissolution of anode, however, may not proceed by pit nucleation and propagation and follow the second approach by establishment of the onset of dissolution at the metal/oxide interface rather than pit nucleation. In this case, the as-cast oxide layer containing topographical changes resulted from indium's primary role is penetrated by chloride ions and once the aggressive ions reach the metal beneath the layer the onset of dissolution is established. The continuous activation of anode is guaranteed by segregated layer covers all around of the anode's grains and prevent fast thickening of the renewal oxide layer by causing the aluminum atoms and oxygen ions to be less available to support the repassivation process.

In other words, the secondary role of indium is the build-up of indium atoms beneath the renewing oxide, resulting in a loss of availability of aluminum atoms at the interface to provide conditions for fast growth of the oxide layer. This very thin newly-formed oxide layer does not therefore sustain any resistance to the corrosive electrolyte and readily dissolves or allows passage of chloride ions.

The novel technology of CDS can potentially overcome the poor castability of anode alloys and by using this process it should be possible to ensure the presence of the activator element in the microstructure for its multifunctional role in the activation process of aluminum galvanic anodes.

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