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Pitting corrosion of aluminum

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Abstract

This review describes the experiments performed during the last few decades which enhance knowledge of the pitting of aluminum. Specifically, metastable and stable pits, pit chemistry and the effect of intermetallics on pitting are discussed. The properties of metastable alloys and inhibition of Al are also discussed. © 1999 Published by Elsevier Science Ltd. All rights reserved.

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1. Introduction

Most of this article reviews some aspect of the passivity and pitting of Al and Al-alloys. It has been suggested that anodic oxide films might control the corrosion resistance of the base metal. It is known that different factors influence the pitting of other metals and alloys the same way as that of aluminum and aluminum alloys and that the existing hypothesis of pitting mechanisms in halogen environments apply to other metals and alloys as well. Recently, the interest in localized corrosion and inhibition of Al-alloys has been revived intensely because of aging of Al-alloys which are used extensively in the aerospace industry and because of increasing use of Al-alloys in the automotive industry.

Four stages of pitting corrosion can be distinguished: (1) processes occurring on the passive film, at the boundary of the passive film and the solution; (2) processes occurring within the passive film, when no visible microscopic changes occur in a film; (3) formation of so-called metastable pits which initiate and grow for a short period of time below the critical pitting potential and then repassivate (this is an

intermediate step in pitting); and (4) stable pit growth, above a certain potential termed the critical pitting potential.

A vast number of papers have been published through the years on the growth of stable pits. Metastable pits were first described qualitatively about 30 years ago, but quantitative studies were not reported until the 1980 s [1].

Concerning the first two stages—the processes which lead to the breakdown of the film, hence the interaction of Cl^- with an oxide film—little is known. These stages are certainly dependent upon the composition and structure of the oxide film. The structural characteristics of the oxide depend on the material composition, the presence and distribution of micro-defects (vacancies, voids, etc.) as well as macro-defects (inclusions, second phase particles its size and shape), crystal structure and the degree of noncrystallinity of the oxide. Its also depends on the electrolyte composition, potential and temperature.

In neutral (roughly between pH 4–9) noncomplexing solutions, the oxide film on aluminum has very low solubility. Its electronic conductivity is also very low; hence the redox reactions are blocked. However, a small current is measured during metal polarization as a result of the presence of defects in the oxide film.

The air-bourne oxide on the Al was observed to be amorphous, whereas, the structure of the oxide obtained by thermal oxidation of Al was strongly dependent on the temperature. Anodic films that were grown in a borate and tartaric acid solution on the Al are thin, dense, coherent and amorphous, whereas films grown in sulfuric and phosphoric acids contain layers which are thick, porous and crystalline. Hence, the structure of the oxide film on aluminum can be different resulting in different chemical and physical properties.

Vijh [2] has shown that the corrosion potentials of Cu, Ni, Sn, Pb, Fe, Al and Zn in chloride solutions can be related to the estimated band gap values of the corrosion reaction films most likely to be formed. Highly insulating films tend to be associated with more cathodic potentials; a fact which has been qualitatively explained in terms of electron-hole participation in the partial reactions proceeding on the film covered electrode during open-circuit corrosion.

The oxide films grown in aqueous environments on the majority of metals and alloys display semiconductive properties. There are many papers studying the semiconductive properties of iron and steels but only few papers exist that deal with electronic properties of aluminum passive film. The semiconductive properties of passive films were observed to vary with environmental and material variables. For example, depending upon the heat treatment, the passive films on stainless steels exhibited either *p*- or *n*-type of defects. At higher electrolyte temperatures, the oxide films on 304 stainless steel behave predominantly as an *n*-type conductor [3]. When higher anodic voltages are applied, the space charge region can be inverted to a *p*-type for an *n*-type conductor, and to an *n*-type for a *p*-type semiconductor [4]. The number of pits was greater when the films were of the *n*-type rather than the *p*-type [5].

Several researchers have intended to correlate the intrinsic properties of oxide films with pitting susceptibility, studying the semiconductive properties of oxides using AC-impedance and photoelectrochemical techniques. The photo-effect easily

can be related to the semiconducting nature of the passive film. The concentration of carriers near the surface can be increased by illumination. Lenhard et al. [6] found a significant decrease in the number of pits and an increase in the breakdown potential, when the nickel oxide (*p*-type) was illuminated. At the same time the pitting potential moved to a more positive potential. The same phenomenon was found on steel [7]. Morach et al. [8] found that materials with a lower number of localized states have better resistance to localized corrosion.

Bulk Al_2O_3 is an insulator with a band gap 8–9 eV [9] but the passive film on the Al exhibits a band gap ~ 3 eV [10]. Menezes et al. [10] measured the photocurrent as a function of potential for pure Al, and AA 7075 and AA 3003 alloys in chloride, molybdate and sulfate solutions. They found that the flat band potential is dependent upon the kind of electrolyte present and shifts to a more positive value with increasing susceptibility to pitting, which is probably associated with a defect structure of the oxide (i.e., deviation from stoichiometry). According to the authors, the diminished photoresponse at positive potentials suggests that the defects (O vacancies or Al interstitials) migrate toward the interface and oxidize.

Kobotiatis et al. [11] studied the electronic properties of a passive layer grown anodically on Al 70775 in chromate and oxalate solutions using electrochemical impedance spectroscopy. The Mott–Schottky plots were obtained from the measurements of capacitance at different potentials. Flat band potentials and the density of the energy state were calculated from these plots. Differences were found in semiconducting properties of the passive layer formed in chromate and oxalate solutions. These differences were related to the inhibition properties of chromate and oxalate to pitting. The oxide developed in the presence of chromate (good inhibitor) exhibits a less-noble flat-band potential and a lower average density of state. No effect of the electric potential was found on the flat band potential and the density of the energy states. Hence, in both of the above papers, the flat band potential was less noble in conditions when the susceptibility of Al to pitting is low as stated in the literature.

The effect of the electronic structure on pitting can be explained by a point defect model [12]. This model assumes that the chloride ions incorporate to the passive film by occupying anion vacancies. This results in a decrease of anion vacancies and increases the cation vacancies. When the cation vacancies start to pile up at the metal interface, a breakdown of the films occurs.

2. Interaction of chloride anions with passive film

In an effort to establish the interaction of chloride ions with a passive film, e.g., if chloride ions are adsorbed on the Al-oxide film and/or are incorporated in the oxide film. Different analytical techniques have been used.

Analytical techniques such as autoradiography [13] SIMS [14] and X-ray photoelectron spectroscopy [15] revealed adsorption of Cl^- ions on passive films of Al at the open circuit potential as well as at applied anodic potentials. The

metal surface was found to be inhomogeneous, consisting of a number of defects, and the adsorption energy varied from site to site. Accordingly, the adsorption of chloride ions was determined to be local.

Berzing [13] measured the adsorption isotherms on corroding Al with Cl^{36} as a radioactive tracer. The amount of chloride adsorbed w_{Cl} , was a function of the chloride concentration (Cl) and time according to the equation:

$$\log w_{\text{Cl}} = 0.64 (\log(\text{Cl}) + \log t) - 7.8$$

where w_{Cl} is expressed as g cm^{-2} , (Cl) as mol^{-1} and t (min). Chloride adsorption was primarily localized to the corroding pit sites. The adsorption of chloride ions on the passive Al was found to increase linearly with the potential. Addition of nitrate or sulfate delayed but did not prevent the uptake of chloride. The log of delay time was a function of the log chloride concentration and inhibitor species. It was concluded that a corroding aluminum surface has a variety of adsorption sites with different adsorption properties; only a minority of these sites are active for pitting corrosion. According to the authors the results suggest that there is no threshold for the chloride concentration below which pitting will not occur. Similarly, the presence of an inhibitor will delay but not prevent the onset of pitting.

Using the XPS method, Augustynski [15] found chloride ions incorporated at the corrosion potential in the first 10–15 Å of the oxide/solution interface. At more anodic potentials a significant amount of chloride is also present inside the oxide film. An increased adsorption of Cl^- was observed at high temperatures probably as a result of increased porosity of the passive film.

3. Metastable alloys

There are not many metals which dissolve in aluminum above a few atomic percent, those that do dissolve are Mg, Zn and Li. The equilibrium solubility of copper, one of the most important elements in aluminum alloys, is only 5.7 at%. When copper is in a solid solution pitting is inhibited [16]. None of the existing commercial alloys have very good resistance to localized corrosion. Therefore, there have been several efforts to produce “stainless” aluminum with a high resistance to localized corrosion in a chloride solution. To obtain this goal, chemically and physically homogeneous supersaturated Al alloys were produced by adding different elements exhibiting good resistance to pitting. It is expected that alloying elements which may be incorporated into the passive film will influence not only the chemical properties but the electronic structure of the film as well. These metastable alloys were produced only in the form of thin films (using nonequilibrium methods) which are useless for technical purposes. However, many papers dealing with nonequilibrium Al-alloys provide interesting fundamental information on the effect of alloying elements on pitting. The pitting potential of aluminum can be substantially increased by the addition of such

elements as W, Ta, Mo, and Cr [17–22]. Fig. 1 taken from ref. [21] shows anodic polarization of different Al-alloys in 0.1 M KCl. As can be seen, all of these elements increase the pitting potential in a neutral chloride solution. In the case of Al-9% W the pitting potential is shifted to more than IV in a more positive direction. Surface analyses were made for oxides on Al-Ta, Al-Cr [19], Al-W [21] and Al-Mo [23]. The passive film on Al-Mo, Al-Cr, Al-Ta has a considerable amount of oxidized solute (5–10%) but only 0.1–0.2% of W was detected in the oxide on the Al-W alloy.

Frankel et al. [24] studied pitting of thin (1000–2000 Å) sputter deposited Al-binary alloys (mainly Al-Nb, Al-Mo and Al-Cr). Measurements of the pitting and repassivation potential show that stable pits initiate at potentials only about 30 mV higher than they repassivate (Fig. 2). Hence the contribution of the passive film in inhibiting pitting is low, and pit growth is dependent upon events occurring within pits [24].

Other evidence that incorporation of alloying elements into the passive film does not play a fundamental role in pitting is given by Krishnakumar and Smialowska [25]. They studied passivation characteristics of a sputtered metastable Al-Cr and Al-Ta alloy by electrochemical impedance spectroscopy. It was

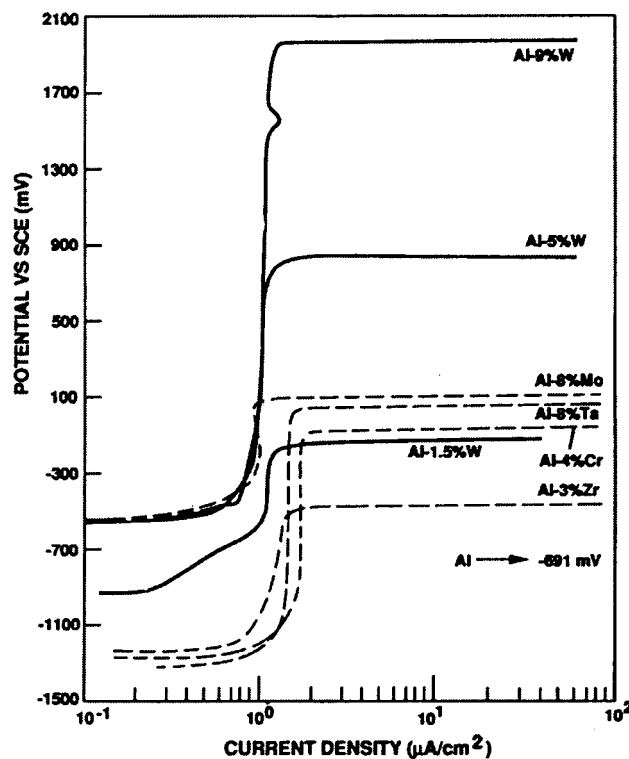


Fig. 1. Anodic polarization curves for Al alloys in deaerated 0.1 M NaCl solution [21].

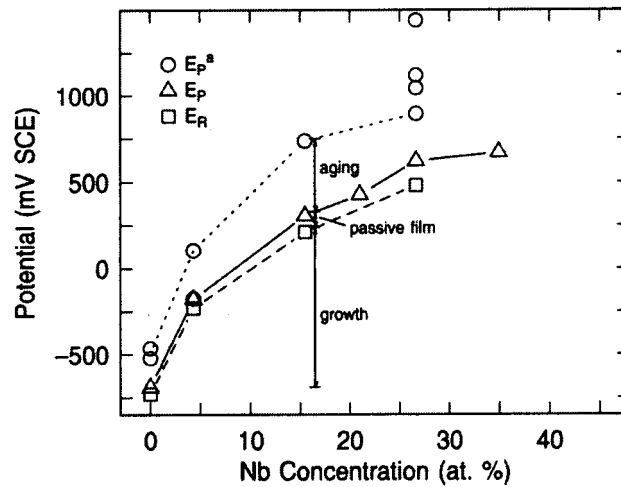


Fig. 2. Pitting potentials for freshly deposited samples, E_{pit} , and aged samples E_p^a , along with repassivation potentials, E_R , for pure Al and AlNb alloys [24].

demonstrated that the oxide film resistance shows a peak at potentials where a sharp increase in the enrichment level of the alloying elements in the oxide occurs. However, the film resistance decreases and the passive current increases after the enrichment peak is observed (Fig. 3). A decrease in resistance is observed at

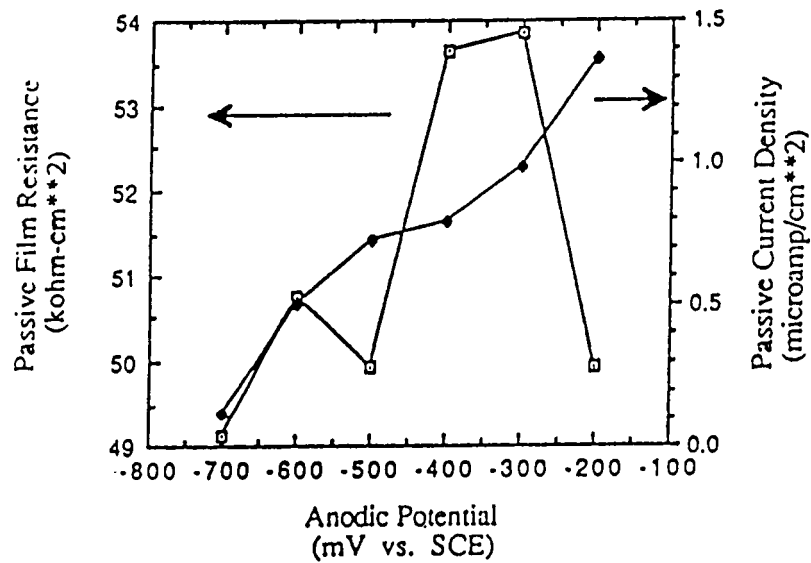


Fig. 3. Variation of passive film resistance and current density with potential for Al-10% Ta film in 0.3wt% NaCl solution [25].

potential higher than 500 mV for Al–4%Cr and 800 mV for Al–10%Ta and Al–9%Cr cathodic to the pitting potential despite further enrichment of alloying elements. It was found by others that the ratio of oxidized alloying elements Ta, Cr [17] and W [22] to the oxidized Al increases with potential in a chloride solution (Fig. 4). This indicates that enrichment effects in the passive film do not play a significant role in determining the pitting potential. The resistance on pure bulk Al also start decreasing at a potential well below the pitting potential. No resistance decrease was observed in the sulfate solution (Fig. 5).

There are different points of view concerning which processes within a pit inhibit its growth. It was suggested that inhibition is determined by the oxide solubility in acid of alloying elements [20,26], that the alloying element decreases the pit dissolution kinetics [24], and still another point of view [21] combines enrichment of the solute specie (hence solubility of alloying elements) with the potential of zero charge model [27,28]. According to this model the solute-rich metal region below the film inhibits the pit formation by forming an oxidized solute barrier layer and reduces Cl^- adsorption because of localized reduction in the pH_{zch} . Note that there is a linear dependence between the solubility of oxides in an acid solution with the potential of zero charge of the oxides [26]. The observed increase in the pitting potential of an AlMn alloy [29] can not be explained by the solubility of manganese oxide which is very high. However, it can be explained by the kinetics of a pit dissolution. It is known that the presence of Mn in Al increases cathodic polarization, hence decreases the corrosion rate.

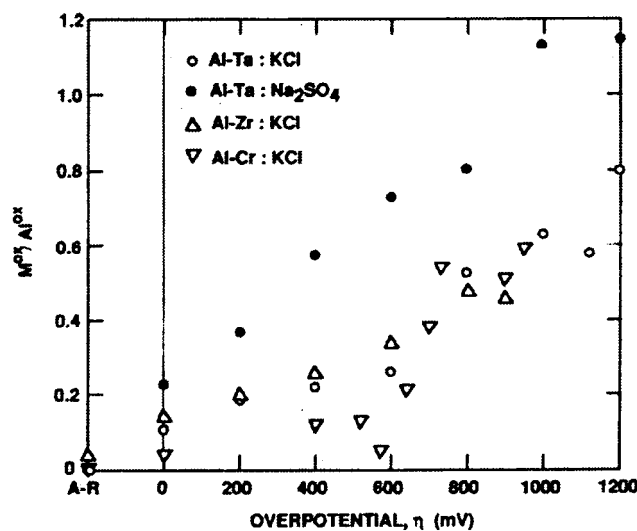


Fig. 4. Ratio of oxidized Al as a function of overpotential for Al–Cr and Al–Ta alloys in deaerated 0.1 M KCl; and for Al–Ta alloys in 0.1 M Na_2SO_4 [17]. OCP for Al–Ta in KCl = -1280 mV (SCE); OPC for Al–Ta in Na_2SO_4 = -1315 mV (SCE); OPC for Al–Cr in KCl = -1126 mV (SCE).

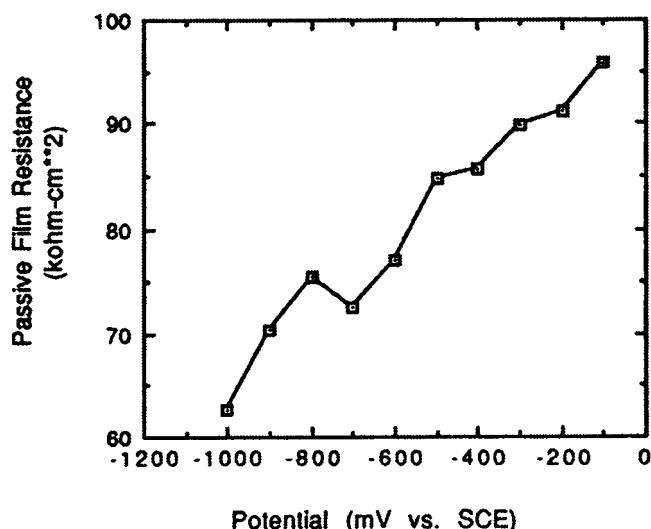


Fig. 5. Variation in passive film resistance with potential for Al-10at% Ta in sodium sulfate solution [25].

It is probable that depending upon the kind of alloying element a different process can determine the rate of pit growth.

4. Intermetallics

Intermetallics in aluminum alloys, are either intentionally developed to obtain the desired mechanical properties or are present in the alloys as natural impurities. Depending upon the alloy different second-phase particles are present [30]. For example, 1xxx alloys contain Al_6Fe and Al_3Fe , (alloys contain particles with Cu and 3xxx have $AlMg$ and $AlMnMg$ particles. There are intermetallics which when present in the alloy decrease significantly the resistance to localized corrosion (such as particles with Cu and Fe in 2xxx and 1xxx alloys, respectively) and the particles which seem to not adversely affect corrosion resistance. The behavior of the intermetallics depends mainly upon the potential difference between the particle and the matrix in a solution. The phases which are electrochemically more noble than the matrix play the role of cathodes while to the inclusions matrix undergoes anodic dissolution.

From the literature, Buchheit [31] collected the corrosion potential values for intermetallic phases (mainly in NaCl solutions) common in Al alloys which can help to predict the galvanic cell formation in Al-alloys.

Many papers were published on the influence of the Al_3Fe phase on pitting [32–36]. Nisancioglu [34] studied the electrochemical behavior of Al_3Fe , $\alpha Al(Fe, Mn)Si$ and $\delta AlFeSi$ in NaOH solutions. He made the measurements in an alkaline

solution because a high pH is established around intermetallics acting as the cathode for oxygen evolution. Similar to the earlier result of Golubev and Ronzhin [35], Nisancioglu found that near the corrosion potential the Al_3Fe undergoes a selective dissolution of Al and the surface of the Al_3Fe crystals becomes richer in Fe. Enrichment with Fe is detrimental to cathodic behavior. Oxidation of Fe into a protective Fe_3O_4 occurs at more anodic potentials. A formation of iron oxide inhibits the aluminum dissolution. The presence of Mn or Si in the phase reduces the effect of Fe on both the anodic and cathodic reaction rates.

Metzger and Zahavi [36] examined anodic films on Al–1%Fe and Al–4%Fe containing particles of Al_3Fe . They did not find dissolution of particles but from transmission and replica studies they deduced that the particles were undermined by local pitting.

Mazurkiewicz and Piotrowski [37,38] studied the behavior of Al_2Cu at the open circuit potential and under anodic polarization in sulfate solutions and found dissolution of this intermetallic with the formation of Al^{3+} and Cu^{2+} . The latter are reduced on the electrode in the range of potentials corresponding to the stability of metallic copper. On the basis the electrochemical studies on laboratory synthesized Al_2Cu , other researchers also found that this particle is cathodic with respect to aluminum [39].

Buchheit et al. [40] determined the chemical composition of the particles in AA 2024-T3 and studied its behavior in 0.1 M NaCl at pH 4.2. They found four main types of particles: 60% were AlCuMg (S-phase), 12% were Al (Cu, Fe, Mn), AlCuFe and (Al, Cu) Mn. The S-phase occupied 2.7% of the total surface area. This phase was active and Mg and Al selectively dissolved, leaving a pit where the particle was present. The S-phase dealloying left Cu-rich particle remnants, which were cathodic to the matrix and therefore caused the peripheral formation of pits around the particle. It is interesting to note that some of the Cu-rich particles decomposed into small mobile clusters and could be carried out from the pit probably by mechanical action.

In another paper [41] the localized corrosion behavior of AA 2090 was studied. Two types of pitting were found. The first type was attributed to the dissolution of the subgrain boundary phase T_1 (Al_2CuLi). A direct correlation between increased subgrain boundary precipitation and increased subgrain boundary pitting was noted. The second type of pitting involved an enhanced local galvanic attack of the matrix material surrounding the AlCuFe constituents which occurred randomly throughout the plate. They also measured the pH solution within an artificial crevice. The pH first increased to 7 (from pH 5) and after 100 min decreased to nearly constant value of 4.

There are many second phase particles which seem to be harmless to corrosion, for example AlMgMn, AlMnCr, AlMnSi particles, which are not cathodic to the matrix. However, it might be expected that these particles would still be the sites where pits will preferentially nucleate, because dissolution of these particles will produce small holes whereas agglomeration of aggressive species can occur.

Zamin [42] studied the role of Mn in the corrosion behavior of Al–Mn alloys.

The positive effect of an increase on manganese in a solid solution results in the shift of potential of the matrix in the cathodic direction whereas an increase in the Me/Fe ratio in the intermetallic shifts their potential in the anodic direction. In effect the potential difference between the matrix and the intermetallic decreases.

Some authors suggest that the geometry of the intermetallic influence the susceptibility to pitting. The differences in the pitting behavior of 6056 and 2024 alloys were explained by differences in the behavior of the coarse particles in the alloys [43].

5. Metastable and stable pits

Many years ago several researchers observed oscillations of current anodic polarization curves and a constant potential below the pitting potential for different metals and alloys in chloride solutions [44]. The occurrence of these oscillations was explained by the consecutive formation and repassivation of microsize pits. However, until the last decade no studies of these micropits were performed in detail. The metastable pits are very small in size and grow and repassivate in less than a few seconds. It was expected that the knowledge of the processes occurring during the formation and repassivation of the metastable pits would be helpful in understanding the processes which determine the stable growth of pits. The most important issues in the metastable pit studies are the processes leading to the formation of metastable pits and the electrochemical factor or factors that influence the transition of metastable to stable pits.

When the metastable pits occur first the current increases as the pits nucleate and begin to grow, and then decreases after a short time. It was found that metastable pits on stainless steel are covered by a remnant of passive film [1]. It is well established that metastable pits form sometimes several hundred millivolts below the pitting potential and during the induction time for stable pit formation. The metastable pitting events occur more frequently at potentials close to the pitting potential. There are many studies of metastable pits on steels [1,45–47] but few on aluminum. The most profound research on metastable pits on steel was made by Williams et al. [45]. They established the criterion for pit stabilization, namely: that $I_{\text{pit}}/r_{\text{pit}}$ must exceed 4×10^{-2} A/cm for stable growth. I_{pit} is the current within the pit, and r_{pit} is the radius of the pit. Below this value metastable pits are formed. This criterion also applied to aluminum alloys (Fig. 6).

As shown by Pride et al. [48] the number of metastable pits on pure aluminum increase with an increase of the anodic potential (until the pitting potential) of a constant concentration of chlorides, and with increasing concentration of chloride at a constant potential. (Figs. 7 and 8). The background current also increased with chloride concentration and potential. As the concentration of Cl^- increased the current spikes increased and the rate of metastable pit nucleation increased. The same trend was observed when the potential was increased. The authors found that stabilization of the pits also occur on aluminum when $I_{\text{pit}}/r_{\text{pit}}$ is higher than 10^{-2} A/cm.

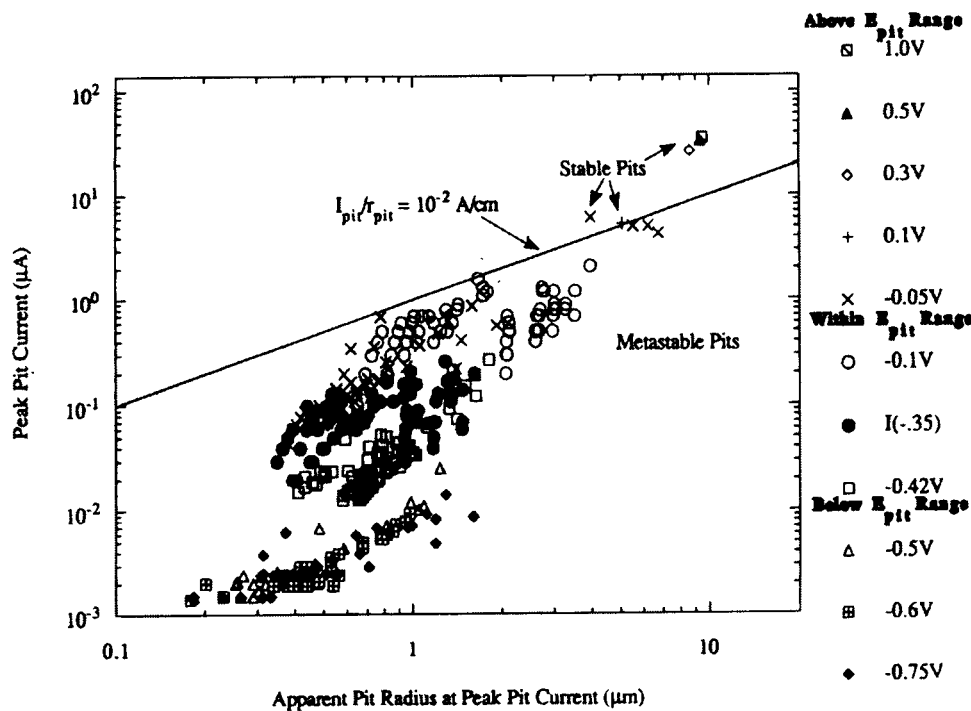


Fig. 6. Relationship between peak pit currents and apparent pit radii at peak pit current for a large population of metastable and stable pitting current spikes [48].

Pride et al. found that the apparent metastable pit current density is ~ 0.1 to 10 A/cm^2 and the apparent metastable pit radius is ~ 0.1 – $6 \text{ }\mu\text{m}$.

Scully [49] also studied the metastable pitting of Al–Cu thin films in a diluted HF solution and discovered that the θ -phase plays a dual role: it raises the potential to promote the metastable pitting initiation and supports cathodic reactions to sustain the pit growth. He suggests that metastable pitting at the open circuit potential may be cathodically limited.

Buzza and Alkire [50] demonstrated that the pit stability depends on the pit size, the duration of time lapse at the open circuit the potential and upon applied potential. These results were interpreted to mean that at a particular applied potential the critical concentration adjacent to the pit surface is required if the pit is to remain active.

Frankel et al. [1] suggested that metastable pitting formed on stainless steel is stabilized by the ohmic drop associated with the porous pit cover and that repassivation is expected to occur if the pit cover ruptures. When the cap on the pit is broken the pit solution is diluted and repassivation occurs.

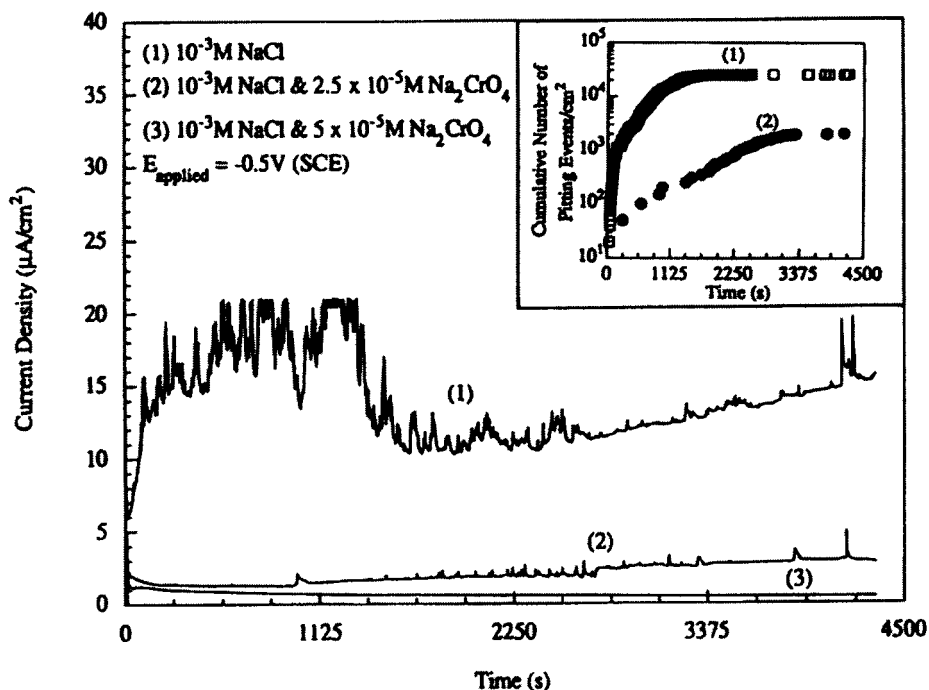


Fig. 7. Time series showing effect of potential on anodic current spikes associated with metastable pitting [48].

It is obvious that a pit will develop when the conditions within the pit are such that the pits are in the active state. Many years ago, Galvele [51] suggested that the stable pits would grow continuously if the critical value of $x \cdot i$ (pit depth times pit current density) were exceeded. He developed this rule taking into consideration the acidification of the pit solution. It is well known that pits (with some exceptions) occur only in halogen solutions. Hence, both acidification and chloride ions are necessary for pit development. The magnitude of the pH is coupled with the concentration of chloride ions in the pit solution. (The pH is lower when the concentration of chloride is higher until a solid metal salt is formed.) As is generally accepted, a necessary condition for stable pit growth is the presence of a salt film at the pit bottom. The presence of a salt film is the result of a high dissolution rate within the pit and the consequent acidification. The chloride salt films stable only in a high acidic solution.

Note that often crystallographic pits are observed especially in the initial stage of pit development. In this case no salt layer could be present within the pit and pit is probably growing under ohmic control.

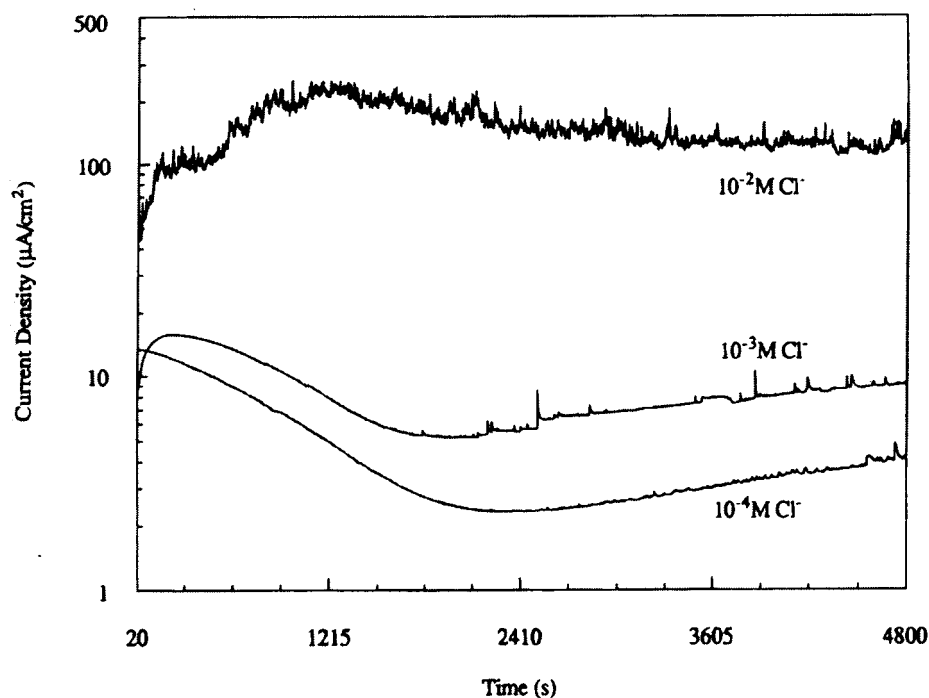


Fig. 8. Time series showing the effect of Cl^- on the anodic current spikes associated with metastable pitting. Potentiostatic control at a fixed potential -0.6 V [48].

6. Pit growth

The prediction of pit growth is important from a practical point of view, therefore many works have been performed to establish the kinetics of pit growth. Different types of experiments were made; measurements of the pit growth on natural and artificial pits at and open circuit potential and at an applied potential. In addition to establishing the pit depth and radius, the number of pits was counted as a function of time. Most of the experiments were done on steel [52].

One of the first investigations of pit growth kinetics on aluminum was made by Godard [53] who found that the pit depth was proportional to $t^{1/3}$. By predicting the pit depth from this relationship, he obtained a good agreement with the pitting in service.

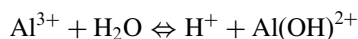
Hunkeler and Boehni [54] measured the time required for pits to perforate aluminum foils of different thickness in chloride solutions and in a chloride solution containing different anions at a constant potential. They found that the pit growth is ohmically controlled because the rate of pit growth is related to the conductivity of the bulk electrolyte. The pit depth is a function of time ($d \approx t^{1/2}$) as is pit current density ($i \approx t^{-1/2}$). Similar values were obtained when studying artificial pits: $d \approx t^{0.45}$, $i \approx t^{-0.48}$ [50].

The experimental results showing that the pit radius (in hemispherical pits) or the depth increased with the square root of time and that the pit current density decreased with the square root of time are consistent with both a diffusion controlled and an ohmic controlled pit growth rate. In the case of the experiments performed by Buzza and Alkire [50] on an artificial pit initiated by a laser pulse, the pit growth rate was not dependent on the applied potential (at applied potential -0.7 and -0.54 V) therefore they came to the conclusion that the pit growth was diffusion controlled. The discrepancy between the results reported in [54] and [50] might be caused by different experimental conditions.

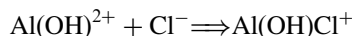
It is interesting to find the pit current at an early time of pit development. Frankel [55] and Sehgal et al. [56] studied the growth of a 2-dimensional pit in a thin aluminum film by video monitoring the development of a pit at a constant potential. They converted the corrosion rate of the pit wall to current. A very high current density which increased linearly with the potential and reaches a limiting value at a high potential was found. Hence at the beginning the pit growth was under ohmic and after some time under mass transport control. The maximum current noted during the pit growth in 0.1 M NaCl was 120 A/cm^2 [56].

7. Chemistry of pits

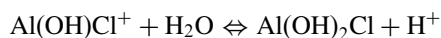
It is well documented that within Al pits the salt layer exists, if not during pit nucleation and the first stadium of pit growth, then during a later period of pit growth. As noted by Vijn [57] on metals such as Mg, Zn, Al, Fe, Ni and Zr (i.e., metals that suffer pitting) the dissolution product MeCl_x forms a solid salt in pits. It is almost unanimously accepted that a salt film stabilizes the pit. However, there is no clear knowledge on the composition of the salt layer. In the literature two different types of pit's salt are mentioned: Aluminum chloride (AlCl_3) and aluminum oxychlorides $\text{Al(OH)}_2\text{Cl}$ and Al(OH)Cl_2 . Depending upon the kind of a salt different pH of the solution within the pit can be expected. In the case of the presence of AlCl_3 the pH should be as low as 1, because the pH of saturated AlCl_3 is -0.3 [58]. On the other hand, the saturated solution of $\text{Al(OH)}_2\text{Cl}$ exhibits a pH 3 [57]. According to Hagyar and Williams [60] the following sequence of reactions occurs, ionization of the bare surface of Al occurs rapidly and Al^{3+} undergoes hydrolysis very rapidly.



aluminum hydroxide reacts with chloride



and then with water producing acidic conditions



Note that 15–20% of current is consumed for hydrogen evolution within the pits. The aluminum NMR spectrum of the solution extracted from artificial pits was found to be $\text{Al}(\text{OH})_2\text{Cl}$ and $\text{Al}(\text{OH})\text{Cl}_2$ [59]. According to Foley and Nguyen [61] these kinds of compounds are present during dissolution of Al in an aqueous chloride solution.

The pH of the solution measured in pure Al pits was found to be between 3 and 4 by using a freezing method when the pH of the bulk solution was 11 [59]. However Kaesche [62] found a pH 2 in the pits and Hoch measured a pH 1 at the active heads of the filiform corrosion [63]. pH 3 was observed in a simulated occluded cell [64] and in crevices [65]. Alavi and Cottis [66] studied conditions in simulated crevice using 7475-T651 alloy in a 0.6 M NaCl solution. They measured the pH in part of the crevice to be 3–4 but within a deeper part the pH was 8. This alkaline pH was probably caused by an occurrence of both anodic and cathodic reactions within the long (8 cm) crevice.

Several authors measured the local pH near intermetallics in aerated chloride solution. Direct measurements of the pH around the AlFe intermetallic were made by Park et al. [32]. Using an ion selective microelectrode they found an alkaline solution in the pits formed around the inclusions. AlFe_3 is the cathode which provides sites for oxygen reduction. (Fig. 9). This cathodic reaction generates hydroxide ions which dissolve aluminum. In another paper Rynders et al. [67] studied the corrosion at the AlFe_3 inclusion using in situ atomic force microscopy. They observed that circular pits are formed around the inclusion. The radial size of the trench was an order of magnitude greater than the trench depth. It was found that the application of a cathodic overpotential to the region of water

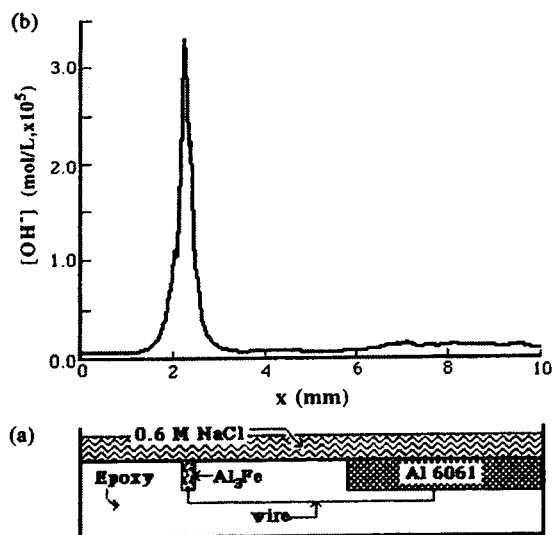


Fig. 9. (a) Schematic of galvanic cell formed by connecting Al_3Fe and Al 6061. (b) Hydroxide ion concentration over Fe_3Al in contact with Al 6061 [32].

reduction accelerated the dissolution process. They expressed the view that iron-rich inclusions act as cathodic sites for oxygen reduction and generate a high local pH that initiates pitting corrosion. It seems that Nisancioglu et al. [68] were the first to suggest that the dissolution of Al near the AlFe_3 particle is a result of a local alkalization. Alkaline pits were found around the AlFe_3 particles although the alkalization probably occurs at other cathodic particles. However, no data are available in the literature. It seems that alkaline pits form below pitting the potential and repassivate. However, the repassivated film is weak and is still prone to pit nucleation. Further experiments should be performed to find if this suggestion is correct.

Alodan and Smyrl [69] used fluorescence microscopy to investigate topographical and chemical changes during the corrosion of aluminum alloys. They reported that chloride solutions attack Al 6061 through the Mg, Si and Al inclusions in the early stages, and the inclusions partly dissolve and form corrosion products. During the exposure to a chloride solution, Mg selectively dissolves. On the basis of their results and mathematical model, they came to the conclusion that the pH does not change over the active sites. However, the pH of the bulk solution was rather low (pH 4) and small changes in the pH might not be noted.

Except for the data in paper [66] which shows an alkaline condition within the crevice, all other researchers found acidic conditions within the crevices and pits. However, the alkaline solution within the pits formed around cathodic inclusions was present when the cathodic reaction is oxygen reduction. The alkaline pits form according to a different mechanism.

8. Inhibitors

The effect of inhibitors on the pitting corrosion was evaluated mainly by measuring the pitting potential. The most—studied and the most—important inhibitors for aluminum alloys are chromates. Therefore, mainly the studies of chromate inhibitors will be discussed.

Augustynski [15] used the XPS method to study the effect of NO_3^- and CrO_4^- ions as corrosion inhibitors for Al. Films formed on Al in the presence of chromate anions were thought to be composed of hydrated chromium III and Al III oxide as well as a significant amount of adsorbed (incorporated) VI species. The results show that the interactions between Al and various aggressive (chloride) or inhibiting ions from the solution exist at potentials distinctly more negative than the critical potential for pitting. He found that the inhibitors studied undergo reduction inside the protective oxide film. Somewhat similar results were reported by Rabbo et al. [70]. Using the SIMS method a rapid uptake of chromium by alumina was assumed to be associated with the reduction of $\text{Cr}_2\text{O}_7^{2-}/\text{CrO}_4^{2-}$ at the tips of flaws in the surface film; a more gradual uptake of chromium was also found that was presumed to be associated with the

penetration of $\text{Cr}_2\text{O}_7^{2-}/\text{CrO}_4^{2-}$ in the outer layer of the film. It was suggested that chromates inhibit action blocking the incorporation of Cl^- into the oxide film. It was hypothesized that the reduction of the inhibitive oxyanions supplies oxygen atoms that allow displacement of Cl^- from the metal/oxide interface.

Hawkins et al. [71] studied the interaction of chromate species with Al supporting air-formed and anodic films using fluorescence detection of X-ray absorption. They observed the presence of different valency Cr species depending upon the thickness of the oxide layer. Cr (III) was present after immersion of a specimen with an air formed film into a chromate/chloride solution. On the other hand, a significant amount of Cr (VI) was found in a thick anodic film. In an intermediate thickness film (6 nm), both Cr (III) and Cr (VI) were present. The authors claim that rapid reduction of chromate species proceeds at the flaw bases. For air formed films, it is envisaged that the penetrating chromate species may be reduced by an electron conduction process through the residual film, when its outer region has been disaggregated or dissolved.

X-ray studies of the valency of Cr in aluminum have shown that III- and VI-valent Cr species may be present in a passive film on aluminum [72]. Trivalent Cr is incorporated in the oxide film when aluminum is anodized in a chromate solution [72] and is found to be present to some depth in the oxide.

Pride et al. [48] reported that the chromate also affect metastable pits; the metastable pit nucleation decreases at a given potential and Cl^- concentration.

The experimental results indicate without a doubt that after immersion of Al (or steels) to neutral chromate solutions, two phenomena occurs; adsorption of chromate and its partial reduction. Several possible actions of chromates can be taken into consideration: (1) chromates can adsorb in defective spots, decreasing the active area of the surface and therefore increasing the passive properties of a film; and (2) chromates can incorporate into the defective sites of the film, and can be reduced into chromium oxides increasing the protectiveness of the film against the chloride attack; (3) chromates and/or chromium oxides can change electronic properties of the passive film. Except for paper [4] no studies have been made on the effect of inhibitors on the electronic properties of aluminum passive film.

Cartledge [73] claimed that chromates act as an adsorption inhibitor in non-reduced form. He found that in a neutral solution containing chromates and air, a faster the cathodic reaction is a fast reduction of oxygen and no reduction of chromate. Hence, in this case the real passivator is oxygen and the inhibitor acts by decreasing the critical passivation current as a result of the adsorption of chromate on the metal surface. Thomas and Nurce [74] came to the same conclusion on the basis of potentiostatic measurements.

Breslin et al. [75] studied the electrochemical behavior of aluminum in aggressive chloride solutions containing molybdate and dichromate. They noted the increase of the pitting potential in both solutions. They measured the uptake of chromium by Al powder in a solution of different concentrations of Cl^- and $\text{Cr}_2\text{O}_7^{2-}$. The smaller uptake of chromium was in the more concentrated chloride solutions (0.2 M). At this concentration of Cl^- the pitting potential practically

does not change with the content of $\text{Cr}_2\text{O}_7^{2-}$ from 0 to 0.2 mol/dm². They suggested that reduction of molybdate and chromate species occurs at the flawed region of the passive film.

As shown in the past by many researchers, to inhibit pitting the corrosion of Al and steel (by increasing the pitting corrosion potential) the concentration of the inhibitor or chloride is not as important as the ratio of Cl^- to the inhibitor concentration [76]. There is a linear dependence between log of c_{Cl} and log c_{inh} . This relationship seems to indicate that the competitive adsorption of Cl^- and the inhibitor occurs. Because the surface of the non-noble metals is always inhomogeneous, it is clear that adsorption occurs first of all at some defective spots.

Fig. 1 in the Breslin paper is interesting as shows polarization curves of Al in 0.5 mol/dm³ NaCl with an addition of 0.1 and 0.05 mol/dm³ $\text{Na}_2\text{Mo}_2\text{O}_7$ at pH 7. The passive current is lower (hence exhibits better passive properties) for a lower concentration of molybdate but the pitting potential is less positive. At a higher concentration of molybdate, the passive current is higher and the pitting potential is also higher. This result shows that more protective film measured by current density will not always lead to better resistance to pitting.

A high pitting potential associated with a high passive current was also noted for chromate concentration from 1.5×10^{-4} to 0.01 M. However, at 0.1 M chromate, passive current was the lowest and the pitting potential was the most positive (Fig. 10) [77]. This figure presents polarization curves on 2024 Al in 0.1 M NaCl with different concentration of chromate. The pitting potential increases and the corrosion potential decreases as the chromate concentration increases (Fig. 11). In the region of chromate concentration studied the pitting potential increases linearly with pH (Fig. 12). These results clearly show that pH plays an important role in chromate inhibition. Unfortunately, there are no studies of the effect chromates pH in inhibition of Al. Perhaps, there exist a synergistic effect between chromate and hydroxide ions. It is worth mentioning that the same value of the pitting potential of aluminum alloys 8090 and 2014 was measured in 1–10wt% of NaCl solutions at pH 2, 6 and 11 [78]. The pH was adjusted using HCl or NaOH. In another paper [79] a constant pitting potential was measured at controlled pH between 6 and 8.

It should be noted that many inhibitors which are not incorporated into the passive film increase the pitting potential of Al. Citrate, tartrate, benzoate and acetate increase the pitting potential of Al but to a lesser degree than nitrate and phosphate [80].

The studies of chromate conversion coating enlighten to a certain degree the action of chromates at the corrosion potential. When Al with the Alodine converting coating is immersed in a NaCl solution, a small quantity of chromates are released [81]. As shown by polarization measurements (Fig. 13), the presence of 15 ppm of chromate in chloride solution decreases the corrosion potential into the region where no pitting corrosion occurs; hence, the region of potential below the pitting potential is enlarged. This effect is probably caused by the increasing pH of the solution. For example, the pH of 1 M NaCl is 5.7 and in the same

Polarization Curves of Al 2024-T3 in 0.1 M NaCl + X M K_2CrO_4 Stagnant Solutions

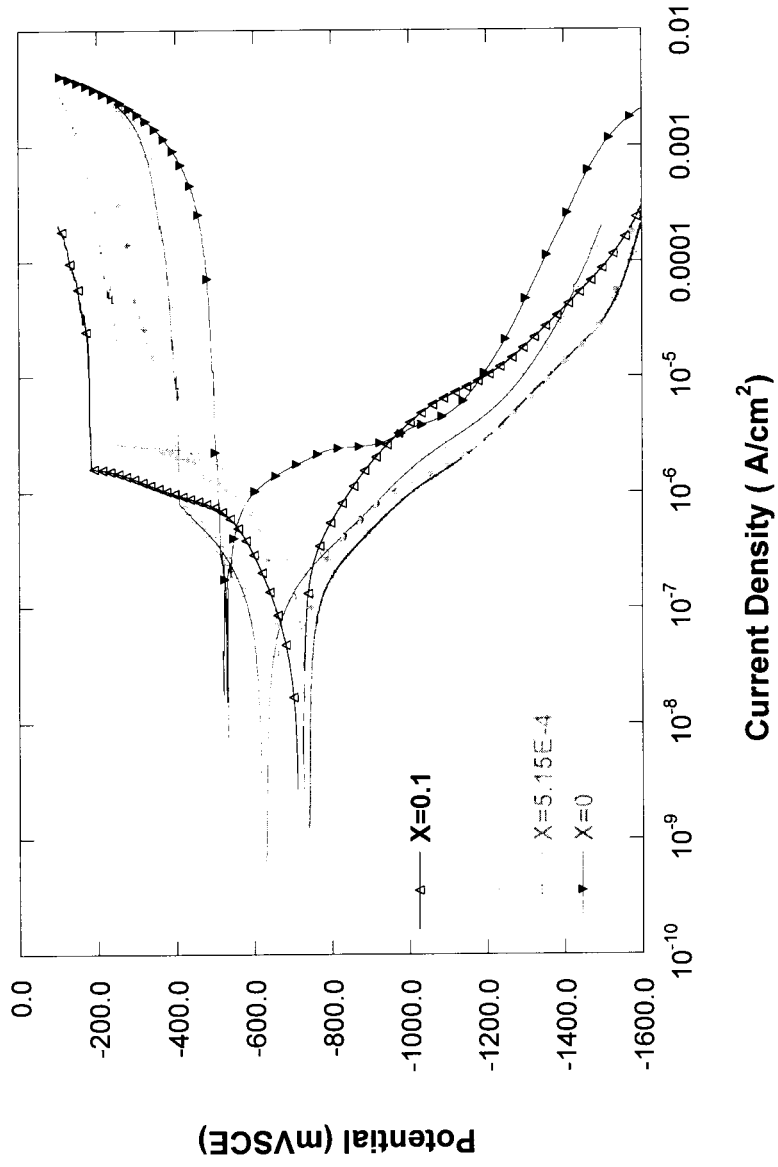


Fig. 10. Anodic polarization curves for Al 2024-T3 in 0.1 M NaCl with different concentration of potassium chromate [77].

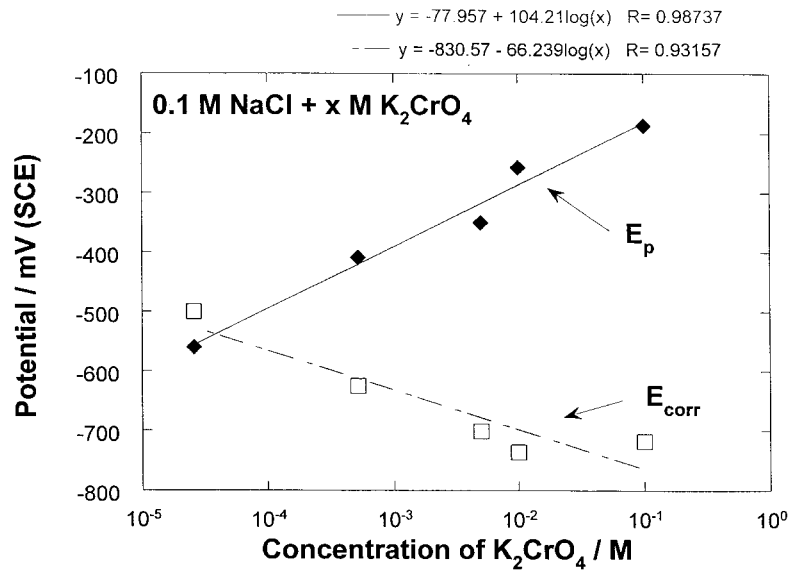


Fig. 11. Dependence of corrosion (E_{corr}) and pitting (E_p) potentials on chromate concentration [77].

solution with 100 ppm of chromate the pH is 7.4. This change in pH corresponds to a decrease of about 100 mV in the corrosion potential. An addition of about 0.01 M chromate increases the pH to 8.2 which corresponds to corrosion potential decrease of about 150 mV. As seen in Fig. 12 potential changes 50 mV for one

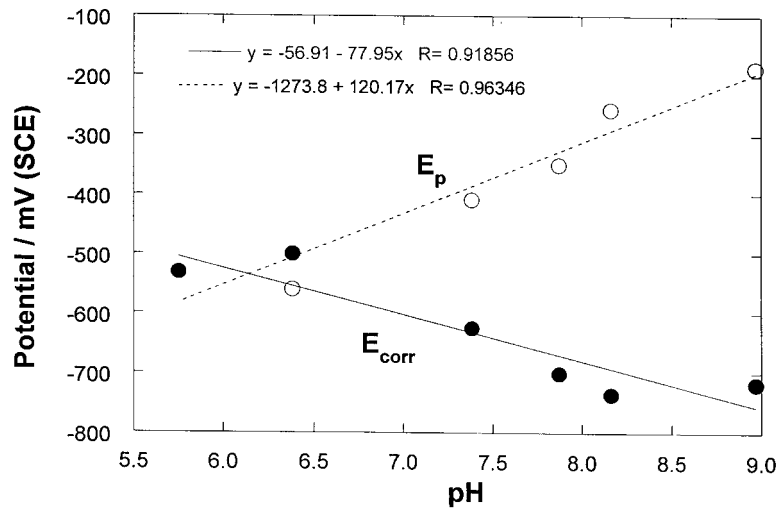


Fig. 12. Dependence of corrosion and pitting potential on pH of chromate solutions [77].

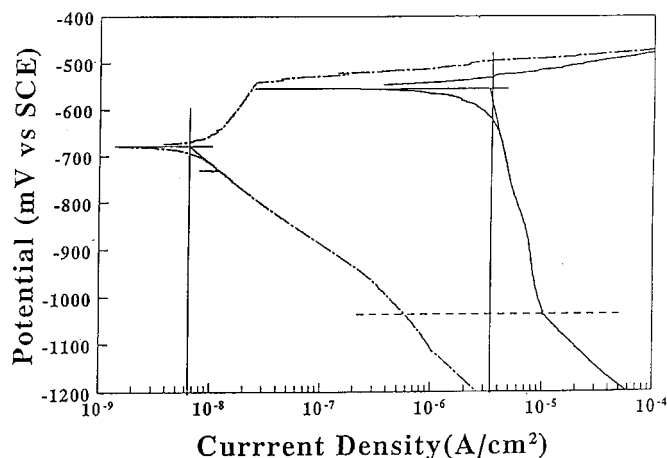


Fig. 13. Polarization curves measured after 45 h in 0.1 M NaCl with 15 ppm of K_2CrO_4 (dashed line) and without K_2CrO_4 (solid line) [81].

unit of pH. No systematic studies have been performed to find the contribution of chromate in the decreases of the open circuit potential of Al.

Hunkeler and Boehni [54] studied the effect of different anions on the pit growth in aluminum and found the inhibitive action of the chromate and nitrate. These anions were added to the chloride solution during the pit growth stage, and the possible inhibiting effect on pit nucleation was eliminated. They reported that a 10^{-3} and 10^{-1} M addition of NO_3^- and CrO_4^{2-} , respectively, are needed to inhibit the pit growth of aluminum in 10^{-2} NaCl of pH 11. It seems the effect of chromate on pit growth is complicated because Sehgal et al. [56] who studied a two-dimensional pit found, that the low concentrations of chromate in 0.1 N NaCl have no effect or even increase the pit growth, while only very high concentrations inhibit the pit growth.

In conclusion, chromates as inhibitors of pitting corrosion can act in different ways. But the mechanism of their action is still not known. Chromate anions can increase the pH in neutral solutions and the increase the cathodic polarization reaction decreasing the corrosion potential. They can increase the pitting potential as a result of an increasing pH in neutral solutions; they can improve the film against pitting corrosion by a restriction of adsorption of chloride anions on the surface or by restriction of the entrance of chloride to the passive film with incorporated chromium oxide plugging the flaw sites in the passive film and they can change the electronic structure of the passive film. The action of chromate on pit growth is not clear, but it seems that only a high concentration of chromate will decrease pit growth.

Despite the large number of papers published, more systematic research has to be done to learn about the mechanism of a chromate action in chloride solutions.

9. Conclusions

The experiments performed during the last decades enhance our knowledge of the mechanism of pitting of aluminum, however, unresolved questions still remain.

—The passive film on Al-alloys exhibits semiconductive properties which are the result of nonstoichiometry of the composition and local structural inhomogeneities.

—Because of inhomogeneity of the surface, Cl^- adsorption on the surface and absorption of Cl^- in the outer layer of the film occurs in localized sites.

—Pitting susceptibility (measured by pitting potential) depends upon electronic properties of the passive film. Less noble flat-band potentials correspond to higher pitting potentials. This means that a less defective oxide film, with lower localized states, is more resistant to pitting.

—In chloride solutions, the aluminum passive films are weakened (measured by current in the passive state) at much lower potentials than the pitting potential. Electrical resistance of the passive film formed on metastable alloys decreases at the potential several hundred millivolts below the pitting potential. In a sulfate solution no decrease of film resistance occurs. It can therefore be assumed that Cl^- ions adsorbed/absorbed in the outer layer of the film increase the number of the space charge.

—Intermetallics weaken the passive film and are sites for pit nucleation. The cathodic intermetallics produce a galvanic cell with an aluminum matrix and act as a cathode for oxygen reduction. These particles selectively dissolve and remnants from the particle dissolution—metallic Cu and Fe, are still more cathodic than the intermetallics.

—Deterioration of passive film properties at lower potentials than the pitting potential permits a rupture in the passive film and produces metastable pits. When the film covered metastable pit breaks down, the pit repassivates because the pit current is too low to sustain the aggressive solution. The metastable pit current is too low to obtain the i_x higher than 10^{-2} A/cm required for stable growing pits.

—Pit growth is determined by events occurring of the metal/pit solution interface. The physical and chemical properties of the passive film mainly influence the initiation of pits but play a secondary role in pit growth. For stable pit growth a high concentration of Cl^- and a low pH in the pit should develop to produce such an aggressive condition within the pits that repassivation is hampered. In the initial stage, the stable pit might grow under ohmic control as a result of presence of hydrogen bubbles in the pit solution or/and a presence of a high resistance salt. After longer times pits growth tends to be diffusion controlled. Presence of the salt layer regulates the transport of ions in and out of the pits restraining the pit solution and the pit passivation.

—It seems that the difference between stable and metastable pits is that in contrast to stable growing pits, in the case of metastable pits only the first step of pit development occurs, namely, formation of aggressive solution aggressive solution, however a salt film is absent.

The following problems influencing pitting of Al and Al-alloys which has been

not sufficiently explored should be studied:

1. the effect of semiconductive properties of the oxide films on pit initiation
2. time necessary for salt precipitation in the pit
3. formation of pits at the cathodic intermetallics
4. the condition of crystallographic pit formation—and their transformation into spheroidized shape (effect of inclusions)
5. pitting inhibition by inorganic compounds (chromate, nitrate phosphate): studies of the solution pH with dissolved inhibitor, influence of inhibitor on cathodic reactions and on the magnitude of passive current and influence of inhibitor on electronic structure of passive film
6. deterministic factors in pit initiation e.g., second phase particle size, aspect ratio, chemistry, etc.

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