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Electrochemical Study of Aluminium Alloy AA 5083 Corrosion Induced by Elemental Mercury in LNG Industries

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Abstract: Electrochemical corrosion studies of industrial Aluminium alloy AA 5083 corrosion in natural gas containing mercury metal and water as impurities showed to be a complex process. Single scan voltamograms of amalgamated electrode presents peaks of electrochemical oxidation around $E = -1.4$ volt/SCE and a corrosion potential $E_{cor} = -1.6$ volt/SCE showing an active amalgamated surface. Oxydation peak, I_p relating rate of electrochemical oxidation of aluminium was depending on three factors: thickness of amalgam and diffusivity of aluminium in amalgam, rate of chemical dissolution of aluminium in mercury which is the limiting step at high scanning rate potential and low immersion time. Diffusional step which controls kinetics at highest immersion time and lowest scanning rate and an intermediate step which controlled by the two kinetics.

Key words: Corrosion, aluminium alloy, mercury, amalgam, natural gas

INTRODUCTION

Aluminium alloys are successfully used in industries because they have a good corrosion resistance, good thermal and electrical conductivity and low density, which make them very competitive material for the heat exchangers in liquefaction of natural gas industry.

However, impurities like moisture and mercury (Kinney, 1975) which meet in different layers of natural gas and interact with the metal equipments and cause sometimes, a significant corrosion (Phannenstiel *et al.*, 1976).

Aluminium alloys weakly resist corrosion in aqueous medium in the presence of mercuric compounds because aluminium and its alloys are very reactive when they are not protected by their oxide film.

The mechanism of reactivity is due to the adsorption of mercury, formation of amalgam film and activation of aluminium surface (Wongkasemjit and Wasenkatom, 2000).

Many interesting studies of mercury elimination are in process. These results are not satisfactory because they do not allow a complete elimination of mercury. Concentrations of about 10 nanograms of mercury per normal cubic meter of gas and more are frequently encountered and corrosion appears after physical adsorption and local concentration of residual mercury in the equipments.

Mechanism of corrosion depends on many factors like adsorption of mercury on aluminium surface,

electrochemical oxidation and intergranular diffusion of mercury in aluminium bulk (Bennet and Pinnel, 1972). However this study showed that diffusion of aluminium in amalgam can be the limiting step of corrosion process.

Electrochemical behaviour of amalgamated industrial aluminium alloy type AA 5083 in aqueous medium containing chlorides ions were investigated. Single voltamograms using rotating disk electrodes preamalgamated were plotted to identify the determinant stage of the process of corrosion.

Objectives of this study is a contribution of understanding corrosion phenomena occurring in cryogenic exchangers in LNG industries by using electrochemical techniques on rotating disk electrodes.

MATERIALS AND METHODS

This study was conducted in materials laboratory of university of sciences and technology of Oran (Algeria) in the years 2002-2005.

The samples were supplied by the Algerian industry of natural gas and have a chemical composition data given by Table 1.

Samples were mechanically formed with a cylindrical form of 3mm diameter. These samples were inserted under press in Teflon ends adapted to the device of a rotating disk electrode EDX type.

Electrolytes were prepared from distilled water by the addition of KCl crystal, its concentration was

Table 1: Chemical composition of aluminium alloy type AA5083

Element	Mass (%)
Mg	4-5
Zn	0.25
Si	0.4
Fe	0.4
Cu	0.1
Mn	0.4-1
Ti	0.25
Cr	0.05-0.25
Other	0.15
Al	Remainder

1 mole L⁻¹ for all experiments. pH were adjusted to approximate value of 7 by the addition of HCl or KOH. All reagents are PROLABO products of analytical grade.

Amalgamated electrodes were prepared separately by cathodic deposit of mercury on mechanically and chemically cleaned surface of the samples at a constant potential: $E = -0, 15$ volt/ECS. HgCl₂ solution of concentration of 10⁻⁴ mole L⁻¹ was used. Time of mercury deposits were 6 to 48 min according to experiments. Temperatures were measured before and after each experiment and were approximatively 20±1°C.

Voltammograms were plotted using a potentiostat Type Tacussel 40-1X driven with pilot type Servovit and enregistred on XY table model Leybold. Saturated calomel reference electrode (SCE) and counter-electrode of 2 cm² area of platinum plate were used.

Scans start from cathodic potential $E_i = -1.8$ volt/SCE to an anodic potential

$E_f = -0.8$ volt/SCE. Rotations of electrode were 5000 rpm for all experiments.

RESULTS AND DISCUSSION

Experimental results:

Electrochemical behaviour of non amalgamated alloy:

Figure 1 curve a shows an electrochemical behaviour of non amalgamated electrode in KCl 1 M at pH = 7 and temperature 20±1°C. Potential window was limiting to: $E = -1$ volt/SCE in the anodic side by aluminium pitting corrosion and $E = -1.8$ volt/SCE in the cathodic side by hydrogen reduction. This result showed a classical electrochemical behaviour of aluminium and its alloys in aqueous solutions containing chloride ions

Electrochemical behaviour of amalgamated alloy:

Figure 1 curve b, represents the electrochemical behaviour of alloy AA5083 after 10 min of preamalgamation in a separated cell at constant potential of -0.15 volt/SCE and after 6 min of immersion in the experimental electrolyte (KCl 1 M) before starting scanning.

Results shows an anodic oxidation peak at potential $E_p = -1.4$ volt/SCE, current peak was $I_p = 25$ mA and gave

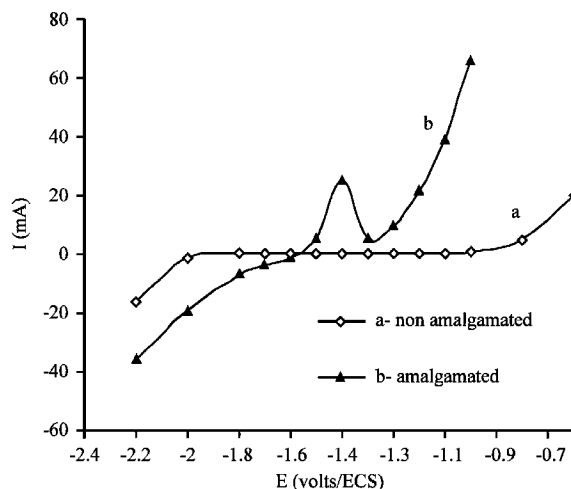


Fig. 1: Voltammograms for amalgamated and non amalgamated alloy AA5083 in KCl 1M

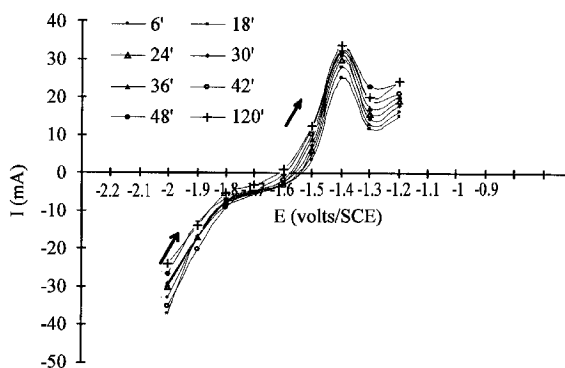


Fig. 2: Voltammogram for amalgamated alloy AA5083 in KCl 1 M for different times for immersion

a value of corrosion potential of $E_{cor} = -1.6$ volt/ECS, the cathodic area shows the reduction of hydrogen.

Evolution of oxidation peak in different conditions:

Experimental conditions of preparative amalgamated electrodes were changed: Three conditions were investigated: the time of immersion of amalgamated electrode, the time of mercury deposited and the scanning rate potential.

All specimens were amalgamated in 10⁻⁴ HgCl₂ solution and immersed for definite time in the experimental solution (1 M KCl). Rotation of electrode was 5000 rpm for all experiments.

Time of immersion: Specimens were amalgamated for a period of 10 min and then immersed in experimental solution for: 6, 18, 24, 30, 42, 48 and 120 min, respectively. Scanning of 300 mv min⁻¹ (5 mv s⁻¹) was started immediately after those preparative preliminaries.

Voltammograms (Fig. 2) shows an increased in current peak I_p with time of immersion.

A plot of the current peak I_p with presented time shows two zones (Fig. 3): the first zone at a time less than 36 min, the curve was nonlinear and it increases rapidly with an increment of $233 \mu\text{A min}^{-1}$; the second zone at a time beyond 36 min, variation of I_p becomes linear and stabilized at an increment relatively low of $21 \mu\text{A min}^{-1}$.

Time of amalgamation: Electrodes were amalgamated in 10^{-4} M HgCl_2 solutions at different times: $t = 6, 18, 24, 30, 36, 42$ and 48 min, respectively, then were immersed in an experimental solution of KCl (1 M) during 30 min, at a potential scan rate of was 300 mv min^{-1} (5 mv s^{-1}) and rotation of electrode of 5000 rpm .

Results in Fig. 4 shows an increase in amplitude of current peak with the time of amalgamation.

The dependence of current peak with the time in Fig. 5 exhibited two parts, the first one is at a time less than 30 min approximately, the current peak increases

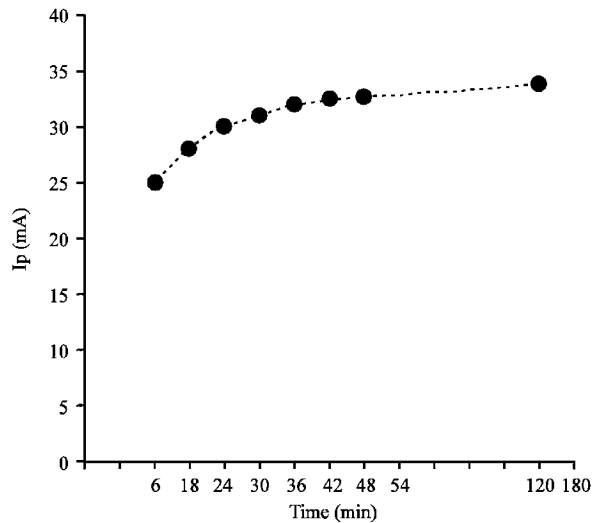


Fig. 3: Current peak evolution vs time of immersion

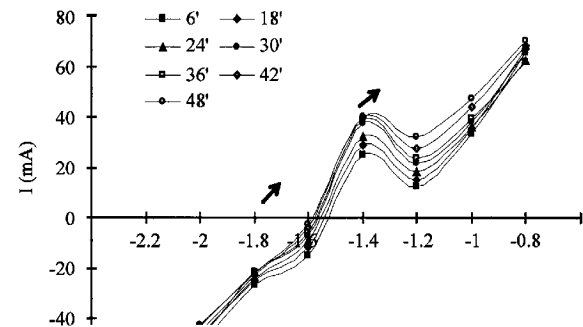


Fig. 4: Voltammogram of alloy AA5083 for different times of amalgamation

linearly with rate of deposit mercury at a time longer than 30 min, corresponding to the second part of the curve, current peak tends to stabilize and the variation of peak current becomes stationary indicating a complete electrolysis of mercury.

Scanning rate potential: Electrodes were amalgamated in 10^{-4} M HgCl_2 solution during 30 min and then immersed in experimental electrolyte for 36 min. Times adopted correspond to the second part of the curves of Fig. 3 and 5. Scanning rates were: $v = 50, 100, 200, 300, 500, 800, 1000 \text{ mv min}^{-1}$.

Results in Fig. 6 shows a decay of peak with the increased in scan rates.

For a lower scanning rates: $v < 100 \text{ mv min}^{-1}$, the slope was:

$$\frac{dI_p}{dv} = -0.27 \text{ mA/mv-min}$$

Evolution of I_p with a potential scan rate is represented in Fig. 7 which shows two linear different dependencies: For relatively low scanning rates: $v < 100 \text{ mv min}^{-1}$, the decay was:

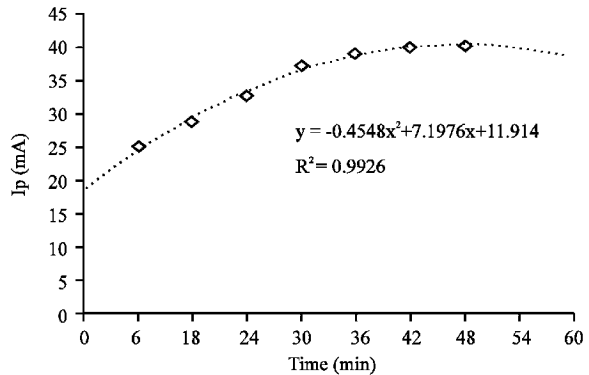


Fig. 5: Current peak evolution vs time amalgamation

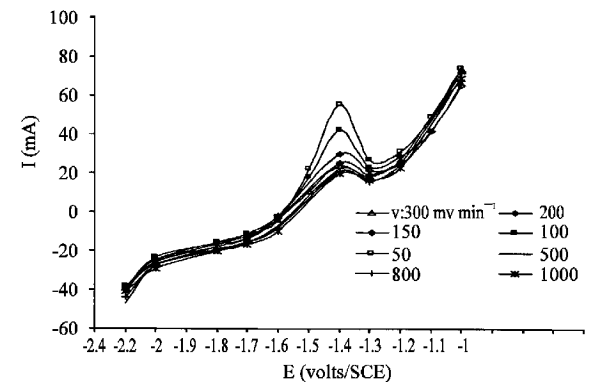


Fig. 6: Voltammograms for different scanning potentials

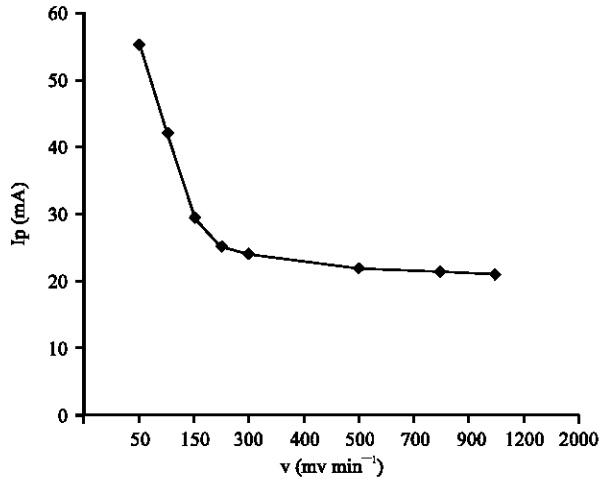


Fig. 7: Variation of current peak vs scanning rates potential

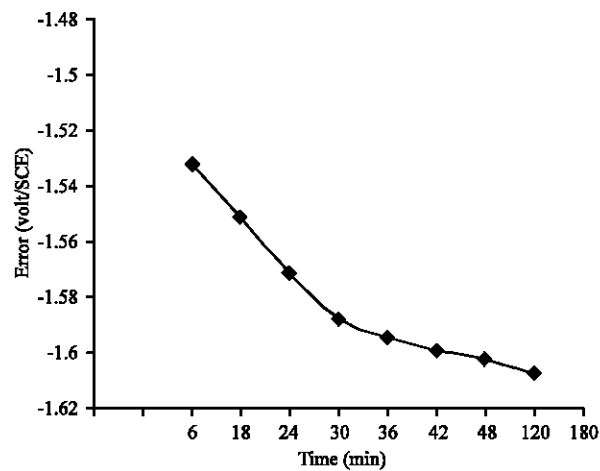


Fig. 8: Error vs time immersion

$$\frac{dI_p}{dv} = -0.27 \text{ mA/mv-min}$$

For the rates higher than 300 mv min⁻¹, the variation was much slower with a decay of:

$$\frac{dI_p}{dv} = -0.013 \text{ mA/mv-min}$$

Corrosion potential: Corrosion potential showed a negative value -1.52 volt to -1.60 volt/SCE and depends on experimental conditions.

Corrosion potential is shifted towards more negative values for longer time of immersion (Fig. 8).

DISCUSSION

Corrosion of amalgamated aluminium alloy AA5083 in neutral aqueous medium containing chloride showed a complex process on amalgamation.

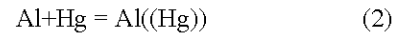
The non amalgamated alloy exhibits a classical electrochemical behaviour with a spontaneous passivity and then activation (Fig. 1a).

Different behaviour was unregistered when electrode was amalgamated, voltammograms showed, in their anodic area, an oxidation peak at a potential: $E_p = -1.4 \text{ volt/ECS}$, attributed to the reaction (Wongkasemjit and Wasankatorn, 2000):



Reaction (1) is well known and showed a catalytic reaction in which mercury is regenerated from the amalgam and will continue the process of amalgamation. That reaction occurs at interface amalgam/water as indicated by Fig. 9 and is electrochemically dependant.

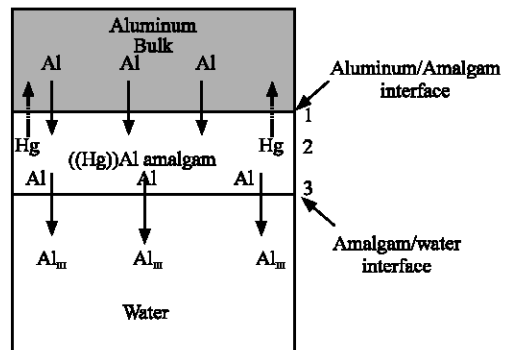
Amalgamation of aluminium (reaction 2) is a chemical process which obeys a chemical kinetic with a rate constant k_c occurs at interface amalgam/bulk aluminium.



Reaction 2 reached at a stationary level when the amalgam becomes aluminium saturated. However, reaction 1 is an aluminium consumer and a gradient of aluminium concentration occurs so a diffusional process takes place.

The scheme of the general process is represented in Fig. 9.

The two parts enregistered on curves in Fig. 3-6 showed 2 determinant steps on the process.



- 1- Chemical reaction: $\text{Al} + \text{Hg} = ((\text{Hg}))\text{Al}$
- 2- Diffusion of Al in Mercury
- 3- Electrochemical oxydation of Aluminium: $\text{Al} = \text{Al}_m + 3\text{e}$

Fig. 9: Process of aluminium corrosion induced by Mercury

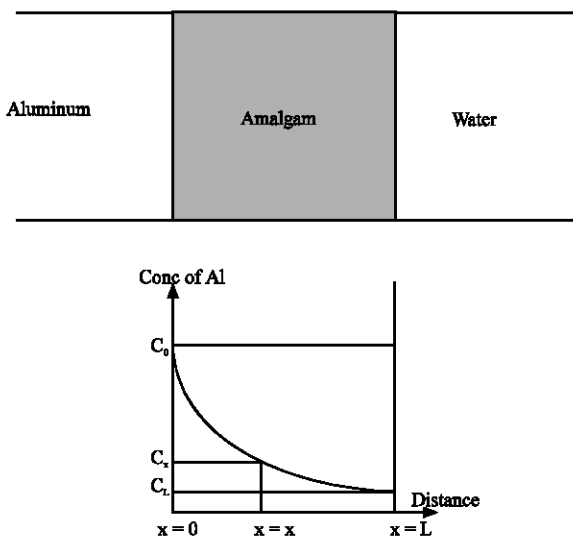


Fig. 10: Profile of concentration of aluminium in amalgam

At lower times of direct contact of mercury with the active surface of aluminium (times of immersion) chemical reaction of amalgamation (reaction 2) is a process controlled, while at a longer period of direct contact, amalgam tends to be saturated according to solubility of aluminium in mercury and then diffusion of aluminium which controls the general process.

During amalgamation period, chemical process controls the general kinetics, because rate of mercury deposited on electrode increases and the saturation cannot occur before the total electrolysis of mercury ions. However, for a determined concentration of mercury solution, total electrolysis occurs at a limited period and then diffusional control takes place.

Variation of I_p with scan rates of potential showed the impact of chemical and diffusional steps on electrochemical corrosion.

For low scan rate diffusion controlled the process (first part of Fig. 7), for higher values the process becomes

chemically dependant. Current peak in similar cases (thin film of mercury) is given by the relation (Bard and Faulkner, 1983):

$$I_p = n^2 F^2 / v / l A C_{Al((Hg))} / 2,7 R T \quad (3)$$

For a total electrolysis of 50 mL of Hg^{++} solution, the calculated thickness of the amalgams l was 10.05 μm for a surface of electrode of 7.06 mm^2 . Slope of the function I_p vs v has a value of -0.27 mA/millivolt/min or 0.00021 A.s/volt (Fig. 7). The deduced concentration

$C_{Al((Hg))}$ at interface amalgam/water was approximately 1 mg/100 g of mercury.

The concentration of saturation of the aluminium in mercury at 20°C, given by literature, was 2 mg/100 g of mercury.

Profile of concentration of aluminium in amalgam according to process proposed by Bard and Faulkner (1983) are represented Fig. 10.

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