

CONDUCTANCE MEASUREMENTS IN CORROSION STUDIES OF ALUMINIUM

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دراسة تآكل الألومنيوم بالقياسات التوصيلية

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تم اقتراح طريقة جديدة للحكم على معدلات نوبان طبقة الأكسيد المتكونة فوق فلز الألومنيوم أو سبائكة في محلول 3 مolar من حمض الهيدروكلوريك في درجات حرارة 30°م حيث يتم تنشيط طبقة الأكسيد باذابتها فيزداد التوصيل الكهربائي (أكسيد الألومنيوم عازل كهربائي) وكلما كانت طبقة الأكسيد أسماك أو من النوع العازل كلما استغرق نوبانها وقتاً أطول . ومن المعروف أن الألومنيوم وسبائكة تكون مغطاة بطبقة أكسيد في الهواء الجوي ، كما أن استخدام التيار المتردد يؤدي إلى تكون طبقة أنودية على سطح الألومنيوم وسبائكة . وقد استخدمنا الطريقة الجديدة المقترحة هنا والمبنية على قياس التوصيل الكهربائي في دراسة الظروف المختلفة لتكون الطبقة الأنودية ، كما استخدمت هذه الطريقة في الحكم على تأثير المعالجة بالماء المقطر المغلي (اللحام) في طبقة الأكسيد المتكونة في الهواء الجوي . وقد أتضح أن جهد التيار المتردد المستخدم في المعالجة الأنودية ، كذلك زمن المعالجة يؤثران بوضوح في مقاومة طبقة الأكسيد للنوبان في حمض الهيدروكلوريك كما تبين أن المعالجة بالماء المقطر المغلي تحسن من مقاومة الألومنيوم بشكل واضح ولا تؤثر كثيراً في مقاومة سبيكة الألومنيوم مع المنجنيز . وقد استخدمت طريقة قياس التوصيل الجديدة المقترحة هنا في التعرف على تأثير بعض المثبطات العضوية المختلفة على معدلات نوبان طبقة الأكسيد على سطح الألومنيوم وسبيكة الألومنيوم مع المنجنيز .

وتقدم الطريقة الجديدة المبنية على قياس التوصيل الكهربائي وسيلة سريعة وكمية لدراسة معدلات نوبان (تنشيط) طبقة الأكسيد سواء المتكونة في الهواء الجوي أو نتيجة للمعالجة الأنودية للألومنيوم وسبائكة كذلك يمكن استخدامها في دراسة تأثير مثبطات التآكل على الألومنيوم وسبائكة .

Key Words: Air borne oxide film, Alternating current, Anodization, Aluminium, Aluminium-manganese, Anodic film, Barrier layer conductance, Corrosion inhibition, Oxide film, Sealing.

ABSTRACT

A new method is suggested for studying the rates of dissolution of oxide film on aluminium and its alloys. The method is based on measuring the conductance between two aluminium (or its alloys) electrodes immersed in 3.0 M HCl solution at 30.0°C. the oxide layer is activated and dissolved, which means an increase in the electric conductance (aluminium oxide is dielectric). The thicker oxide and films of the barrier type will take longer time to activate. It is known that aluminium and its alloys are usually covered with an air borne oxide film. Also the application of alternating current (AC) leads to the formation of anodic films. This newly suggested method based on conductance measurements was utilized for studying the different

conditions of formation of the anodic films. This method was also used to control the sealing effect of air borne oxide films. From this study it could be concluded that the AC voltage and time of anodization clearly affect the corrosion resistance of the oxide film in HCl solution. Sealing with boiling distilled water enhances the corrosion resistance of aluminium distinctly while its effect on the Al-Mn alloy is rather insignificant.

The suggested conductance method was used to study the effect of some organic inhibitors on the rate of dissolution of the oxide film on the Al and Al-Mn surface.

INTRODUCTION

The anodic oxidation of Al is useful for the improvement of corrosion resistance, abrasion resistance, hardness and decorativeness. Anodic films are those layers produced by anodically polarizing metals and alloys at high fields where the films nucleate and grow directly at the anode surface [1-7]. The conditions under which different types of films are formed at the anode are discussed in earlier papers and reviews [8-15].

Impedance measurements identified four regions through the thickness of the barrier type anodic films proceeding from the metal outwards [16]:

- a- An n-type region containing excess metal ions and trapped electrons.
- b- A less defective n-type region.
- c- A region where OH⁻ ions have replace some O²⁻ ions, and finally.
- d- An outer oxygen rich region.

The films formed in H₂SO₄ yield an outer layer containing a mixture of crystalline ν -Al₂O₃ and boehmite α -AlO(OH), whereas the inner layer is amorphous Al₂O₃ [17]. Water incorporated into the film slowly converts the amorphous oxide into monohydrate.

AC as well as DC can be applied for anodization of Al and its alloys. The success of AC anodizing depends on [18]:

- a- Simple conventional oxidative reactions on the anode half-cycle, and
- b- No reversion of the anodic reaction during the cathodic half-cycle.

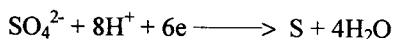
The possible reactions are:

a) Anodic Reactions

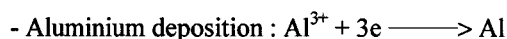
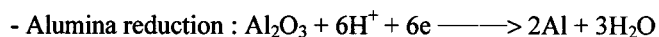
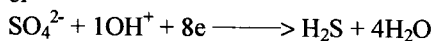
- Dissolution : $\text{Al} \longrightarrow \text{Al}^{3+} + 3\text{e}$
- Film format : $2\text{Al} + 6(\text{OH}) \longrightarrow 2\text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} + 3\text{e}$
- Oxygen evolution : $4\text{OH}^- \longrightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}$
- Oxidation of sulphate: $2\text{SO}_4^{2-} \longrightarrow 4\text{S}_2\text{O}_8^{2-} + 2\text{e}$

b) Cathodic Reactions

- Hydrogen evolution : $2\text{H}^+ + 2\text{e} \longrightarrow \text{H}_2$
- Reduction of sulphate:



or



The presence of Cl⁻ ions promotes active stages in the anodic process (dissolution), while sulphate ions promote passivity (film formation).

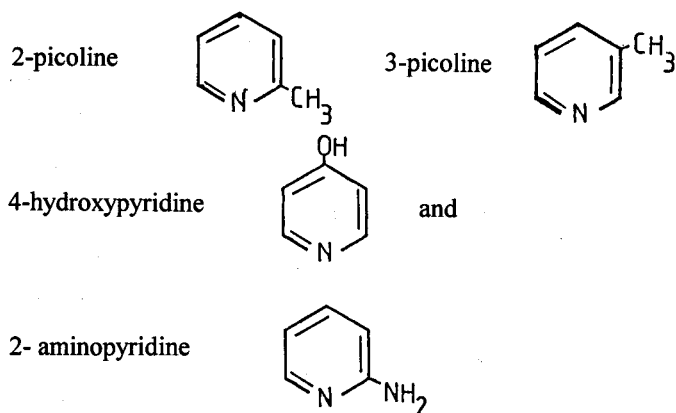
The main cathodic reaction in an acid solution is inevitably hydrogen evolution and as such as widely accepted.

Generally, Al and its alloys are known to have an air borne passive film which is mainly composed of oxides and hydrated oxides of Al. These air borne films and films formed by anodization (DC or AC) are very poor conductors. Wood [19 & 20] considered that some of the water in porous films is absorbed at room temperature. He used the presence of such water on the pore walls to explain the electrical properties of the films. We made use of the poor conductance of the oxide films on Al and its alloys, and their ability to dissolve in acid solutions (HCl), and suggested a new experimental technique based on conductance measurements. This technique is applied here for investigating corrosion, AC anodization and inhibition of Al and Al-Mn Alloy.

EXPERIMENTAL

Sealing of Al and Al-Mn specimens was conducted in boiling distilled water for 20.0 minutes. AC Anodization was carried out in the special cell where two identical electrodes 3.0 cm apart were immersed in anodizing solution. The effect of different parameters of anodization was studied using three different methods. Mylius temperature, Hydrogen evolution, as well as the conductance method suggested in the present work.

The inhibition of Al and Al-Mn corrosion caused by four organic compounds was investigated using the newly suggested conductance method. these compounds are:



The advantage of AC anodization in its best version includes the ability to anodize two electrodes simultaneously.

Conductance measurements during the dissolution of the specimens (untreated, sealed or anodized Al and Al-Mn alloy) was carried out in a special conductivity cell. In this cell, two identical electrodes (Al or Al-Mn) exactly of the same dimension (1.0 x 2.0 cm²) are immersed in 20.0 ml of 3.00 M HCl solution. The electrodes are kept parallel and 2.0 cm apart. The temperature was kept at 30.0°C by an ultrathermostat. A highly precision laboratory instrument (YSI model 35) was used to measure the conductance on a digital display. The rate of dissolution and depassivation (activation) is evaluated from the regression analysis of κ-τ relationship (κ-conductance and τ-time). The results of each experiment were correlated in the following manner:

(i) Linear regression

$$X = A + By, \text{ or } t = A + B\kappa \quad (1)$$

(ii) Logarithmic regression

$$X = A + B \log \text{ or } t = A + B \log \kappa \quad (2)$$

(iii) Power regression

$$X = A y^B \text{ or } t = A \kappa^B \quad (3)$$

and (iv) Exponential Regression:

$$X = A 10^{By} \text{ or } t = A 10^{B\kappa} \quad (4)$$

where A and B are the constants in the regression equations, κ- the conductance and τ-the time.

RESULTS AND DISCUSSION

(i) The effect of Sealing:

The behaviour of the sealed Al in the conductance cell is illustrated in Fig. 1. In this figure, data obtained from the Mylius temperature and the hydrogen evolution methods are also illustrated for comparison. The rate by which κ is distinctly slower in case of the sealed than the untreated A. The correlation of data yielded satisfactory values of r-the correlation coefficient and t-the student criterion for both the linear and logarithmic regressions.

$$r = (n \sum xy - \sum x \sum y) / [\{ n \sum x^2 - (\sum x)^2 \} (n \sum y^2 - (\sum y)^2)]^{1/2} \quad (5)$$

$$t = [r^2 (n-2) / (1-r^2)]^{1/2} \quad (6)$$

Values of r and t were rather low for the power and exponential regressions. The correlation through linear regression is restricted to the portion of the κ-τ curve far enough from the first stage. On the other hand, the three other regression relations are concerned with the first portion of the curve (Fig. 1).

It is worthy to note that the excellent correlation (r=1.0) in a linear regression between κ and τ is most probably related to the continuous activation and thinning in the anodic film (Sealed or untreated Al) on one hand and depletion in the concentration of HCl on the other hand. The lack of a reasonable correlation for power and exponential regressions can not be simply attributed to a single reason. Most probably, the complex behaviour of κ with τ is due to changes in the surface nature and the formation of Al³⁺ ions in solution together with the local microscopic high deficiency in HCl concentration inside the surface pores. These factors together give rise to poor correlation in both power and exponential regressions.

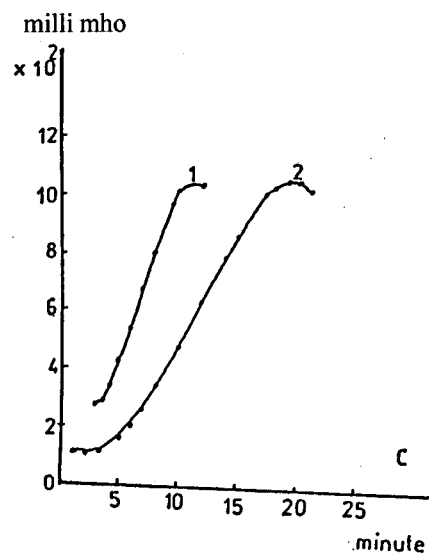
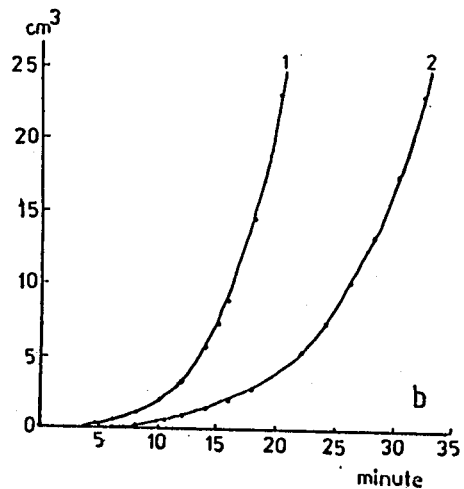
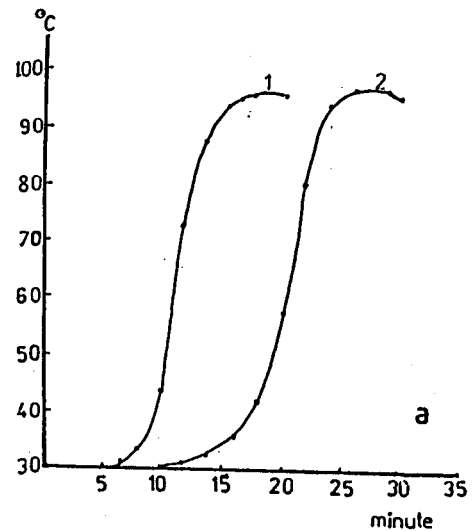


Fig. 1: Effect of sealing of aluminium by boiling (1.0 x 5.0 x 2 cm²) on a) t-τ, b) V_H-τ and c) κ-τ [MCTI] curves in 3.00 M HCl at initial temperature t₀ = 30.0°C.

- 1- Untreated aluminium.
- 2- Sealed aluminium (by boiling).

It is interesting to mention that the first look at the κ - τ curves shows a distinct nonlinear behaviour at the beginning passing into a linear one after a certain time interval. The transition of the nonlinear into a linear character is mainly attributed to the leveling interaction of the different factors and the resulted compensating effect on the κ values. These factors are, the HCl concentration, the formation and accumulation of Al^{3+} ions, the state of the metal surface (nature and thickness of the anodic film) and the local temperature. As the anodic film becomes very thin, the HCl concentration factor predominates and the linear growth of κ with τ passes through a maximum.

(ii) The effect of AC anodizing:

The effect of AC anodization voltage on the κ - τ behaviour of anodized Al and Al-Mn in 3.00 M HCl at 30.0°C is displayed in Figure 2. This figure obviously demonstrates the increase in the dissolution resistance of anodized Al and Al-Mn alloys upon increasing the applied AC voltage during anodization from 10 to 100V. In the mean time the use of 1.0V for anodization gives rise to more readily dissolving Al and Al-Mn alloys than the untreated specimens.

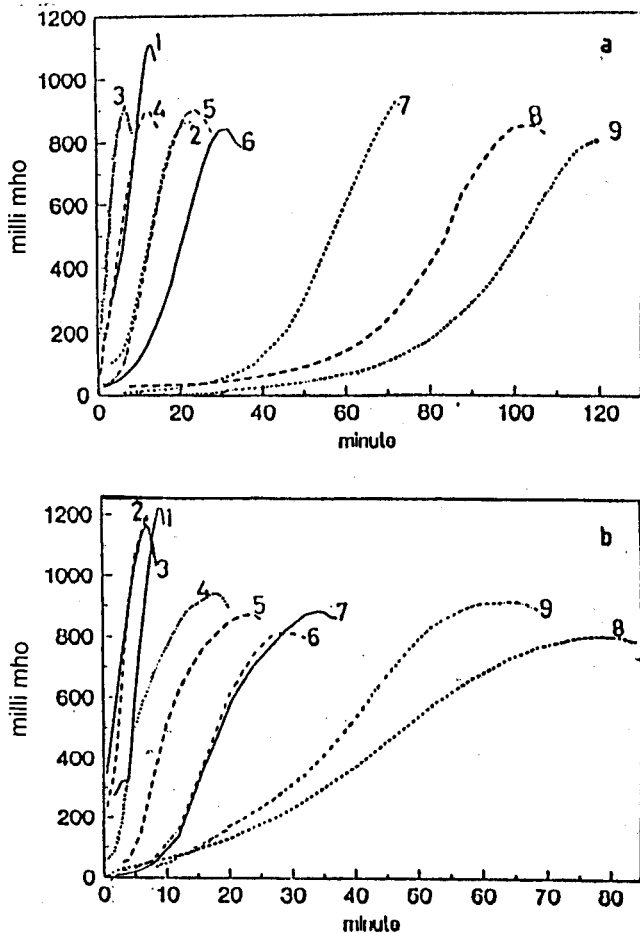


Fig. 2: κ - τ [MCT2]curves for a) Al and b) Al-Mn ($1.0 \times 5.0 \times 2 \text{ cm}^2$) anodized in 0.100 M oxalic acid at different AC voltage for 20.0 minutes at 30.0°C, in 20.0 ml 3.00 M HCl at 30.0°C.

- 1- Untreated.
- 2- Sealed.
- 3- Anodization using 1V AC.
- 4- Anodization using 5 V AC.
- 5- Anodization using 10 V AC.
- 6- Anodization using 20 V AC.
- 7- Anodization using 50 V AC.
- 8- Anodization using 100 V AC.
- 9- Anodization using 150 V AC.

Sealing of Al by boiling leads to an improvement in the dissolution resistance which is not as high as that caused by anodization at 20.0V. On the other hand, sealing of Al-Mn alloys gives rise to a less resistant surface towards dissolution in HCl than the untreated alloy. It seems that the existence of Mn in the alloy prevents the sealing effect i.e. the closing of the pores in the air borne film by hydration and hydroxylation. Moreover, boiling in distilled water brought about more active surface of Al-Mn alloy.

In Figure 3, the κ - τ behaviour is displayed for Al and Al-Mn alloy anodized for different time intervals. It is evident that the anodic film thickness and in turn its protecting properties is directly proportional to the anodization time. The κ - τ dependence obtained for the dissolution of the formed anodic films after anodization in different concentration of the acid shows the proportionality between the protecting properties and the acid concentration.

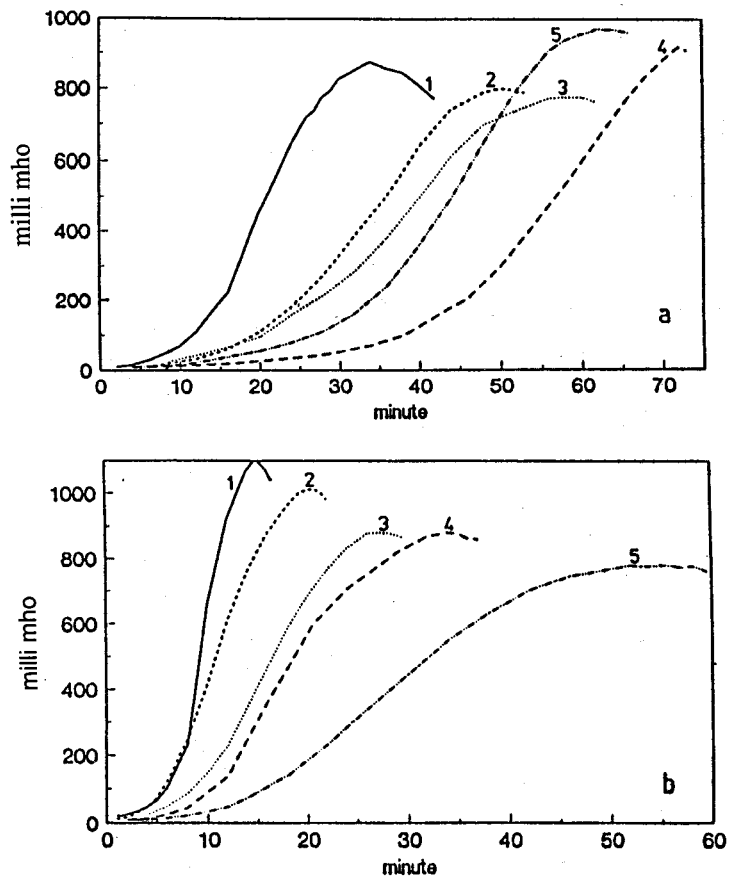


Fig. 3: κ - τ [MCT3]curves for a) Al and b) Al-Mn ($1.0 \times 2.0 \times 2 \text{ cm}^2$) anodized in 0.100 M oxalic acid at 50 V AC for different times at 30.0°C, in 20.0 ml 3.00 M HCl at 30.0°C.

- 1- 1 minute.
- 2- 5 minutes.
- 3- 10 minutes.
- 4- 20 minutes.
- 5- 50 minutes.

(iii) The effect of Organic Additives:

The influence of the four studied organic additives on the dissolution behaviour (κ - τ curves) of Al and Al-Mn alloy is illustrated in Figure 4. All the organic additives exhibit

qualitatively the same behaviour. They were found to retard the dissolution of Al and Al-Mn presumably by their adsorption on the metal surface. The extent of retardation (inhibition) obviously depends on the degree of surface coverage. Thus κ - τ curves may serve as a measure of differentiating the weak and the strong adsorption. In other words, the κ - τ curves provide a quantitative estimation of the inhibition caused by organic inhibitors (additions).

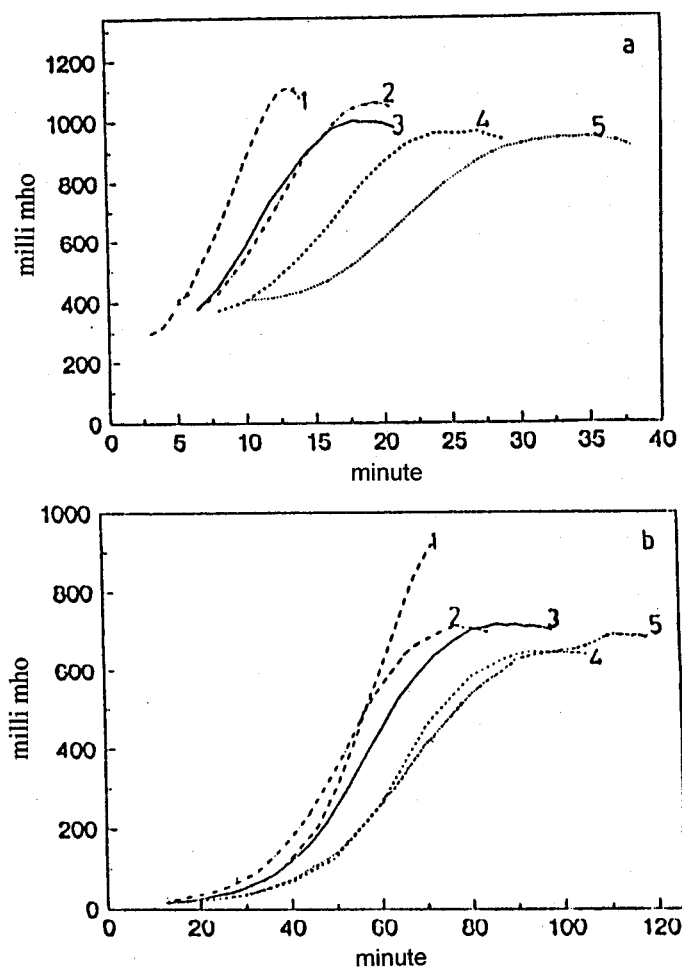


Fig. 4: κ - τ [MCT4] curves for a) untreated Al and b) untreated Al-Mn ($1.0 \times 2.0 \times 2 \text{ cm}^2$) anodized in 20.0 ml 3.00 M HCl (in presence and absence of 0.100 M of different inhibitors) at 30.0°C.

- 1- Free
- 2- 2-picoline.
- 3- 3-picoline.
- 4- 4-hydroxypyridine.
- 5- 2-aminopyridine.

It is obvious that the efficiency of inhibition varies with the type of the additive. The order by which the efficiency of inhibition decreased is as; 2-aminopyridine > 4-hydroxypyridine > 3-picoline > 2-picoline. The observed high efficiency of the studied compounds [21] in acid medium may be attributed to the cationic nature of the additive in the medium on one hand and the highly negative potential of dissolution of Al relative to its own zero-charge point on the other hand [22]. This makes the adsorption of the cationic substances more effective than the nonionic or the anionic

species. Moreover, all the studied compounds have N atom as the key atom for adsorption process in addition to the delocalized π -electrons on the ring which makes the molecule more plane and a new center of adsorption is introduced.

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