Anodic Polarization of Anodized Aluminum Alloy 5052

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Abstract

Aluminum alloy 5052 had been anodized by sulfuric acid as an electrolyte under constant voltage and the anodic oxide film produce will be testing by potentiostatic anodic polarization .Two variables, which were considered as important variables, were studied. These variables are anodizing time 15,30 min. and sealing time 10,20 min., and the test by potentiostatic anodic polarization through electro chemical polarization measurements in solutions of 1N na2 so4 (PH= 1). The results are discussed in light of the rate of ionic current flow through the coating during anodic polarization measurements.

Introduction

When aluminum is exposed to the atmosphere, aluminum oxide can be formed on the aluminum surface. This oxide film is called (natural oxide film). The thickness of the air formed oxide film is very small therefore it can not be used as a protective film for preventing corrosion (L.Young 1961). Anodizing is a method of producing a `thickened oxide film on aluminum alloys by electrolytic means (Burns 1967). Anodizing also can be defined as an electro-chemical process by which the surface of a metal material, commonly aluminum is oxidized to form a porous and durable surface coating. The aluminum part, which becomes the anode, is submerged in a solution, commonly sulfuric acid, while a current is applied

The anodizing process using sulfuric acid process, which is common, has advantages of lower cost, rapid action and comparatively low operating voltage. The latter is a consequence of the high conductivity of the electrolyte and its ability to penetrate the film to the underlying metal. The electrolyte has a solvent action upon the film which affects its character (Franklin 1961). This process was patented by Gower and Brien in 1927 (Gower, Brien 1927).

A wide range of operating conditions was used to meet specific requirement such as temperature, current density, concentration of acid, processing time, and the basic metal used (New Man 2002). A normal process involves a 5-20% by volume solution of sulfuric acid and generally is operated at temperature of 20-25oC and at an anodizing current density of 1.2-1.6 A/dm2 at 18-24 V, processing times vary from 15-60 min., depending on the alloy treated and film thicknesses desired. The film thickness by this process is up to 25 μm (Canning 1970) (Henley 1982), (Defence Stun 1997).

Sealing

Sealing of the oxide film is the final chemical operation in anodizing. It is well established that the anodic coatings formed on aluminum in sulfuric acid, phosphoric acid, or oxalic acid electrolyte consist of two portions, a very thin non-porous barrier oxide layer and relatively thick porous layer. The highly porous oxide films contain a huge number of tiny cells, each with a central pore. It is understandable that the porous structure, with a very high specific surface area, has a strong tendency to absorb water

and other aggressive agents from the surrounding environment, leading to structural and physical damages of the anodized aluminum.

Sealing is a post treatment of anodizing to fill and close or plug the micro pores of anodic coatings by means of chemical conversion, physical absorption, or chemical impregnation that takes place within the pores. The understanding of Sealing is essentially based on the investigation of the hydrothermal process carried out in hot water or steam at temperatures above 95°C. It is generally accepted that in hydrothermal sealing process the anhydrous oxide (Al2O3) in an anodic coating is partially hydrated to form boehmite–like crystals AlO(OH).The basic reaction of hydrothermal sealing may be expressed by the following transformation taking place at temperatures above 90°C (Metalast 2001).

$$Al_2O_3 + H_2O \rightarrow 2AlO(OH)$$
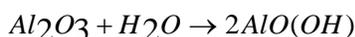
The most common sealing treatment consist in exposure to boiling water or steam for a period of time about equal to that of the anodic treatment. During this treatment the an hydrous aluminum oxide on the surface is converted to crystalline alpha monohydrate (boehmite).

The hydrated product is essentially the same as that formed when aluminum reacts with water under the same conditions (Spooner 1961). The density of the monohydrate is less than that of the oxide, the accompanying volume increase seals the mouths of the pores to a depth depending on the treating time. Thin films will be completely hydrated, including the barrier layer, but normal coatings, in which the pore diameter is small relative to pore depth, will not be completely hydrated. (Hunter 1959). On heating sealed anodic films, loss of weight at temperatures well below the decomposition temperatures of the monohydrate indicated that not more than 20 % of the water content (Spooner 1961).

The sealing operation must be carefully controlled to obtain a uniform product. Sealing in demineralized water provides better protection than dose treatment in tap water at a corresponding pH. The PH of the sealing water is important. In commercial practice a pH in the range of 5.6 - 6.6 is used . (Henley 1982). Sealing process is achieved by means o f boiling water.   (Mason and Slunder 1947).

Sealing by salt hydrolysis, using solutions of nickel or cobalt acetate at 90oC, is suitable for sealing dyed coatings. The salts are hydrolyzed and precipitated as the hydroxides, which are nearly colorless, and help stabilize the color (Burns 1997).

Physical sealing used when substances provided a physical blocking of the coating pores. A wide range of organic materials has since been used for physical sealing. They have some advantages in special applications. For example sealing in lubricating oil or graphite / oil suspensions provides a lubricating surface that has been used for piston (Henley 1982)
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Polarization

The change of potential of electrode due to the passing of current from or out of it is called polarization measurement is probably the most used method for studying the corrosion behavior of metal in corrosive media. Metallic surfaces can be polarized by the application of an external voltage which causes current flows between anode and cathode caused a change in the electrode potential. This change is termed as polarization and it affect the rate of corrosion. Direct polarization measurements of potential versus current density not only provide the basis for computing the corrosion rate at any given potential , but from comparison with different models of electrode reactions often indicate the mechanism by which the reactions occur.(Burns 1967).

Polarization is important in understanding corrosion behavior and corrosion reaction mechanism. It is of primary importance to know whether a metal is active or passive in a given environment, and significant information on this point can be obtained from polarization studies.

Polar graphic methods may be used to determine the initial rates of corrosion of metals in aqueous media since they are suitable for the detection of trace amounts of metal ions in solution. Electrochemical studies usually provide the most fundamental knowledge of corrosion mechanism.

Polarization curves obtained by the potentiostatic technique, in which a given potential is impressed on the specimen and the resulting current measured, are particularly valuable in studying the formation and growth of passive films (Greene 1962).

Experimental Work

This work is to study the formation of anodic oxide film on the aluminum alloy 5052 by means of sulfuric acid as an electrolyte under constant voltage , the electrolyte concentration: 15 wt % H_2SO_4,

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temperature: 45°C, current density: 1.4 A/dm2 , time of anodizing: 15,30 min., sealing time: 10,20 min. and the anodic oxide film produce will be testing by potentiostatic anodic polarization through electro chemical polarization measurements in solutions of na2so4 (PH= 1) .When the anode is aluminum alloy 5052, the cathode in commercial practice, is stainless steel or lead. The current is passed through the electrolyte, such as sulfuric acid. Most of the oxygen that would have been liberated combines with the aluminum to form a layer of porous aluminum oxide while hydrogen is librated at the cathode. The specimens used into dimensions of $(1 \times 2 \times 0.2)$ cm. The chemical composition of the aluminum alloy 5052 according to UK or USA specification (Trethewey and Chamber lain 1996) its composition was found as follows: 2.5%   Mg , 0.25% Cr , 0.4% Si Max. and the reminder is aluminum. The chemical composition for the material according to the analysis of AL-NASER COMPANY was:(0.008% Cu, 0.311% Fe, 0.045% Mn, 0.012% Zn, 2.43% Mg, 0.299% Si,0.21% Cr, and 96.65% Al)

Description of Anodizing Process

In this process the aluminum specimen was connected to the positive terminal where it becomes anode, while the stainless steel article was connected to the negative terminal to be the cathode. The two electrodes were held by means of jigs and PVC rack to hold them stable in the anodizing tank and this jigs connected to direct current power supply in the anodizing cell to supply the electrodes a maximum current of 0.6A and voltage of 25V. The voltmeter was connected to the electric circuit to measure the voltage applied. The anode and cathode are immersed in the anodizing solution.

Operating Process

To anodizing the specimen the following steps were followed in this stage:

1. The anodizing acid Solution was prepared in desired concentration and placed in the anodizing cell.

2. The specimen was weighed before anodizing (W1).

3. Both electrodes must be well connected directly to the current power supply.

4. Each electrode surface was immersed in acid solution.

5. The temperature of anodizing acid solution was controlled by a thermostat was set to the desired operating temperature.

6. The power supply was switched so that a constant voltage was obtained where the electrodes were immersed in the solution.

7. Maintaining constant voltage at the time of run (15, 30) min.

8. For each run at the end time while the power supply is on and the anode   was removed from anodizing cell immediately. And then the power supply is switched off.

9. After the specimen was removed from anodizing cell rinsed with running water followed by distilled water to remove the excess solution on the specimen.

10. The specimen was dried by air and weighed after anodizing (W2).

11. Sealing process was the final stage where the specimens was immersed in a boiling distilled water with pH= (5.5-6) for different sealing time= (10, 20) mints.

12. The specimen was rinsed with distilled water and dried by air.

13. To calculate the film thickness, the anodic oxide film must be removed by using stripping solution.

14. After the specimen was stripped it was rinsed with running water followed by distilled water to remove the excess stripping solution on the specimen and dried by air.

15. The specimen was weighted after stripping the anodic coating (W3).

16. The above steps were repeated for each run, and the average values for each two runs were taken.

Electro Chemical Corrosion Cell

The test was carried out using a standard glass cell. The cell was equipped with a multi neck cell consisted of working, reference and counter electrode and one of these neck used for thermometer. The working electrode with dimension (1×2×0.2) cm aluminum alloy 5052. The counter electrode was a carbon electrode. The reference electrode was standard Calomel electrode bridged by a laggin-Haber probe. The distance between the electrode surface and the laggin-Haber capillary was set at about the optimum value of 1mm to minimize the experimental error due to IR drop. A thermometer was used to shwon the solution temperature in the cell to be ±1oC by means of a thermostat control in the system.

Polarization Data Measurements

Before each test, the cell and electrodes were washed with running tap water, followed by demonized water, then supplying of 1N na2so4 solution to the cell. When the required temperature was attained, the working electrode was placed in position in the cell and immersed in the solution. The corrosion potential was measured every 1 minute for the remaining one hour by a digital voltmeter. Then the power supply was switched on and the resistances were putted to maximum. The potential was changed by about 50mv in the positive direction .When the potential is about zero current density, the current was observed when stable after about 1 minute. The procedure adopted in this work is that the potential was changed manually at a nearly constant rate and the current value noted when stability was achieved. The procedure described above was used for the unprotected aluminum alloy 5052 and for protected aluminum alloy 5052 by anodizing in sulfuric acid and by seal sample in boiling water under the effect of optimum condition.

Results and Discussion

In this investigation, anodized coatings of different thickness produced from anodizing process at different times and degree of sealing were compared by potentiostatic anodic polarization through electro chemical polarization measurements. The results are discussed in light of the rate of ionic current flow through the coating during anodic polarization measurements.

Open Circuit Potential Measurements

The variation of the ocp of 5052 aluminum alloy with time of immersion in 1N Na2SO4 solution at 30, 45, 60oC have been studied fig.(4) shows this variation with time. It is clear that:

The free corrosion potential shifts to more negative value with increasing in the temperature.

After one hour immersion the steady state potential recorded at 30, 45, 60oC was found to be about -760, -780, -820mV relative to saturated calomel electrode.

When interpreting open circuit potential data, one must consider factors such as oxygen, chloride concentration, and electrolyte all of which have a significant influence on the reading.

Finally, it can be stated that: A more negative reading of OCP is generally considered to indicate a higher probability of corrosion. Evaluation of metal corrosion from the (absolute) free corrosion potential values may mislead engineers and cause errors in judgment if other factors are not taken into account. It must be stressed that the free corrosion potential measurements only reveals the corrosion probability at a given location and time. It is evident that long-term monitoring of the free corrosion potential reading is more meaningful.

The reason of this variation with time depends and affected by many parameters (i.e material purity, surface treatment, oxygen contact ... etc). Sherif and Narayan have suggested in their study that the open circuit potential of aluminum, like those of other corroding metals, is a mixed potential. Equilibria that control this mixed potential include (Sherif and Narayan 1989).

Cathodic Reactions

Reduction of dissolved oxygen (acid solution)

$$O_2 + 4H^+ + 4\bar{e} \rightarrow 4H_2O$$

Reduction of H+ ions

$$2H^+ + 2\bar{e} \rightarrow H_2 \uparrow$$

Anodic Reaction

$$Al \rightarrow Al^{+3} + 3\overline{e}$$

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 3\overline{e}$$
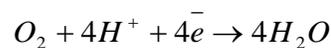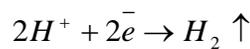
Factors Effecting Anodic Polarization

1. Time of Anodizing

The curves of Fig. (2& 3) show the effect of coating thickness produced from two different anodizing time (15&30 min.) and for different sealing time (10&20 min.). The anodic polarization curve for a bare (uncoated) specimen is also shown in both above mentioned figures for comparison.

The curve for the bare specimen agrees with those published by other studies (Jones D. 1969); for pure aluminum, except that the corrosion potentials of the 5052 alloy in this study are some what more active, because most of the alloying elements in aluminum decrease corrosion resistance and are added to improve mechanical properties.

Fig. (2 and 3) show that anodic polarization in acid sulfate solutions is sensitive to anodizing time, anodized coating thickness and the degree of seal imposed on a coating. Anodized coatings of greater thickness and longer sealing time have higher atmospheric corrosion resistance by passing lower anodic currents through such coatings.

It is also notable that anodic polarization was sensitive to anodizing time and coating thickness at certain sealing time. Its clear that the anodic polarization curves in both above mentioned figure shifts towards potential axis. Compared with the un anodized specimen, indicating the coating thickness increases the resistance to corrosion by decreasing the anodic current density leading to state that: The general effect of increasing anodizing time is associated with an increase in coating thickness, leading to a depress anodic current to lower values at all anodic potential

2. Sealing Time

The initial and principle purpose of sealing is to further improve the corrosion resistance of anodized aluminum. It is generally accepted that in hydrothermal sealing process (i.e., in hot water or steam at temperature above 95 °C), the anhydrous oxide (Al2O3) in an anodic coating is partially

hydrated to form beohmide – like crystles (AlO (OH)). The basic reaction of hydrothermal sealing may be expressed by (Metalast 2001) :

$$Al_2O_3 (anodicCoating) + H_2O \rightarrow 2ALO(OH)(beohmide)$$
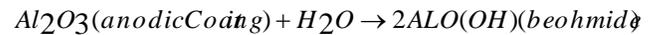
Figs. (4 and 5) show the anodic polarization curves of two different coating thickness produced as a result of different anodizing times for sealed & unsealed coatings.

It is clear from these two figures that:

1. The unsealed coatings permitted considerably higher currents than the sealed coating regardless the anodizing time or coating thickness.

2. The anodic polarization curves representing the sealing coatings shifts toward the potential axis indicating the effectiveness of sealing by decreasing the anodic current values for certain anodic potentials.

3. The anodic polarization curve is quite sensitive to the sealing of the coatings. The 10 and 20 min. seals, are usually considered as edequate for good protection exhibited considerably lower anodic currents than unsealed coating.
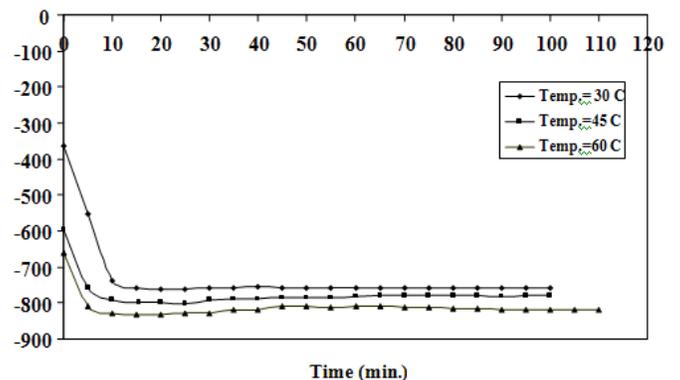
Fig. 1 Free Corrosion Potential 5052 Aluminum Alloy At Different Temperature in 1N Na$_2$SO$_4$, PH=1
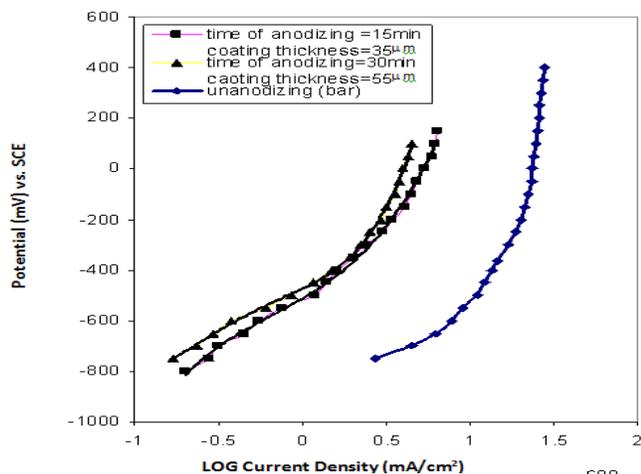
Fig.2 Effect of coating thickness and the anodic polarization of anodized AA5052 at 45°C in 1N Na$_2$SO$_4$, (pH=1), at sealing time of 20 min.
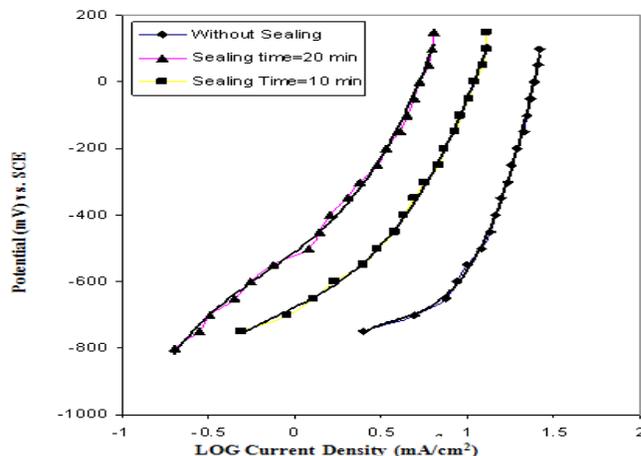
Fig.4 Effect of sealing time on the anodic polarization of anodized AA5052, coating thickness=35μm at 45°C in 1N Na$_2$SO$_4$, (pH=1), at 15 min. anodizing time.
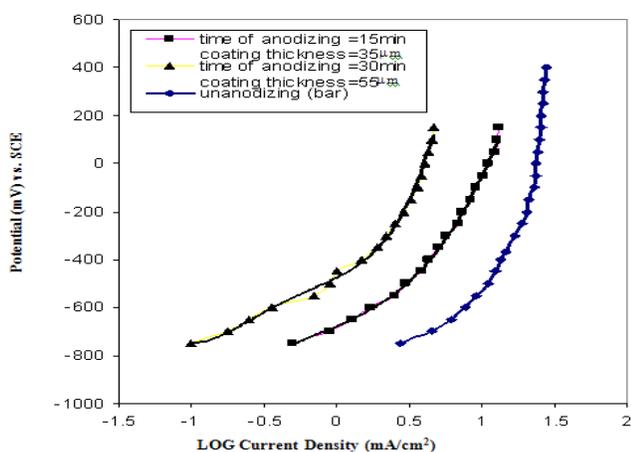
Fig.3 Effect of coating thickness and the anodic polarization of anodized AA5052 at 45°C in 1N Na$_2$SO$_4$, (pH=1), at sealing time of 10 min.
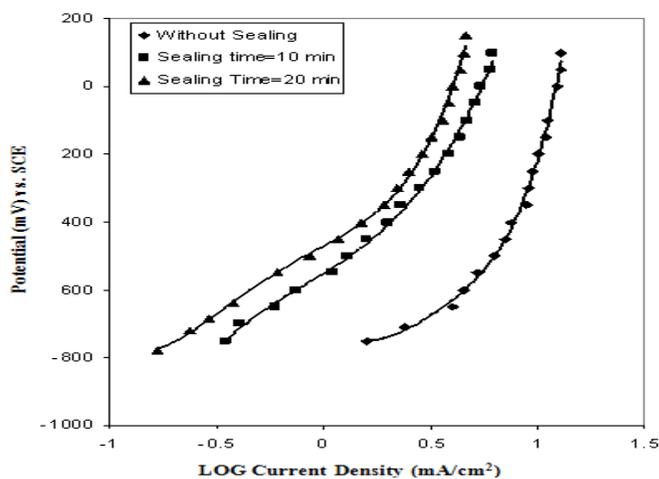
Fig.5 Effect of sealing time on the anodic polarization of anodized AA5052, coating thickness=55μm at 45°C in 1N Na$_2$SO$_4$, (pH=1), at 30 min. anodizing time.

Conclusions

1. Electrochemical polarization measurements are sensitive to the presence of surface films and could possibly lead to improved methods for coating evaluations.

2. Increasing the time of anodizing lead significantly to increase aluminum built-up rate.

3. Anodic currents passed through the anodizing coating are function of coating thickness, degree of sealing and anodizing time.

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الاستقطــاب الانــودي لسبـيكة الالمنـيوم AA 5052 المــؤنودة

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الخلاصة

الهدف من هذا العمل هو دراسة الطبقة الاوكسيدية المتكونة على سبيكة الالمنيوم 5052 بواسطة حامض الكبريتيك كمحلول الكتروليتي تحت تأثير فولتية ثابتة ،تركيز المحلول الالكتروليتي : 15% كنسبة حجمية من حامض الكبريتيك ، درجة الحرارة : 45م°، كثافة التيار: 1.4 امبير/دسم2،زمن الانودة :30.15 دقيقة ،زمن الختم: 20.10 دقيقة و الطبقة الاوكسيدية الناتجة يتم اختبارها بواسطة تقنية الاستقطاب الانودي ذو الجهد الثابت يقاس من خلال المحلول الالكتروليتي (PH= 1) 1N Na$_2$SO$_4$

ان معدل نمو او تعاظم سبيكة الالمنيوم هو مظهر مهم في تخمين كفاءة عملية الانودة .في هذا العمل معدل نمو سبيكة الالمنيوم 5052 تمت دراستها ,مع تغير العوامل :زمن الانودة , سمك الطبقة المتكونة وزمن ختم النموذج المؤنود.النتائج العملية اظهرت انه :

1. ان معدل نمو سبيكة الالمنيوم بصورة عامة ازدادت نوعيا بزيادة زمن الانودة.

2. عملية الاستقطاب الانودي الساكن للطبقة المؤنودة على سطح الالمنيوم كانت حساسة وتتأثر بكل من:سمك الطبقة ودرجة الختم.

3. ان سمك الطبقة المتكونة من عملية الانودة الاكثر سمكا واطول زمنا ختما بصورة عامة تسمح بمرور اقل تيارات موجبة.