

Corrosion Monitoring of Colored Anodized Aluminum Using Frequency Electrochemical Noise and FFT Impedance Measurement Methods

Norouzi¹, P., Moghadesi², M., Ganjali¹, M.R., Mokhtari¹, B., and Gandomkar, F.,
1Department of Chemistry, Faculty of Science, University of Tehran, Tehran, Iran
2Department of Chemistry, Lorstan University, Khoramabad, Iran
E-mail: Norouzi@khayam.ut.ac.ir

(received: 20/4/2003 ; accepted: 12/11/2003)

Abstract

In this work, aluminum electrode was colored with Eriochrom black, using frequency electrochemical noise analysis technique of the FFT impedance response, corrosion resistance of the colored electrode in 0.1 M sulfuric acid solution have been investigated. Scanning Electron Microcopy, also used for monitoring the electrodes surfaces. The electrochemical noise analysis FFT impedance measurements showed that under some applied conditions, coloring aluminum with Eriochrom black could reduce corrosion resistance of aluminum. Where it was realized that application a potential ramp (in range of 0 to 3000 mV) produces an oxidation response associated with a significant noise in the FFT spectrum for the colored aluminum. The noise magnitude in the spectrum strongly depends on the applied conditions during anodizing, coloring and sealing stages. The noise analysis of the impedance and SEM images of the surface colored aluminum, showed a correlation between the number of pitting and the noise in the impedance of the surface.

Keywords: *Eriochrom, Aluminum oxide, Aluminum Coloring, anodizing, noise analysis FFT impedance, Cyclic Voltammetry*

Introduction

Electrochemical noise analysis (ENA) is a generic term describing the phenomenon of spontaneous fluctuations of electrochemical systems (Kearns, *et al.*, 1996). It manifests itself in two guises, as potential noise or as current noise, depending on the mode of measurement. The sources of electrochemical noise may be classified in three categories (Kendig *et al.*, 1993). Charge carrier effects contribute noise whose spectral density, the amount of noise present in a given bandwidth, is essentially constant over a wide range of frequencies and is of low amplitude. This category covers noise originating from thermal agitation of charge carriers, noise caused by charge being transferred in discrete amounts and by other such phenomena. A second source of noise relates to surface processes occurring on the electrodes and specifically to their inhomogeneities. These give rise to fluctuations at frequencies of approximately 1 Hz and below (Granata, 1993). The observed spectral density of these fluctuations in general varies with frequency and the amplitude can be much higher than that caused by charge carrier effects (Bierwagen *et al.*, 1998).

At very low frequencies environmental changes, such as variations of the physical and chemical parameters of the observed system, result in slow fluctuations of the electrode potential or current. These often have the appearance of drift of the electrode potential and can sometimes be accounted for by existing theories of electrode thermodynamics and kinetics (Michelutti, 1998). Therefore, based on these characteristics, use of the ENA as a method for investigating corrosion phenomena has been adopted increasingly. make this technique suitable for study the oxide layer formation at metal surfaces (Buchheit, 2001).

Aluminum and its alloys are susceptible to pitting corrosion in chloride environments, and their corrosion behavior is known to be quite different from that of stainless steels. However, although many studies have been carried out, the basic mechanisms that control the corrosion processes are poorly understood. The aim of this study is to investigate the pitting corrosion mechanisms of aluminum and its alloys by examining connections between the corrosion processes and the electrochemical noises (El-Erat ,2001).

In the previous work the effect of calon on aluminum corrosion resistance was studied (Norouzi *et al.*, 2003). The work described in this paper relates to the measurement and analysis of ENA of the FFT impedance resistance of aluminum electrodes, under applied potential, using frequency analysis technique. Also, Scanning Electron Microcopy (SEM), was used for study the electrode surface.

Experimental

All reagents were analytical grade from Aldrich. The working electrode used in the experiments were plates (3cm x 2cm x 0.1 cm) of 99.5 % pure aluminum which was sealed in polyethylene. The electrode etched at solution NaOH 5%, and washed with solution of HNO₃ 50% w/v and the was placed in the brightening solution (H₃PO₄ 85%, H₂SO₄ 16%, HNO₃ 3% w/v), and finally, was washed with solution of HNO₃ 50% w/v. The prepared specimens were galvanostatically anodized with direct current (DC) at potentials of 12 V (for 30 min) in solution 16% w/v H₂SO₄. For coloring, the specimens were placed in solution of 2 g/L of Eriochrom Black PV(Fig. 1) for 10 min at 50 oC. Sealing process was performed in distilled water at temperatures, 100 °C (for 30 min).

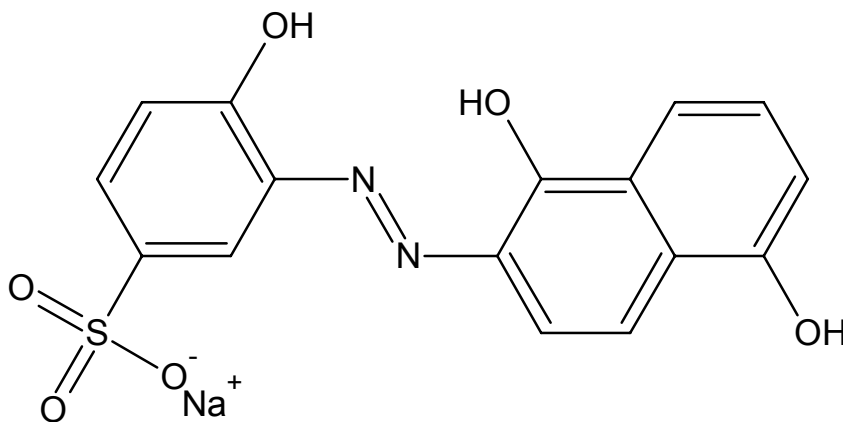


Figure 1 - The structure of the dye used for coloring.

Electrochemical Measurement

All electrochemical experiments were done using a setup comprised of a PC PII Pentium 300 MHz microcomputer equipped with a data acquisition board (PCL-818PG, PC-Labcard Co.) and a custom made

potentiostat . The experimental design of the used system is shown in Fig.2. All data acquisition and data processing programs were developed in this laboratory. The solution of the electrochemical cell was 0.1 M H₂SO₄ solution. In each case, the area of the electrode was 0.25 cm² and the potential scan rate was 50 mV/s at the range 0 mV to 3000 mV. The auxiliary electrode was a Pt electrode (1 cm wire with 0.1 mm in diameter) and the reference electrode was the Calomel (Ag/AgCl) electrode. The initial frequency was 10 kHz and the final frequency was 0.2 Hz.

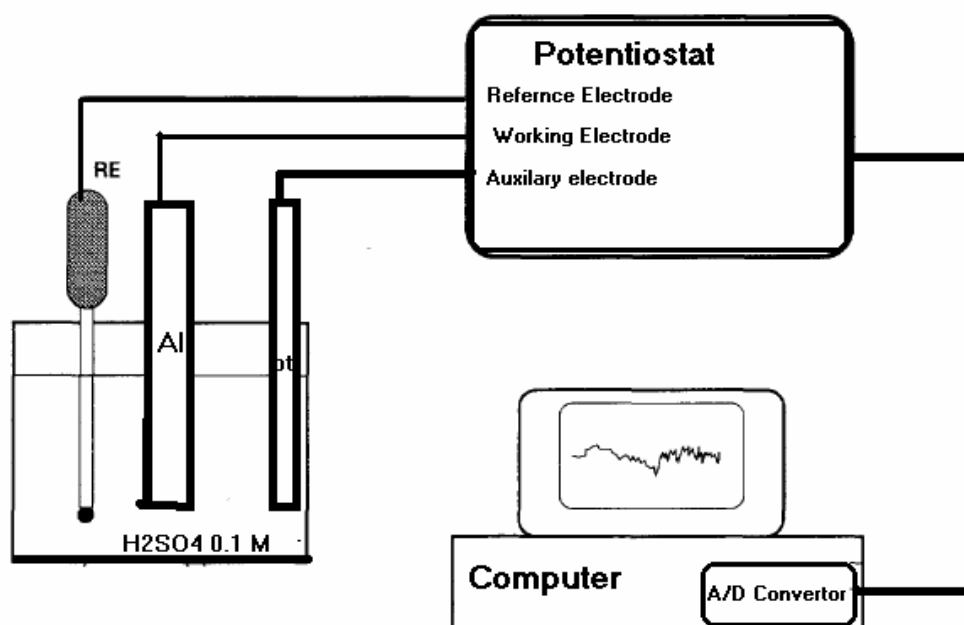


Figure 2 - Experimental approach for collection of electrochemical impedance Measurements.

Data processing

The measurement and analysis of electrochemical noise can be accomplished using either analog or digital equipment and techniques. The digital method employed in the present work offers a number of advantages and can be easily implemented on a microcomputer. The basic steps in the procedure adopted for the present work were: a) Data collection, b) Time record storage, c) Pre-processing, d) Time record analysis, e) Output and classification .

FFT electrochemical impedance

An additional characterization technique was used to study the corrosion behavior in delaminated and intact areas of the oxide film at the electrode surface. Initial experiments on an aluminum specimen with a delaminated formed oxide layer and underlying corrosion incorporated data from FFT Impedance measurement to supplement the corrosion damage data acquired. ENA is an electrochemical technique that can provide a variety of corrosion parameters but was used in this study to evaluate the integrity of the oxide layer and coloring. ENA is used to analyze the response of a corroding sample to small-amplitude alternating potential signals of varying frequencies. The time-dependent current response I_t of an electrode surface to a sinusoidal alternating potential signal E_t has been expressed as an angular frequency (ω) dependent impedance Z_ω as shown in Equation 1:

$$Z_\omega = E_t / I_t \quad (1)$$

Where

$$E_t = E_0 \sin(\omega t) \quad (2)$$

$$I_t = I_0 \sin(\omega t + \theta) \quad (3)$$

and t is time and θ is the phase angle between E_t and I_t . Various processes at the surface absorb electrical energy at discrete frequencies. This causes a time lag and a measurable phase angle between the time-dependent excitation and response signals.

A variety of instrumentation is needed to conduct and interpret ENA. A function generator applies a range of sinusoidal potential frequencies to a potentiostat. The potentiostat applies the signal to the working electrode (the corroding sample). The electrode response is fed to a digital function analyzer that displays the impedance response and phase angle at each frequency. Data collection involves sampling of the measured parameter, potential or current, at predetermined intervals for a required number of samples. The sampling rate should be sufficiently high to cover the frequency range of interest and must be, in order to prevent aliasing, at least twice the highest frequency present in the input signal.

The number of samples taken, i.e. the length of the time record, determines the lowest frequency that may be reliably measured in the collected data and is largely determined by the storage capacity and speed of the computer used. It is wise to choose an integer power of two numbers of samples in order to take a full advantage of some of the FFT algorithms available. The measurement wave form contains multiple SW pulses cycles with a amplitude of E_{sw} and frequency of f_0 , were superimposed on a staircase potential function, which was changed by a small potential step of ΔE . The values of potential pulse of SW (E_{sw}) and ΔE were in a range of few mV (10 to 50 mV). In the computer program, the number of SW cycles, N_c , in each staircase potential step was calculated based on the SW frequency:

$$N_c = f_0 / 1400 \text{ Hz} \quad \text{for } f_0 > 1400 \text{ Hz} \quad (4)$$

and

$$N_c = 1 \quad \text{for } f_0 \leq 1400 \text{ Hz} \quad (5)$$

The values of N_c , f_0 , E_{sw} , $E_{initial}$ and E_{vertex} were the variable parameters in the measurements. Due to this fact that the real signal is located in low frequencies (e.g. < 0.1 kHz) therefore, the signals at the higher frequencies were removed from the data. Application of discrete FFT analysis on the sampled current requires a specific method in current sampling. It required that the number of sampled currents at each pulse cycle must be represented by $2n$ (where n is an integer and greater than 1). Therefore the currents, i_s , were sampled at even time intervals, t_s :

$$t_s = 1 + \frac{s}{4f_0} \quad (6)$$

Where s is an integer number and changes from 0 to 3. Therefore, If currents are sampled (at even time intervals, t_s , $t_s + 1/4f_0$, $t_s + 2/4f_0$ and $t_s + k/4f_0$, then the values of the sampled currents will be:

$$i_k = \sum_{n=1} A_n \sin(kn\pi/2 + 2n\pi f_0 t_s + \phi_n) \quad (7)$$

where k is the number of current data and n is the number of the potential step. To calculate the admittance of the detector response,

first the real and imaginary components of the alternating of current need to be calculated. The real component of I' and E' are given by:

$$I_k' = i_k - i_{k-2} \quad (8)$$

$$E_k' = E_k - E_{k-2} = -2E_s \quad (9)$$

and the equation for the imaginary components are:

$$I_k'' = i_{k-1} - i_k \quad (10)$$

$$E_k'' = E_{k-1} - E_k = 2E_s \quad (11)$$

Pre-processing

Before analysis it is desirable to carry out certain pre-processing operations on the collected time records. The first of these involves the isolation and removal of outliers, data points corrupted during acquisition and far removed from the data mean. These may be isolated using first or second difference procedures and replaced by values equal to the mean of their neighboring data points. It is also useful to compute and remove the mean and trend of the data, i.e. the de value and any slow drift present in the time record. Finally the number of data points may be reduced by the application of digital filtering techniques.

Time Record Analysis

The pre-processed time record may be analyzed in terms of its simple statistics and in terms of its spectral composition. The simple statistical procedures can be the computation of the standard deviation of the data, probability density distribution computations and tests for statistical stationary. Conventional spectral analysis procedures are designed to operate on stationary data, electrochemical noise is usually only weakly stationary and this fact must be taken into account when considering parameters such as confidence limits of the results. Spectra have the useful properties of optimal flatness and minimum phase.

Experimental results

Fig. 3a shows a typical three dimensional FFT impedance obtained on an anodized Al specimen in solution of 0.1 M H₂SO₄. The potential fluctuations exhibit a distinctly asymmetrical probability density distribution and non-stationary. Fig. 3b shows a FFT spectrum of this data, while Fig. 3c presents SEM of the electrode surface. Anodizing of the electrodes were preformed by applying a direct current (dc) at potentials of 12 V (for 30 minutes) in 18% w/v H₂SO₄ solution and then for coloring, one of them was placed in a solution of 2 g/L of Eriochrom black for 10 minutes at 50 °C. Sealing of the electrodes were performed in distilled water at 100 °C (for 30 minutes). First, it was noted that the color of the electrode did not change during the experiment, even after 1000 potential cycles. Second, the recorded voltammogram of an anodized and sealed aluminum electrode (uncolored) in solution containing 2 g/L of the dye and 0.1 M H₂SO₄, did not show a similar response as seen in curve b. Therefore it can be suggested that the existing difference between the voltammograms a and b can be due to interaction of the dye with the oxide layer (see the discussion section).

Fig. 4a shows a typical three-dimensional FFT impedance obtained on an anodized colored Al specimen in solution of 0.1 M H₂SO₄ under the same conditions described in Fig. 3. Fig. 4b shows a FFT spectrum of this data, while Fig. 3c presents SEM of the electrode surface. In those figures the FFT impedance measurements were performed with ac amplitude 20 mV, potential scan rate 50 mV/s. Also, the range of potential was set within corrosion process took place. The declining of the electrode impedance in specific frequencies can result of a higher rate of corrosion process. In addition, the existence of noise at some frequencies for the colored electrode indicates progress of corrosion process at the electrode surface. Whereas, in case of the uncolored electrode, such noise dose not exists, which can be due to high corrosion resistance of the surface at that potential range.

Fig. 5a and b show a typical three dimensional FFT impedance obtained on an anodized colored Al specimen in solution of 0.1 M H₂SO₄ under optimum conditions Anodizing of the electrodes were preformed by applying a direct current (dc) at potentials of 10 V (for 20 minutes) in 18% w/v H₂SO₄ solution and then for coloring, one of

them was placed in a solution of 2 g/L of Eriochrom for 15 minutes at 60 °C. Sealing of the electrodes were performed in distilled water at 100 °C (for 20 minutes). In those figures the FFT impedance measurements were performed with ac amplitude 20 mV, potential scan rate 50 mV/s. Also, the range of potential was set within corrosion process took place. The increasing of the electrode impedance in specific frequencies can result of a higher rate of corrosion process.

As seen in Figure 3a, the sealing process of an anodized electrode (in absence of the dye), produces a uniform surface, and apparently the pits were sealed very well, whereas in case of the colored electrode, the surface is a little rough and contains some pits (Figure 5b). As will be shown later, the threshold potential of corrosion and current density of the anodic response, as well as, the quality of colored surface, strongly influenced by the applied conditions during coloring procedure. To show this the important parameters were changed individually in the next experiments.

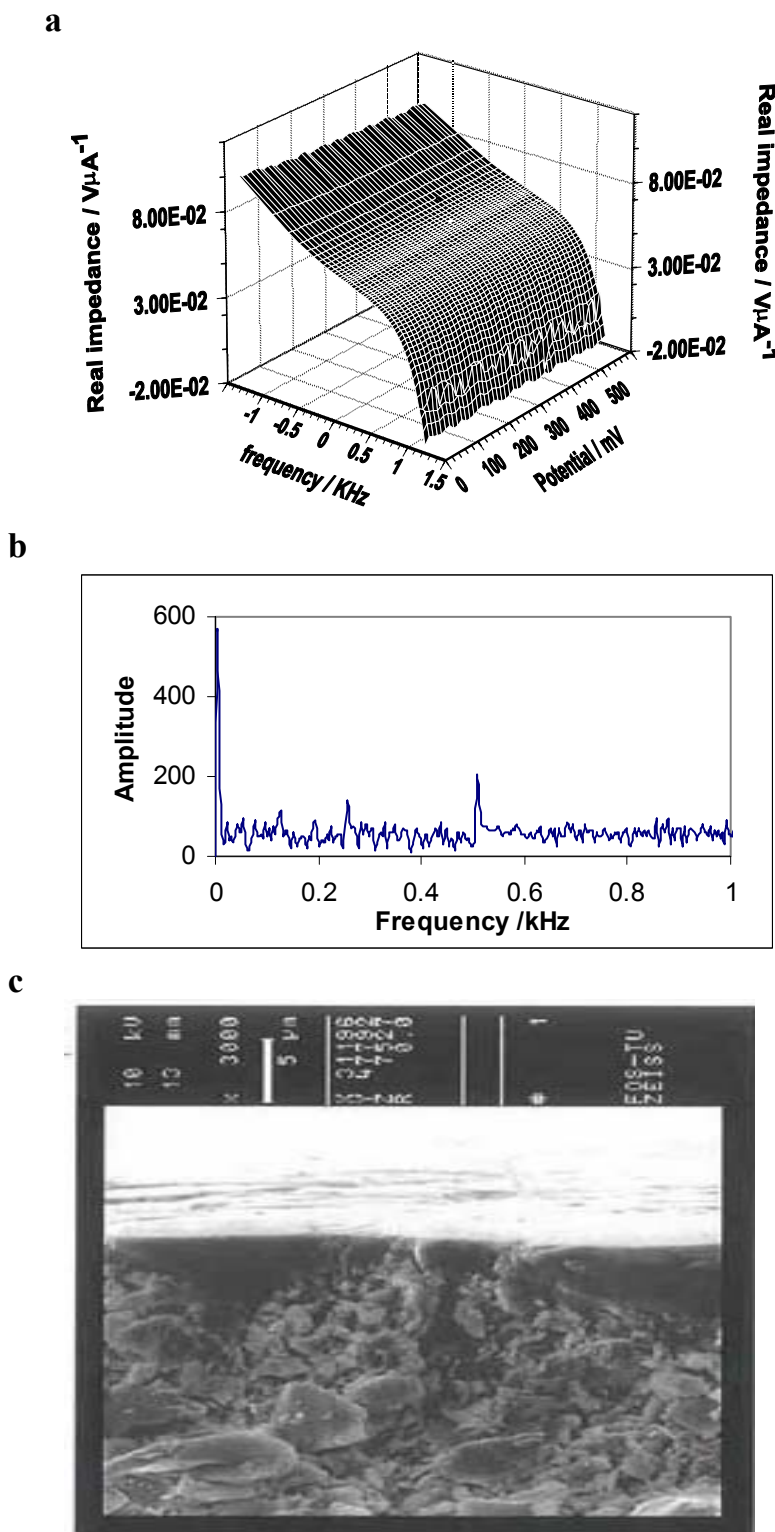


Figure 3 - a) Three dimensional plot for FFT impedance measurement of the electrode colored, b) FFT spectrum recorded at potential 3000 mV, c) SEM images of aluminum electrodes

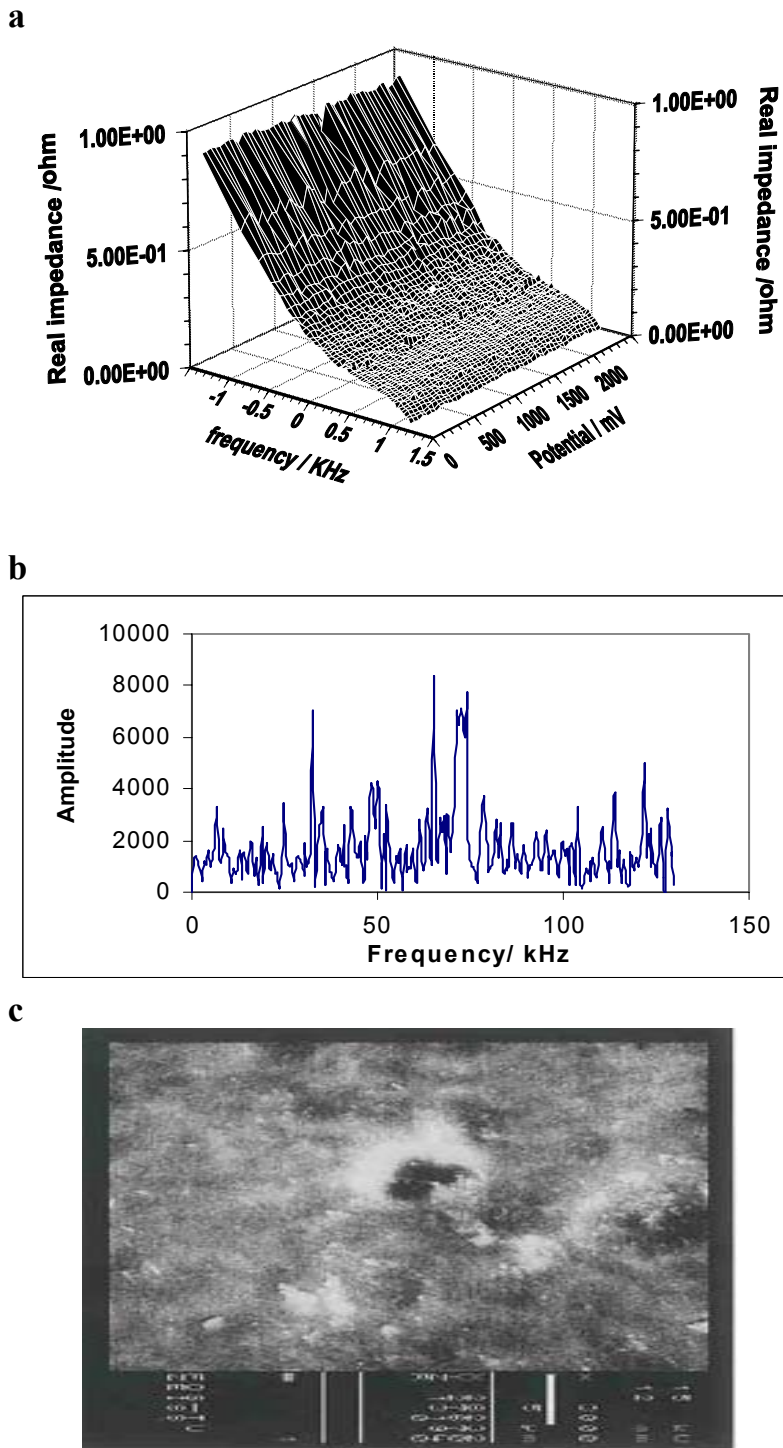


Figure 4 - a) Three dimensional plot for FFT impedance measurement of the colored electrode, b) FFT spectrum recorded at potential 3000 mV, c) SEM images of aluminum electrode.

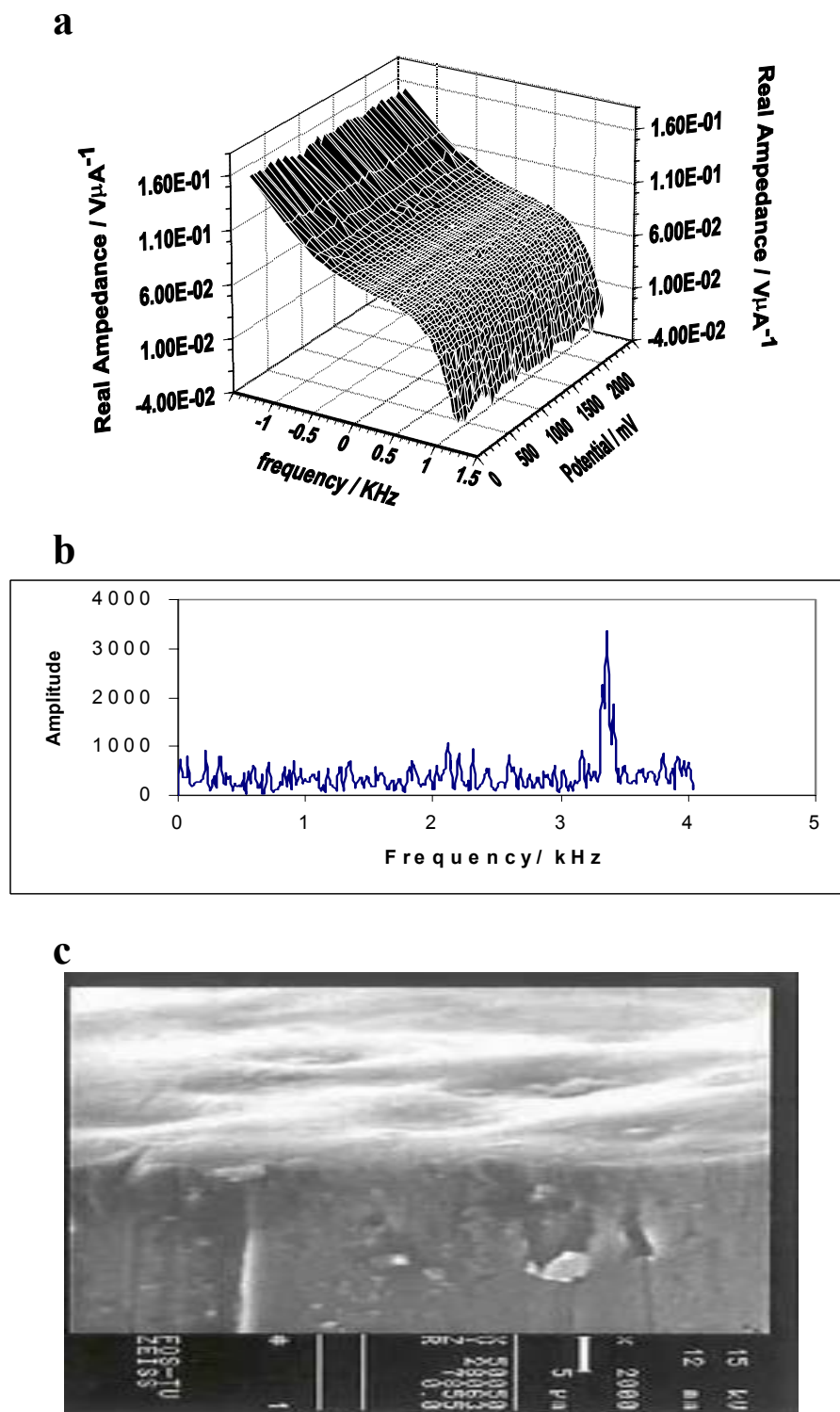


Figure 5 - a) Three dimensional plot for FFT impedance measurement of the colored electrode at optimum conditions, b) FFT spectrum recorded at potential 3000 mV, c) SEM images of aluminum electrode.

Discussion

The FFT impedance measurements of anodized and well-sealed aluminum (in Fig. 3 and 5) show the electrode surface is passive at the potential range 0 to 3000 mV. In fact, due to formation of an oxide film, such electrode should be passive at potentials higher than 3000 mV. However, when the electrode was colored, under special conditions, the surface oxidation process of the electrode takes place at potential lower potentials. Nonetheless, the occurrence of corrosion process at such low potential suggests the possibility of lowering the corrosion resistance of the oxide film by the adsorbed dye. Comparison of the SEM pictures of the surfaces of the two electrodes (Figure 3c and 4c) confirms that dye molecules cause some of the porous still remain open after the sealing process. Unfortunately, little is known about the processes, which occur inside the porous during the coloring procedure. Therefore, we can only make assumptions based on the reported data and our experimental results.

It has been reported that chemically adsorbed organic compound can influence the processes inside porous (Tsangaraki-Kaplanoglou 1997). Moreover, adsorbed species on oxide film can influence the corrosion resistance of aluminum and the structure of the oxide film. Likely, here, there is a possibility that some of the dye molecules bound to the porous wall change the structural characteristic of porous oxide film during the coloring or sealing procedure. This can change the magnitude of the noise in the FFT impedance responses Fig. 3c and 4c.

It is believed that the adsorbed dye inside the porous can be in two forms; physically bound (or free form) and chemically bound to the porous wall. Based on this, it can be speculated that the chemically bonded dyes influence the structural characteristics of the oxide during the coloring and sealing process. Because in cases there are just a physical penetration the dye molecules separate from the surface, and has a very low effect on the corrosion resistance of the electrode. Therefore, the observed phenomena can be interpreted in term of adsorption of the dye molecules and interference with the closure of the porous during sealing. Some supporting evidences for the chemical bound dye come from the results of studying the effect of pH of the coloring bath on the voltammogram. The recorded noise

spectrum for the electrodes colored at various pHs showed less noises for the electrodes, which were colored at pHs, lower than 7 or higher than 8. At this pH range, there is the possibility that the dye molecules via functional group, $-O^-$ or $-SO_3^-$, attach to the oxide film. However, at higher pH due to a higher concentration of OH^- there is a lower chance for the dye to adsorb.

Also, due to this fact that Eriochrom black is an anion salt, it will be in a more protonated form in acidic pHs, consequently the dye can not chemically bond to the oxide film. Moreover, it is reported that the barrier layer may become permeable during oxide growth, resulting in penetration of species in the electrolyte. According to the mechanism for field assisted dissolution of oxide film, in acidic solutions, during applying positive potentials, the process $Al \rightarrow Al^{3+} + 3e$ takes place at the $Al-Al_2O_3$ interface. This produces an equivalent amount of aluminum ions which enter the oxide bulk. Which can increase noise in the spectrum.

While the migration of Al^{3+} species from the oxide surface towards the $Al-Al_2O_3$ interface takes place, the Al^{3+} ions become free from the surrounding anions in the oxide lattice and solvated by water molecules and move toward the film surface driven by electrical field. Based on this mechanism, for unsealed oxide film, the anodic process at the electrode surface during scanning of the potential is similar to the anodizing process, and accordingly, the existing oxidation response at impedance curves is the result of formation of Al^{3+} . The FFT impedance response of the colored electrode was strongly influenced by the increasing temperature of the anodizing bath. As mentioned above, anodizing at temperatures $35\text{ }^\circ\text{C}$ cause the noise at the voltammogram to be significantly enhanced. Increasing temperature of the bath during anodizing causes oxide film to lose its uniform structure, which is associated with defects in the barrier layer. This can explain the observed the large oxidation response and high noise level in the impedance voltammograms.

Considering that the important processes in the film formation take place within a thin barrier layer of non-porous oxide, a thicker barrier layer resulting from anodizing at high voltage (or current density) provides greater corrosion resistance. This may because of slower migration Al^{3+} , SO_4^{2-} and O^{2-} species.

For some cases in acidic solution the oxide film dissolves in acidic solution and, in consequence the adsorbed dye released in the cell. One possible reason for losing color of the specimens (with a low color stability) in the cell solution is that in such cases the dye may be in free form or just physically adsorbed into the oxide film. This situation, most likely occurs for the oxide film that has a thick amorphous hydrated (gel) oxide on the top, or for a not well-sealed surface. Due to this fact that, sealing can cause notable changes in surface development of porous aluminum oxides, unplugged porous facilitate the ejection of Al^{3+} ion into the solution. It was reported that the movement of point defects, such as cation vacancies and oxygen vacancies through the anodic oxide film contributes to the formation of the film

Conclusion

The FFT impedance voltammetric and SEM imaging study indicate that coloring aluminum is accompanied with extensive changes in the electrochemical properties of the anodized surface. However, under some conditions, the coloring of aluminum with Eriochrom balck can change the resistance of the surface toward corrosion and may decrease the breakdown potential of the barrier layer. There is a possibility of chemisorption of the dye to the oxide layer. This could be via $-\text{O}^-$ of $-\text{SO}_3^-$ of the dye molecules, which penetrate in the presence of vacancies in the oxide. Also, the results showed that stability of coloring in high concentrations of the dye or anodizing at high voltages (above 12 V) result in higher noise response of colored specimens. Based on these results, it can be said that the dye, also, prevent sealing. This can accelerate the surface oxidation by ejection of Al^{3+} ions from the surface into solution at positive potentials. In general, obtaining a good quality colored electrode accompanies with lowering corrosion resistance of the surface in acidic solutions.

Acknowledgment

This work is supported by the research council of university of Tehran under grant number 514/1/482.

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