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Electrochemical Impedance Spectroscopy of Anodic Passive Film on Alloy 600 at Room Temperature

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Abstract

Electronic structure of the metal/passive film/solution system was modeled based on the Point Defect Model and the work of Armstrong et al and its characteristics was investigated by potentiodynamic polarization and Electrochemical Impedance Spectroscopy(EIS) measurement for a commercial alloy 600 at room temperature.

The modeling of metal/passive film/solution system showed the system could be described by well developed equivalent circuit. From EIS measurement of the passive film on Alloy 600 diffusivity of oxygen vacancies was estimated to 2.0724×10^{-14} cm²/sec.

I. Introduction

Alloy 600 is a material commonly used to construct the tubing in steam generators(SG) of pressurized light water reactors(PWR). The properties of thin oxide film of Alloy 600 in PWR environment are closely related with corrosion behavior of this alloy. As a fundamental experiment to achieve this goal, potentiodynamic polarization and Electrochemical Impedance Spectroscopy(EIS) experiments have been performed at room temperature.

II. Electronic Modeling of Passive Film

Overall reactions occurring at the working electrode can be divided into three processes which occur at the metal/film interface, film and film/solution interface[2].

Then, total impedance Z_T of the overall reaction can be written as

$$Z_T = Z_{m/f} + Z_f + Z_{f/s}$$

where $Z_{m/f}$, Z_f , $Z_{f/s}$ are impedances of metal/film interface, film and film/solution interface

1. Metal/Film Interface

Impedance response at the metal/film interface was assumed by Armstrong and Edmondson as the parallel connection of one capacitor (C_∞) and two charge transfer resistance, that is, electron charge transfer resistance (R_e) and cation charge transfer resistance (R_c) [2]. But generally $R_e \ll R_c$ can be assumed [7].

2. The Film

According to Point Defect Model (PDM) developed by Chao, Lin, Macdonald in the early 1980s [1][3][5], total current through passive film can be divided into 4 components, that is, (1) electronic current due to the transport of electrons (e') (2) electronic current due to the flow of electron holes (h) (3) ionic current due to the transport of anion vacancies (V_O'') (4) ionic current due to the movement of cation vacancies (V_H^{\bullet}).

Thus,

$$I = I_{e'} + I_h + I_{V_O''} + I_{V_H^{\bullet}}$$

Accordingly impedance can be written as

$$1/Z_f = 1/Z_e + 1/Z_h + 1/Z_O + 1/Z_M$$

Impedance function for electrons and electron holes are modeled as pure resistances because rate controlling step for electron or hole movement is at the interfaces [1].

$$Z_e = R_e$$

$$Z_h = R_h$$

Impedance functions for vacancies were derived based on the movement of anion and cation vacancies within the film under the influence of concentration and electrical

potential gradients by Macdonald at el[1]. Equation of Fick's first and second law was Fourier-transformed and the solution was found using appropriate boundary conditions from PDM. The impedance was calculated to have the form

$$Z_M = \sigma_M \omega^{-1/2} (1-j) \quad \text{for cation vacancies}$$

$$Z_O = \sigma_O \omega^{-1/2} (1-j) \quad \text{for anion vacancies}$$

where

$$\sigma_O = RT/F^2(32D)^{1/2} \{ [C_{V_o}(m/f)]_{dc} (1-\alpha) \}$$

$$\sigma_M = RT/F^2(2\chi^A D)^{1/2} \{ (\alpha-1) [C_{V_m}(m/f)]_{dc} \}$$

From the above expressions, impedance of the film appears like Warburg impedance.

Two limiting case can be defined (1) movement of cations vacancies alone ($\sigma_O \gg \sigma_M$) and (2) movement of anion vacancies alone ($\sigma_M \gg \sigma_O$)

3. Film/Solution Interface

According to Armstrong and Edmondson[2] impedance at the film solution interface was calculated based on the time dependence of the excess of cations over anions in the surface layer as,

$$Z_{f/s} = \frac{1}{Y_{f/s} + j\omega C_\infty}$$

where C_∞ is the double layer capacitance.

$$\begin{aligned} Y_{f/s} &= \frac{1}{R_{\infty 1}} + \frac{1}{R_{\infty 2}} + \frac{k}{k+j\omega} \cdot \left(\frac{1}{R_{01}} + \frac{1}{R_{02}} \right) \\ &= \frac{1}{R_{\infty 1}} + \frac{1}{R_{\infty 2}} + \frac{1}{j\omega \left[\frac{1}{k} \left(\frac{1}{R_{01}} + \frac{1}{R_{02}} \right)^{-1} \right] + \left(\frac{1}{R_{01}} + \frac{1}{R_{02}} \right)^{-1}} \end{aligned}$$

The impedance appeared parallel connection between one charge transfer impedance and double layer capacitance. Charge transfer impedance consists of two infinite frequency resistance and series connection of one resistance and one inductance.

According to k value in above expression, several behaviors can exist in complex plane

(1) for large k ($k \gg \omega$)

Impedance locus takes the form of a single semicircle in the complex plane resulting from a resistance $R_{\infty 1} R_{01} / (R_{\infty 1} + R_{01})$ in parallel with the capacitance $C_\infty + k R_{\infty 2}$ as described in the Fig. 1 (d)

(2) small k ($k \ll \omega$)

Two semicircles will appear in the complex plane according to the relative values of

A and B

$$A = \frac{R_{\infty 1} R_{01}}{R_{\infty 1} + R_{01}}$$

$$B = \frac{R_{\infty 1} R_{\infty 2}}{R_{\infty 1} + R_{\infty 2}}$$

For $A > B > 0$ and $B > A > 0$ figures a and b are obtained, whereas $B > 0 > A$ results in figure c.

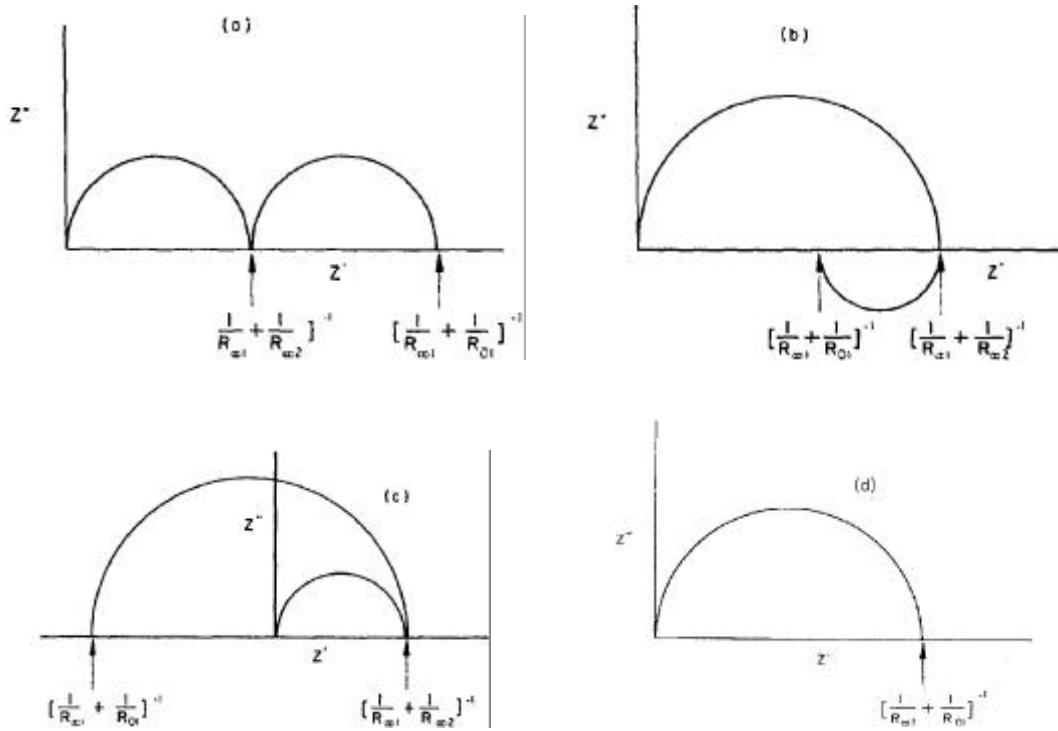


Fig. 1 Complex plane impedance diagrams for film/solution interface. (a)(b)(c) when k is small, (d) when k is large compared to measurement frequency range.

4. Total impedance

Summarizing all the results above, the equivalent circuit for total impedance Z_t can be expressed as below. First, second and the third part represent the equivalent circuit of metal/film interface, film and film/solution interface respectively.

Depending upon the frequency range employed and the relative values of the parameters a variety of impedance loci in the complex plane may be observed.

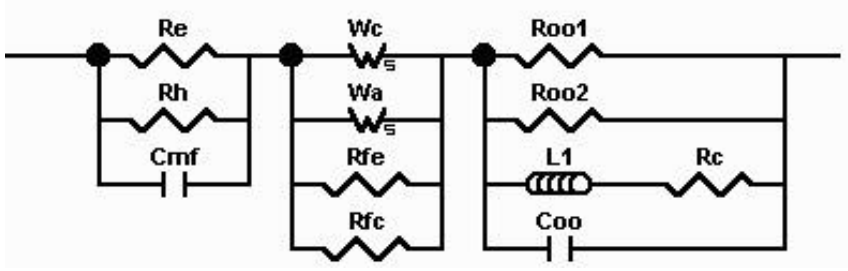


Fig. 2 Equivalent circuit for metal/passive film/solution system. W_c , W_a represent Warburg impedances.

III. Experimental

Alloy 600 were prepared from commercial origin and composition is specified as below.

Alloy	C	S	P	Si	Mn	Ni	Cr	Fe	Mo
Alloy 600	0.1	0.015	0.025	0.31	0.78	74	16	8.63	-

The plate shaped working electrode, 1 cm^2 in area, was abraded with wet SiC paper of decreasing grit size(400, 600 and 1000), polished with alumina($3 \mu\text{m}$), ultrasonically cleaned in distilled water and dried in air. The specimen was mounted in an epoxy resin. A cell with reference electrodes was utilized with a platinum counter electrode and a saturated calomel reference electrode(SCE).

All experiments were carried out at room temperature under continuous deaeration with high purity nitrogen in a PWR primary water chemistry, which is composed of 1000 ppm boron and 2 ppm lithium. The pH was 5.0 at $20 \text{ }^\circ\text{C}$.

Potentiodynamic polarization was measured through following procedure. Corrosion potential was monitored until stable, and then the electrode was polarized cathodically at -1.2 V(SCE) for 2 minutes in order to reduce any oxidized species.

After E_{corr} had again stabilized, the cathodic polarization began at a rate of 0.2 mV/sec and similar procedure was used to measure anodic polarization.

Working electrode was polarized for 1 hour at 200 mV showing passive behavior on potentiodynamic polarization curve before impedance measurement. The impedance scan frequencies ranged from 10^6 to 10^{-2} and its spectra were collected using system consisting of a Solatron Model 1260 FRA, Solatron 1286 potentiostat, and Zplot software. Impedance spectra were analyzed by Zview.

IV. Results and discussion

1. Potentiodynamic Polarization

Corrosion potential was stabilized at about -640 mV and corrosion current density was about $3.5 \mu\text{A}/\text{cm}^2$. Wide passive region was found ranging from -300 mV to 600 mV. Passive current density was about $2 \mu\text{A}/\text{cm}^2$.

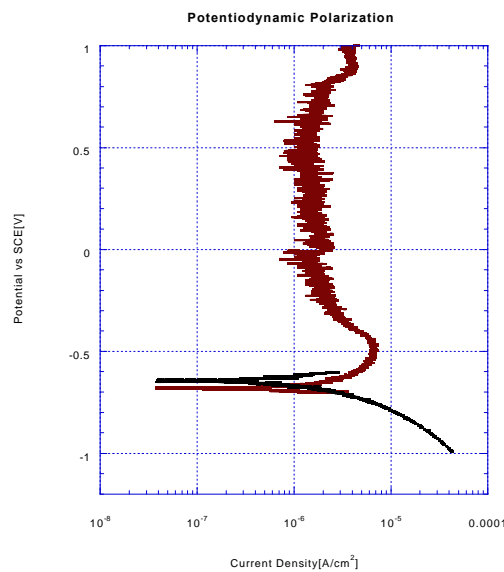


Fig. 3 Potentiodynamic polarization results of Alloy 600. Scan rate is 0.2 mV/sec.

2. Electrochemical Impedance Spectroscopy

Typical Nyquist plot of measured impedance data is shown in the Fig. 4. In very high frequency region (0.1– 1 MHz) negative resistance term appears. The most common source of negative resistance in electrochemical systems results from an interplay between adsorption and electro-dissolution[4]. Inductance term appears in moderately high frequency regions (0.2 – 20 kHz). In low frequency region impedance data show sharp slope and slow process like diffusion in the bulk or inside the film may be responsible for the behavior in this area.

Summarizing above developed equivalent circuit modeling of metal/passive film/solution system, we can conclude that high frequency impedance data reflect electrochemical reactions at the interfaces, and low frequency data are related to characteristics of the film impedance.

Judging from the shape of high frequency data of the experiment this belongs to the case of small k and $B > A > 0$ among the impedance characteristics of the

film/solution interface.

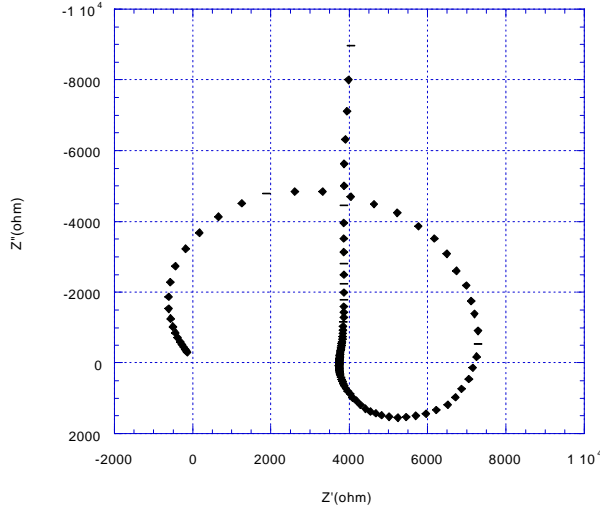


Fig.4 Nyquist diagram for passive film on Alloy 600

From the Nyquist plot of high frequency region we can estimate A, B , and k.

$$A = \frac{R_{\infty 1} R_{01}}{R_{\infty 1} + R_{01}} = 3740$$

$$B = \frac{R_{\infty 1} R_{\infty 2}}{R_{\infty 1} + R_{\infty 2}} = 7195$$

$$\tau = \frac{1}{k} = \frac{1}{\omega^*} \left\{ 1 + \frac{\frac{1}{R_{01}} - \frac{1}{R_{\infty 2}}}{\frac{1}{R_{\infty 1}} + \frac{1}{R_{\infty 2}}} \right\} = \frac{1}{\omega^*} \left\{ \frac{\frac{1}{R_{\infty 1}} + \frac{1}{R_{01}}}{\frac{1}{R_{\infty 1}} + \frac{1}{R_{\infty 2}}} \right\} = 1/ 23121.9$$

where ω^* is the frequency at the maximum of the low frequency semicircle

Assuming these values as initial values, Complex Non-linear Least Square(CNLS) fitting was performed for the high frequency data and the results are shown. Double layer capacitance was estimated about 4.522 pF.

Information about film properties can be obtained by utilizing low frequency region data. Low frequency data can be best fitted as a Warburg impedance parallel with a capacitor. The dominant charge transfer carriers for passive film anodically formed on Alloy 600 is considered as anion(oxygen) vacancies by several authors[6]. When anion vacancy moves far faster than cation vacancy, Warburg impedance can be expressed as anion vacancy impedance alone.

$$Z_f = \sigma_o \omega^{-1/2} (1 - j)$$

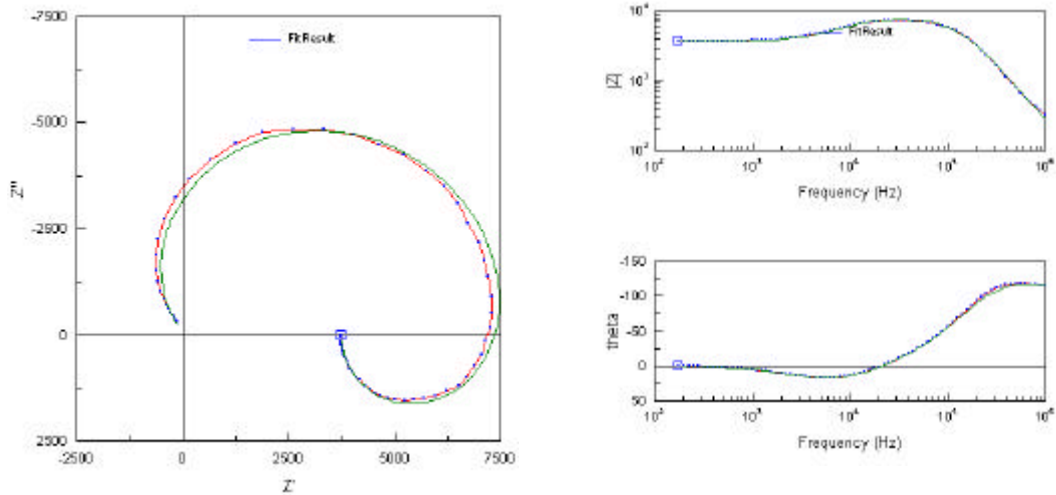


Fig. 5 Complex Nonlinear Least Square(CNLS) fitting for high frequency data

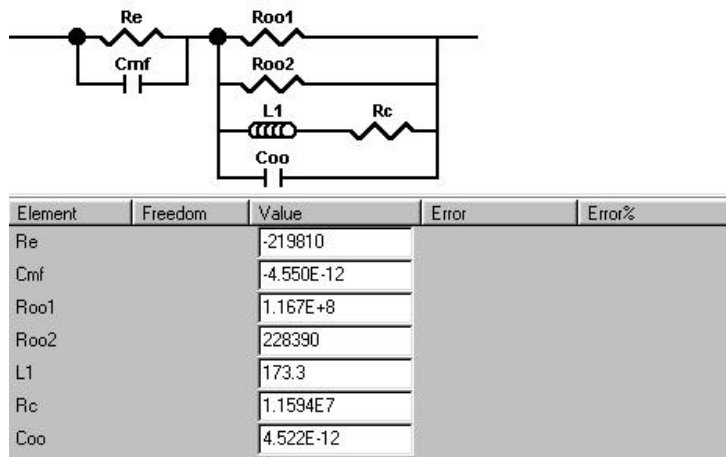


Fig. 6 Equivalent circuit and CNLS fitting result for high frequency data

From the CNLS fitting result of CPE component the Warburg coefficient can be calculated as

$$Z_{CPE} = \frac{1}{T(j\omega)^P} = \frac{1}{TV\sqrt{2}} \omega^{-1/2}(1-j) = \sigma_O \omega^{-1/2}(1-j)$$

$$\sigma_O = 234195 \Omega \text{ cm}^2/\text{s}^{1/2}$$

According to PDM σ_O (Warburg coefficient for the movement of oxygen ion vacancies) can be related with diffusivity of the vacancies as[1]

$$\sigma_O = \frac{1}{I_{dc}} \left(\frac{D_O}{2} \right)^{1/2} \cdot \frac{\epsilon}{1-\alpha}$$

where ϵ is electric field strength

Although reported electric field strength of Alloy 600 in PWR water chemistry, that of Fe -10Cr -10Ni oxide in 0.15 N B(OH)₃/BO₃³⁻ pH = 8.4 was measured by ellipsometry in the literature as[5]

$$\epsilon = 1.72 \times 10^6 \text{ V/m}$$

Assuming $\alpha \approx 0.5$ and electric field strength of the film as above value, and considering $I_{dc} = 1.4952 \times 10^{-6} \text{ A/cm}^2$, D_O can be calculated as

$$D_O = 2 \left[\sigma_O I_{dc} \frac{(1-\alpha)}{\epsilon} \right]^2 = 2.0724 \times 10^{-14} \text{ cm}^2/\text{sec}$$

CNLS fitting results for low frequency data are in Fig. 7, 8.

Capacitance term in low frequency region may result from electron or electron holes in the film. Impedance function for electron or electron holes was assumed as pure resistance in the modeling part by PDM which originally described passive film of pure metal(Ni, Fe etc). But the various composition and interfaces in the passive film of the alloy may result in various capacitance terms in the equivalent circuit.

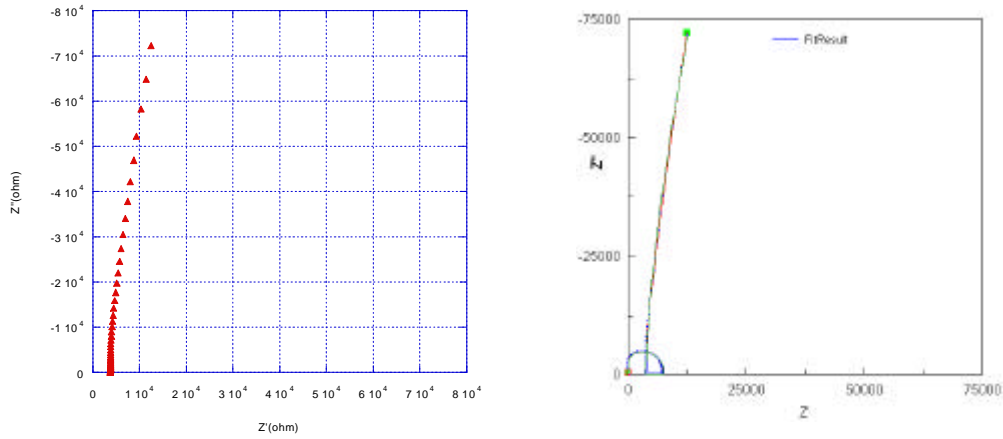


Fig. 7 Nyquist plot of low frequency data and CNLS fitting

V. Conclusion

Electronic structure of the metal/passive film/solution system was modeled based on the Point Defect Model and the work of Armstrong et al and its characteristics was

investigated by Electrochemical Impedance Spectroscopy measurement.

EIS measurement of the passive film on Alloy 600 reveals diffusivity of oxygen vacancies to be $2.0724 \times 10^{-14} \text{ cm}^2/\text{sec}$.

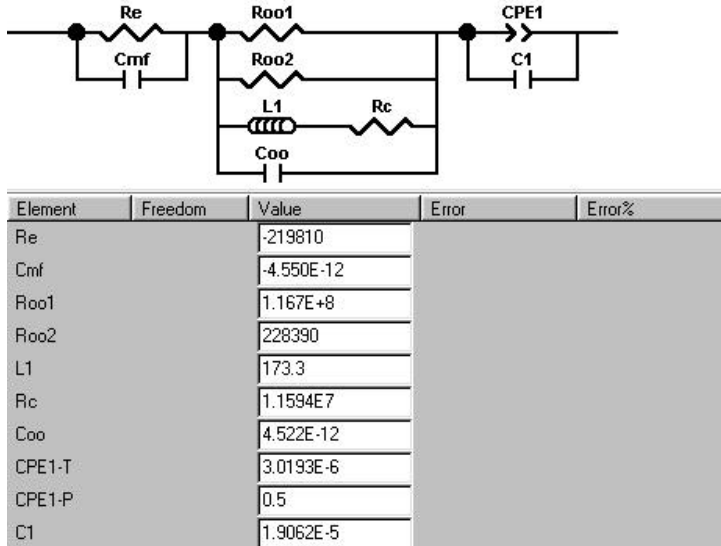


Fig. 8 CNLS fitting result for low frequency data

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