Electrochemical Behavior Assessment of Alloy 22 (UNS N06022) in Hydrochloric Acid Solutions by Electrochemical Impedance Spectroscopy and Mott–Schottky Analyses

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Abstract- In this study, passive behavior and semiconducting properties of Alloy 22 in hydrochloric acid solutions were evaluated. Corrosion and passive current density was measured from potentiodynamic polarization plots. Also, passive film resistance and passive film capacitance were estimated by electrochemical impedance spectroscopy (EIS), and finally defect (donor and acceptor) density was drawn from Mott–Schottky analysis. Mott–Schottky plots revealed that Alloy 22 in hydrochloric acid solutions behave as n-type and p-type semiconductors. Also, this analysis indicated that both donor and acceptor densities are in the range $10^{21}$ cm$^{-3}$ and increased with solution concentration. In conclusion, EIS and Mott–Schottky analysis revealed that dilute hydrochloric acid solutions offer better conditions of the passive film formation on Alloy 22 with higher protection behavior than concentrated hydrochloric acid solutions, due to the growth of a much thicker and less defective films.

Keywords- Alloy 22, Hydrochloric acid, EIS, Mott–Schottky analysis

1. INTRODUCTION

Up to now, six major groups of nickel-base alloys (Ni-Cu, Ni-Mo, Ni-Cr, Ni-Cr-Mo, Ni-Fe-Cr, and Ni-Fe-Cr-Mo) have been developed. Among these alloys, Ni-Cr-Mo (such as
Alloys 625, Alloy22, Hastelloy C-4 and Hastelloy C-276) and Ni-Fe-Cr-Mo (Alloy 825) groups are the most important because of their resistance to corrosion under both oxidizing (due to the presence of chromium) and reducing (due to the presence of molybdenum) conditions. Moreover in these groups, molybdenum provides improved resistance to localized corrosion [1].

The outstanding corrosion resistance of Ni-Cr-Mo alloys is known in a broad range of solutions with pH values ranging from 1 to 13 and temperatures from 25 to 120 °C [2–6]. Also, the passive behavior of Ni-Cr-Mo alloys has been evaluated in relation to the protective characteristics of the passive films. These studies showed that the composition of the passive films depends on many variables such as pH and presence of aggressive anions [7–10].

Generally, there are many industrial processes in which Ni-Cr-Mo alloys have to withstand the acidic and alkaline solutions. However, little information about the passive behavior of Ni-Cr-Mo alloys in acidic solutions (especially hydrochloric acid) is available. Based on ASTM B 575, Alloy 22 (UNS N06022) is a nickel-base alloy and typically contains 57% Ni, 22% Cr, 13% Mo, 3% W and 3% Fe. Although, many studies have been made on the corrosion resistance of Alloy 22 [2,3, 9–14], there is still lack of knowledge on the effect of hydrochloric acid concentration on the electrochemical behavior of Alloy 22. Indeed, based on a literature survey, no previous work has reported the semiconducting behavior of Alloy 22 in hydrochloric acid solutions. The present research, to the best of our knowledge, is the first of its kind that focuses on the effect of hydrochloric acid concentration on the electrochemical and semiconducting behavior of Alloy 22. Therefore, potentiodynamic polarization, EIS and Mott–Schottky measurements of Alloy 22 in hydrochloric acid solutions of various concentrations ranging from 0.01 to 0.30 M have been carried out in this work. Also, an evaluation of microstructure was obtained by optical microscopy.

2. EXPERIMENTAL PROCEDURES

Specimens were fabricated from Alloy 22 with the chemical composition (%): 22.1 Cr, 13.1 Mo, 3.1 Fe, 3.0 W, 2.4 Co, 0.07 Si, 0.01 C, and balance Ni. All Specimens were ground to P2000 (FEPA Standard) grit and cleaned with deionized water prior to testing. Aerated acidic solutions (without purging oxygen or any gas) with five different concentrations were used and the compositions were 0.01, 0.05, 0.10, 0.20 and 0.30 M HCl, respectively. All solutions were made from analytical grade HCl and distilled water, and the tests were carried out at 25±1 °C.

The detailed procedure of three-electrode flat cell is published elsewhere [5,6]. Prior to all electrochemical measurements, specimens were immersed at open circuit potential (OCP) condition for 1200 s to form a steady-state condition. The potentiodynamic polarization curves were measured starting from –0.25 V (vs. Ag/AgCl) to 1.0 V (vs. Ag/AgCl). EIS tests were done at OCP condition and AC potential with the amplitude of 10 mV and
normally a frequency range of 100 kHz to 10 mHz. Also, Mott–Schottky analysis was carried out at a frequency of 1 kHz using a 10 mV AC signal and a step potential of 25 mV, in the cathodic direction [5]. Microstructures of Alloy 22 samples before and after immersion in hydrochloric acid solutions were characterized using an optical microscope.

3. RESULTS AND DISCUSSION

3.1. Polarization measurement

Fig. 1 shows the potentiodynamic polarization curve of Alloy 22 in hydrochloric acid solutions. The current density was found to increase with potential during the early stage of passivation, and no current peak was observed. Similar potentiodynamic polarization curves of alloy C in NaOH solutions [5] and borax solutions [6] have been shown. Also, it is seen that the passive potential range is extended from the corrosion potential to 0.8 V (vs. Ag/AgCl).

![Polarization curve of Alloy 22 in hydrochloric acid solutions](image)

Fig. 1. Polarization curve of Alloy 22 in hydrochloric acid solutions (scan rate=1 mV/s)

Fig. 2 shows the values of the corrosion and passive current density versus the hydrochloric acid concentration. It was observed that both corrosion and passive current density of this alloy increases by increasing hydrochloric acid concentration from 0.01 to 0.30 M.

3.2. EIS measurements

The EIS response of Alloy 22 in hydrochloric acid solutions was measured, and the results are presented as Nyquist, Bode and Bode-phase plots in Fig. 3. Similar Nyquist, Bode and Bode-phase plots for Alloy 22 in 1.0 and 3.0 M HCl solutions have been reported by
Gray et al. [2]. In another study, Gray and Orme [3] obtained similar Nyquist, Bode and Bode-phase plots for Alloy 22 in low pH nitrate and chloride environments.

**Fig. 2.** Dependence of the (a) corrosion and (b) passive current density on the hydrochloric acid concentration

As can be seen in Fig. 3, Nyquist and Bode plots show a resistive behavior at high frequencies, but in the middle to low frequency range there is a marked capacitive response. The Bode-phase curves show one time constant (only one maximum phase lag at the middle frequency range). The phase angle values remained very close to 90 °C. This evolution showed the formation and growth of a passive film. It was observed that the low frequency impedance decreased as the hydrochloric acid concentration increased.

Based on the Nyquist and Bode plots, the equivalent circuit that is shown in Fig. 4 was used to simulate the measured impedance data of Alloy 22 in hydrochloric acid solutions. In this equivalent circuit, $Q_p$ is the constant phase element corresponding to the capacitance of the passive film; $R_p$ is the resistance of the passive film; and $R_s$ shows the solution resistance. This equivalent circuit was composed of one time constant, as proposed by Gray et al. for describing the passive film’s formation conditions on Alloy 22 in acidic solutions [2,3].
Fig. 3. (a) Nyquist, (b) Bode, and (c) Bode-phase plots of Alloy 22 in hydrochloric acid solutions

Fig. 4. The best equivalent circuit tested to model the experimental EIS data [2,3,5]
The impedance and the capacitance of the constant phase element can be calculated from Eq. (1) and (2), respectively [15–17].

\[ Z_0 = [C(j\omega)^n]^{-1} \]  
\[ C = Y_0(\omega_{\text{max}})^{-1} \]  

Where \( \omega \) is the angular frequency (rad s\(^{-1}\)), \( n \) is associated with the roughness of the electrode surface, \( Y_0 \) is the admittance, and \( \omega_{\text{max}} \) is the angular frequency at which the maximum in the imaginary component of the impedance occurs [15–17]. Fig. 5 shows the effect of hydrochloric acid concentration on the resistance and capacitance of the passive film formed on Alloy 22 in hydrochloric acid solutions.

![Graph showing the effect of hydrochloric acid concentration on the passive film resistance and capacitance](image)

**Fig. 5.** Dependence of the (a) passive film resistance and (b) passive film capacitance on the hydrochloric acid concentration

As can be seen in Fig. 5, passive film resistance and capacitance decreased and increased, respectively, as the hydrochloric acid concentration increased. According to the equivalent circuit shown in Fig. 4, the passive film thickness \( (d) \) can be calculated using Eq. (3) [2,3,5]:

\[ R_p = \frac{2\mu F}{k\Omega \text{ cm}} \]
\[
d = \frac{\varepsilon \varepsilon_0}{C}
\]

Where \( \varepsilon \) is the dielectric constant of the passive film, \( \varepsilon_0 \) is the vacuum permittivity \((8.854 \times 10^{-14} \text{ F/cm})\), and \( C \) is the total capacitance of the passive film. Generally, a change in the total capacitance of the passive film can be used as an indicator of change in the passive film thickness. For calculation of the passive film thickness, a value of dielectric constant \( \varepsilon = 20 \), which was estimated by Raja et al. [4], was used for the passive films on Ni–22Cr–13Mo–4W alloy. Therefore, according to Eq.3, the reciprocal capacitance of the passive film \( (1/C) \) is proportional to its thickness, which decreases as the hydrochloric acid concentration increases.

### 3.3. Mott–Schottky analysis

Fig. 6 shows the Mott–Schottky plots of Alloy 22 in hydrochloric acid solutions. As can be seen, \( C^{-2} \) clearly decreased as nitric acid concentration increased. As it is illustrated in each plot of Fig. 6, there are two regions with different slopes. Region (I) with positive slopes indicates that the passive film has n-type semiconductivity, while region (II) with negative slopes represents p-type semiconductivity of the passive film. Therefore, the Mott–Schottky plots show similar semiconducting properties, but with different donor and acceptor concentrations that are specified by different slopes of Mott–Schottky curve.

![Mott–Schottky plots](image)

**Fig. 6.** Mott–Schottky plots of passive film formed on Alloy 22 in hydrochloric acid solutions

According to the Mott–Schottky analysis, the relation between the space charge capacitance \( C \) of n-type and p-type semiconductors and the electrode potential \( E \) can be written as [4, 18]:
\[ C^{-2} = \frac{2}{\varepsilon\varepsilon_0 e N_D} \left( E - E_{FB} - \frac{k_B T}{e} \right) \] for n-type semiconductor \hfill (4)

\[ C^{-2} = -\frac{2}{\varepsilon\varepsilon_0 e N_A} \left( E - E_{FB} - \frac{k_B T}{e} \right) \] for p-type semiconductor \hfill (5)

Where \( e \) is the electron charge \((-1.602 \times 10^{-19} \text{ C})\), \( N_D \) is the donor density for n-type semiconductor \( (\text{cm}^{-3}) \), \( N_A \) is the acceptor density for p-type semiconductor \( (\text{cm}^{-3}) \), \( k_B \) is the Boltzmann constant \((1.38 \times 10^{-23} \text{ J/K})\), \( T \) is the absolute temperature and \( E_{FB} \) is the flat band potential. Fig. 7 shows the calculated donor and acceptor density of Alloy 22 in hydrochloric acid solutions. As can be seen, Mott–Schottky plots indicated that the donor and acceptor densities are in the order of \( 10^{21} \text{ cm}^{-3} \) and increased by solution concentration.

To investigate the effect of hydrochloric acid concentration on the passive film growth, we can use the point defect model. Using this model, we can obtain the analytical expression for the concentration of vacancies within the passive film. This model shows that the cation vacancies are electron acceptors (p-type semiconductor), whereas the oxygen vacancies and the metal interstitials are electron donors (n-type semiconductor) [18].

**Fig. 7.** Donor and acceptor densities of the passive films formed on Alloy 22 in hydrochloric acid solutions.
It is found that a passive film formed on nickel-base alloys in acidic solutions is composed of Cr₂O₃ barrier layer [19]. Therefore, as designated by the Kroger-Vink notation, the present point defects in the barrier layer (Cr₂O₃) are chromium cation vacancy ($V^{3+}_{\text{Cr}}$), oxygen vacancy ($V^{2+}_{\text{O}}$), and chromium cation interstitial ($Cr^{3+}_{\text{i}}$) [20–22].

It can be understood from the point defect model that the transition from n-type to p-type is related to a change in the dominant point defect in the passive film. At low potentials (Region I), the n-type characteristics of the passive film are established by chromium cation interstitial or oxygen vacancy injected into the oxide at the Alloy 22/ barrier layer interface. The switch from n-type to p-type can be related to the generation of chromium cationic vacancy at the barrier layer/solution interface due to the oxidative dissolution of $\text{Cr}^{3+}$ to $\text{Cr}^{6+}$ in the oxide barrier layer [18, 20–22].

3.4. Optical microscopy observations

Fig. 8 shows the optical microscope images of Alloy 22 before and after immersion in hydrochloric acid solutions.

![Optical microscope images of Alloy 22](image)

**Fig. 8.** Optical microscope images of Alloy 22 before (a) and after 1200 s immersion in hydrochloric acid solutions: (b) 0.01, (c) 0.05, (d) 0.10, (e) 0.20 and (f) 0.30 M HCl
It is shown that there is no sign of pitting or any significant change on the surface of the samples before and after the immersion tests. Indeed, Alloy 22 is well passivated even in highly corrosive solutions, which is due to the considerable amounts of alloying elements such as chromium, molybdenum, and nickel in this alloy that play a key role in passivation.

4. CONCLUSIONS

Potentiodynamic polarization curves demonstrated that Alloy 22 shows good passive behavior in hydrochloric acid solutions. Moreover, these curves showed that the corrosion and passive current density increased by increasing the concentration of hydrochloric acid. Mott–Schottky plots revealed the n- and p-type semiconducting behaviors of the passive films formed on Alloy 22 in hydrochloric acid solutions. Also, it was demonstrated that defect densities increased when the solutions concentrations increase while they are in the order of $10^{21}$ cm$^{-3}$. EIS results showed that the thickness of the passive film decreases with increasing solution concentration. This behavior indicates that increasing solution concentration offer worse conditions for forming the thicker passive films. In conclusion, EIS and Mott–Schottky analysis revealed that dilute hydrochloric acid solutions offer better conditions of the passive film formation on Alloy 22 with higher protection behavior, due to the growth of a much thicker and less defective films.

REFERENCES