

Full Paper

Investigation of the Electrochemical Behavior of Alloy C in NaOH Solutions

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Abstract- The electrochemical behavior of alloy C in NaOH solutions under open circuit potential (OCP) condition was investigated in this research by using potentiodynamic polarization, Mott–Schottky analysis and electrochemical impedance spectroscopy (EIS). Potentiodynamic polarization curves suggested that alloy C showed excellent passive behavior in NaOH solutions. Mott–Schottky analysis revealed that the passive films displayed p-type semiconductive characteristics, where the Ni(II) vacancies (over the oxygen vacancies and interstitials) preponderated. Also, the Mott–Schottky analysis indicated that the acceptor density decreases with decreasing NaOH concentration. EIS measurements showed that dilute NaOH solutions offer better conditions for forming passive films with higher protection behavior, due to the growth of a much thicker and less defective films.

Keywords- Alloy C, Passive film, Mott–Schottky: p-type semiconductive, Nyquist plot

1. INTRODUCTION

Ni is widely used in structural alloys, both as Ni-base alloys and as an alloying element in austenitic stainless steels. Generally, pure Ni is extensively used for the containment of alkaline solutions and, while the cost is higher than that of steel, the excellent corrosion performance of Ni over steel at high pH makes pure Ni the material of choice for alkaline service. Moreover, the Ni-base alloys show excellent corrosion behavior in aqueous

aggressive environments, which are attributed to the ability of nickel and chromium to form a stable passive film. Generally, these alloys show excellent outstanding corrosion behavior in a broad range of solutions with pH values ranging from 1 to 13 and temperatures up to 120 °C [1-3]. Therefore, there is an interest in studying the electrochemical (especially passivation) behavior of the Ni-base alloys in various conditions [4-9].

The passivation behavior of the Ni-base alloys has been investigated in relation to the protective characteristics of the passive films. The composition of the passive films formed on the Ni-base alloys has been characterized by using different methods such as X-ray photoemission spectroscopy, time of flight secondary ion mass spectrometry, and atomic force microscopy. These studies indicated that the composition of the passive films depends on many variables such as pH, presence of aggressive anions, and aerating conditions [10-13]. Moreover, the compositional and electrical properties of the passive films formed on the Ni-base alloys have been investigated using surface analytical methods [14,15] and EIS [16-20].

Generally, there are many industrial processes in which the Ni-base alloys have to withstand the alkaline solutions and these solutions can affect the passivation behavior of these alloys. However, little information about the passivation behavior of the Ni-base alloys in the alkaline solutions was available. The aim of this study is to research the electrochemical behavior of alloy C (UNS N10002) in NaOH solutions by using the EIS and Mott-Schottky analysis. Also, this work includes investigation of the passive region of alloy C in NaOH solutions, determination of the semiconductor character and estimation of the dopant levels in the passive film, as well as the investigation of the impedance behavior as a function of NaOH concentration.

2. EXPERIMENTAL

Chemical composition of Alloy C (UNS N10002) used in present investigation is shown in Table 1. All samples were ground to 1200 grit and cleaned by deionized water prior to tests. The alkaline solutions with three different concentrations (0.050, 0.010 and 0.005 M NaOH) were used as the test solutions and made from analytical grade NaOH and distilled water.

Table 1. Chemical compositions of alloy C (UNS N10002)

Elements	Ni	Cr	Mo	Fe	W	Co	Cu	Mn	Si	V	C
Alloy C/wt%	54.4	14.3	17.4	5.14	4.15	2.12	1.53	0.406	0.005	0.128	0.01

All the electrochemical measurements were performed in a conventional three-electrode flat cell under aerated conditions. The counter electrode was a Pt plate, while the reference electrode was Ag/AgCl saturated in KCl. The electrochemical measurements were obtained by using the μ Autolab Type III/FRA2 system controlled by a personal computer. Prior to the electrochemical measurements, the working electrodes were immersed at OCP to form a steady-state passive film.

The potentiodynamic polarization curves were measured potentiodynamically at a scan rate of 1 mV/s starting from $-0.25 \text{ V}_{\text{Ag/AgCl}}$ (vs. E_{corr}) to $1.0 \text{ V}_{\text{Ag/AgCl}}$. The impedance spectra were measured in a frequency range of 100 kHz –10 mHz at an AC amplitude of 10 mV (rms). The validation of the impedance spectra was performed by checking the linearity condition, i.e. measuring spectra at AC signal amplitudes between 5 and 15 mV (rms). For the EIS data modeling and curve-fitting method, the NOVA impedance software was used. The Mott-Schottky analysis were carried out on the passive films at a frequency of 1 kHz using a 10 mV ac signal, and a step rate of 25 mV in the cathodic direction. Each electrochemical measurement was repeated at least three times.

3. RESULT AND DISCUSSION

3.1. Polarization Measurements

Fig. 1 shows the potentiodynamic polarization curves of alloy C in NaOH solutions. By comparing the polarization curves in different solutions, the current density was found to increase with potential during the early stage of passivation and no obvious current peak was observed. Also, all curves exhibit similar features, with a passive potential range extending from the corrosion potential to the onset of transpassivity. In other studies, the anodic behavior of other Ni-base alloys was studied predominantly by the potentiostatic and potentiodynamic methods. These studies indicated that two potential ranges (the passive range and the range of transpassivity) are observed in the measured anodic regions [7, 18, 20, 21]. Moreover, the curves indicated that the corrosion current density decreases with decrease in the concentration of NaOH solutions.

The corrosion current density (i_{corr}) was measured by Tafel extrapolation of the linear part for the cathodic branch back to the mixed potential of zero net current (E_{corr}) with accuracy of more than 95% for the points more negative to E_{corr} by 50 mV [22].

The variations of corrosion current density and corrosion potential in NaOH solutions indicate that the corrosion current density reduces with decrease in the concentration of NaOH solutions (Fig. 1). In addition, the corrosion potential moves towards positive values as the NaOH concentration decreases in the solution (except in 0.005 M NaOH solution).

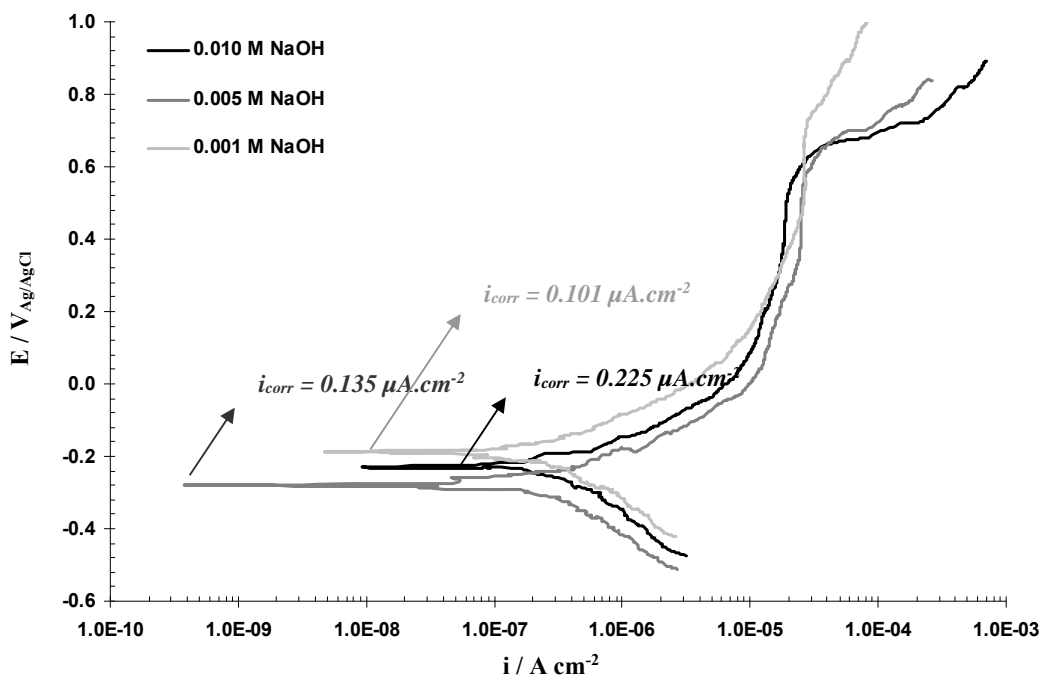


Fig. 1. Potentiodynamic polarization curves of alloy C in NaOH solutions

3.2. Mott-Schottky Analysis

According to the Mott-Schottky analysis, the space charge capacitance of p-type semiconductor was given by the following the Mott-Schottky relationship (1) assuming that the capacitance of the Helmholtz layer could be neglected [23-27]:

$$\frac{1}{C^2} = -\frac{2}{\epsilon\epsilon_0 e N_A} \left(E - E_{FB} - \frac{kT}{e} \right) \text{ for p-type semiconductor} \quad (1)$$

where e is the electron charge, N_A is the acceptor density for p-type semiconductor (cm^{-3}), ϵ is the dielectric constant of the passive film (usually taken as 20 for alloys 22 [1, 24]), ϵ_0 is the vacuum permittivity, k is the Boltzmann constant, T is the absolute temperature and E_{FB} is the flat band potential.

Fig. 2 shows the Mott-Schottky plots of alloy C in NaOH solutions. It should be noted that capacitances clearly increase with solution concentration. Also, all plots show one region in which a linear relationship between C^{-2} and E could be observed. The negative slope in this region is attributed to p-type behavior. Similar plots for Ni in borate buffer solution (pH 8.4) have been reported by Sikora and Macdonald [23].

Fig. 3 shows the calculated acceptor density of alloy C in NaOH solutions. According to Fig. 3, the acceptor densities are in the order of 10^{20} cm^{-3} and decrease with decreasing NaOH concentration. Similar values for the acceptor densities have been reported for Ni in borate buffer solution (pH 8.4) by Sikora and Macdonald [23].

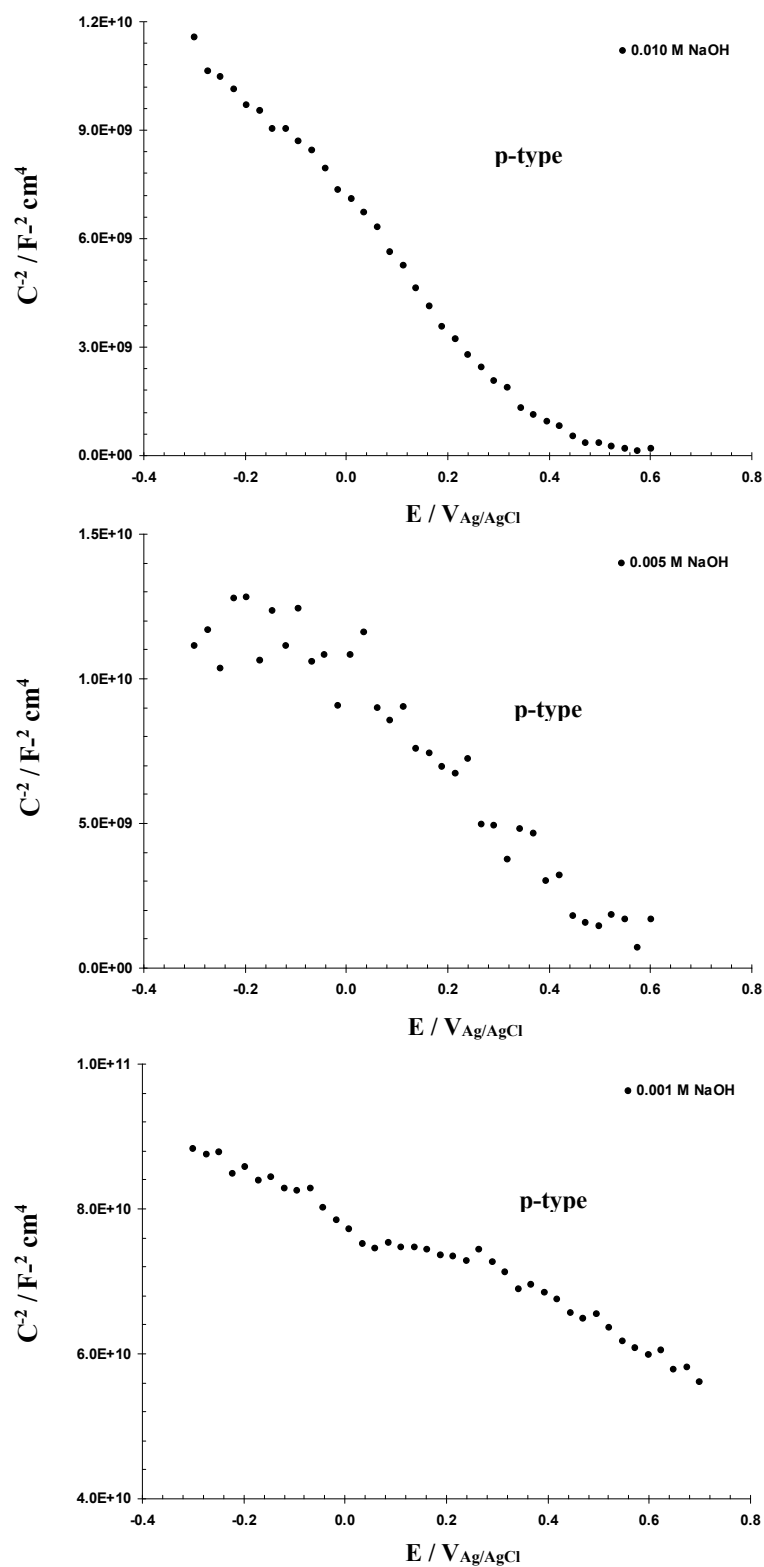


Fig. 2. Mott-Schottky plots of alloy C in NaOH solutions

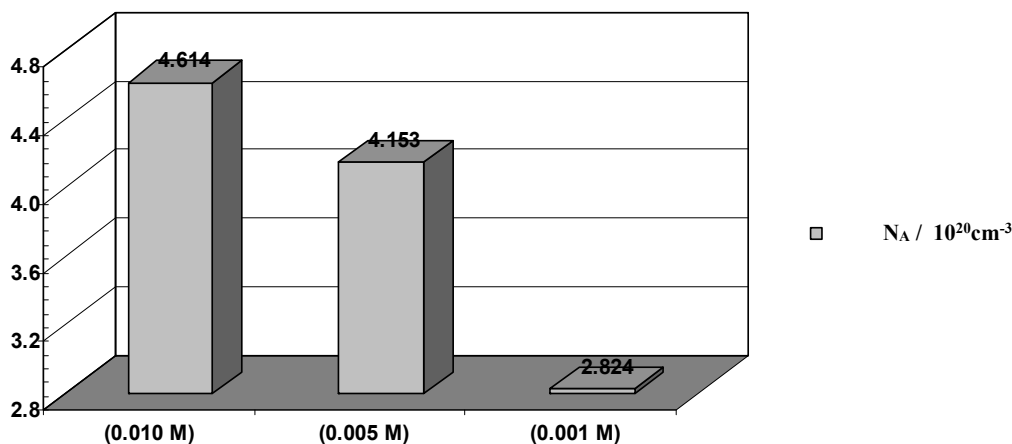


Fig. 3. Calculated acceptor density of the passive films formed on alloy C in NaOH solutions

Indeed, the changes in the acceptor density related to the non-stoichiometry defects in the passive films. X-ray photoemission spectroscopy studies on nickel and nickel alloys show the existence of the barrier layer and outer layer [28,29]. This bilayer structure was found by Nishimura, who stated that the passive film formed on nickel in neutral and weakly alkaline solutions was composed of the barrier layer (NiO) and outer layer (Ni(OH)₂) [30].

In the last decade, many models have been proposed to explain the passivation of materials, a satisfactory description of the phenomenon is still in lack. The point defect model (PDM) [31-33], which was developed by Macdonald et al., described the growth and breakdown of passive film qualitatively from a microscopic perspective. This model is based on the assumption that the passive film contains a high concentration of point defects, such as oxygen vacancies and metal cation vacancies. The growth and breakdown of the passive film involves the migration of these point defects under the influence of the electrostatic field in the film. Therefore, the important parameters in determining the transport of point defects and hence the kinetics of passive film growth is the density and the diffusivity of the defects in film [25-27].

The PDM presupposes that passive films are bilayer structures comprising a defective barrier layer that grows into the alloy and an non-barrier layer that forms via the hydrolysis of cations transmitted through the barrier layer and the subsequent precipitation of a hydroxide, or oxide, depending upon the formation conditions. Moreover, the PDM assumes that the point defects present in barrier layer are, in general, cation vacancies ($V_M^{z'}$), oxygen vacancies ($V_O^{\cdot\cdot}$), and cation interstitials (M_i^{z+}), as designated by the Kroger-Vink notation. Cation vacancies are electron acceptors, thereby doping the barrier layer p-type, whereas oxygen vacancies and metal interstitials are electron donors, resulting in n-type doping [31-38].

Fig. 4 shows the modified PDM of alloy C passivation in alkaline solutions [34]. It is observed that the generation of oxygen vacancies at the alloy/NiO interface (Reaction (3))

and the flux of oxygen vacancy through the passive film, resulting from barrier layer dissolution, are essential to the film growth process. However, oxygen vacancies are electron donors, and like metal interstitials cannot be responsible for p-type electronic character of the barrier layer [31-38]. It seems that the dominant defects are the Ni(II) vacancies, as electron acceptor, thereby doping the barrier layer p-type.

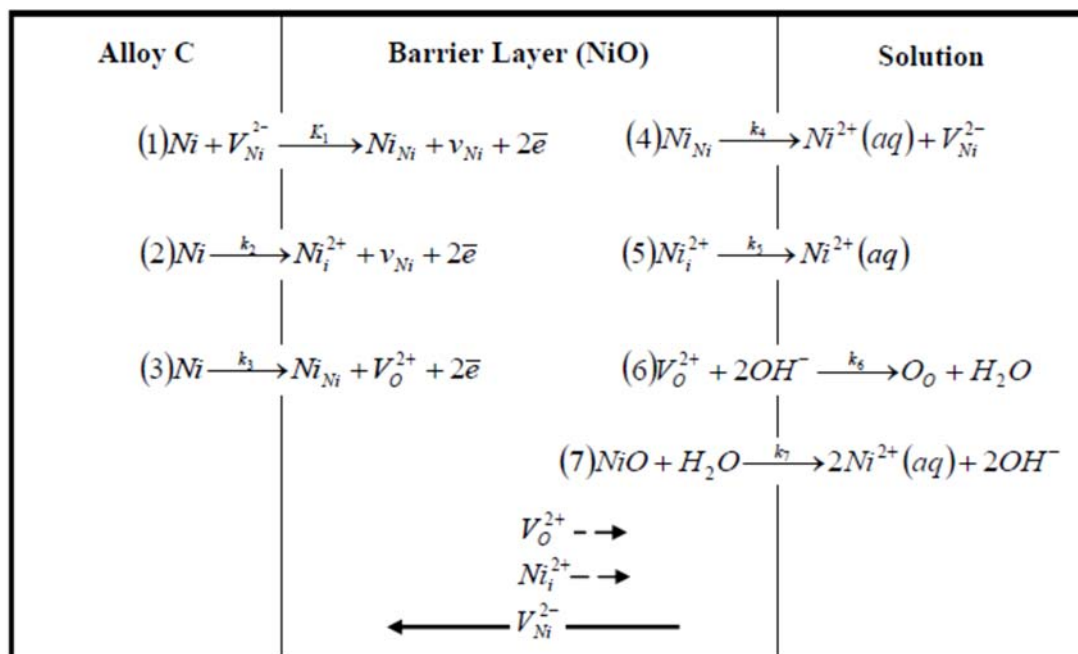


Fig. 4. Modified PDM of passivation of alloy C in alkaline solutions; V_{Ni}^{2-} = nickel vacancy on the nickel sublattice of the barrier layer, Ni_i^{2+} = interstitial nickel, Ni_{Ni} = nickel cation on the nickel sublattice of the barrier layer, V_O^{2+} = oxygen vacancy on the oxygen sublattice of the barrier layer, O_o = oxygen anion on the oxygen sublattice of the barrier layer, $Ni^{2+}(aq)$ = nickel cation in solution [34].

3.3. EIS Measurements

Fig. 5 present the Nyquist plots obtained for alloy C at OCP in NaOH solutions. In order to model the passive film, the equivalent circuit shown in Fig. 6 was used to simulate the measured impedance data.

The Nyquist and Bode plots reveal a resistive behavior at high frequencies, but in the middle to low frequency range there was a capacitive response. The Bode-phase curves show only one maximum phase lag at the middle frequency range (one time constant). Also, in the Bode-phase curves the phase angles values remained very close to 90°. This evolution revealed the formation and growth of a passive film. Also, there was a decrease of the low frequency impedance with the solution concentration.

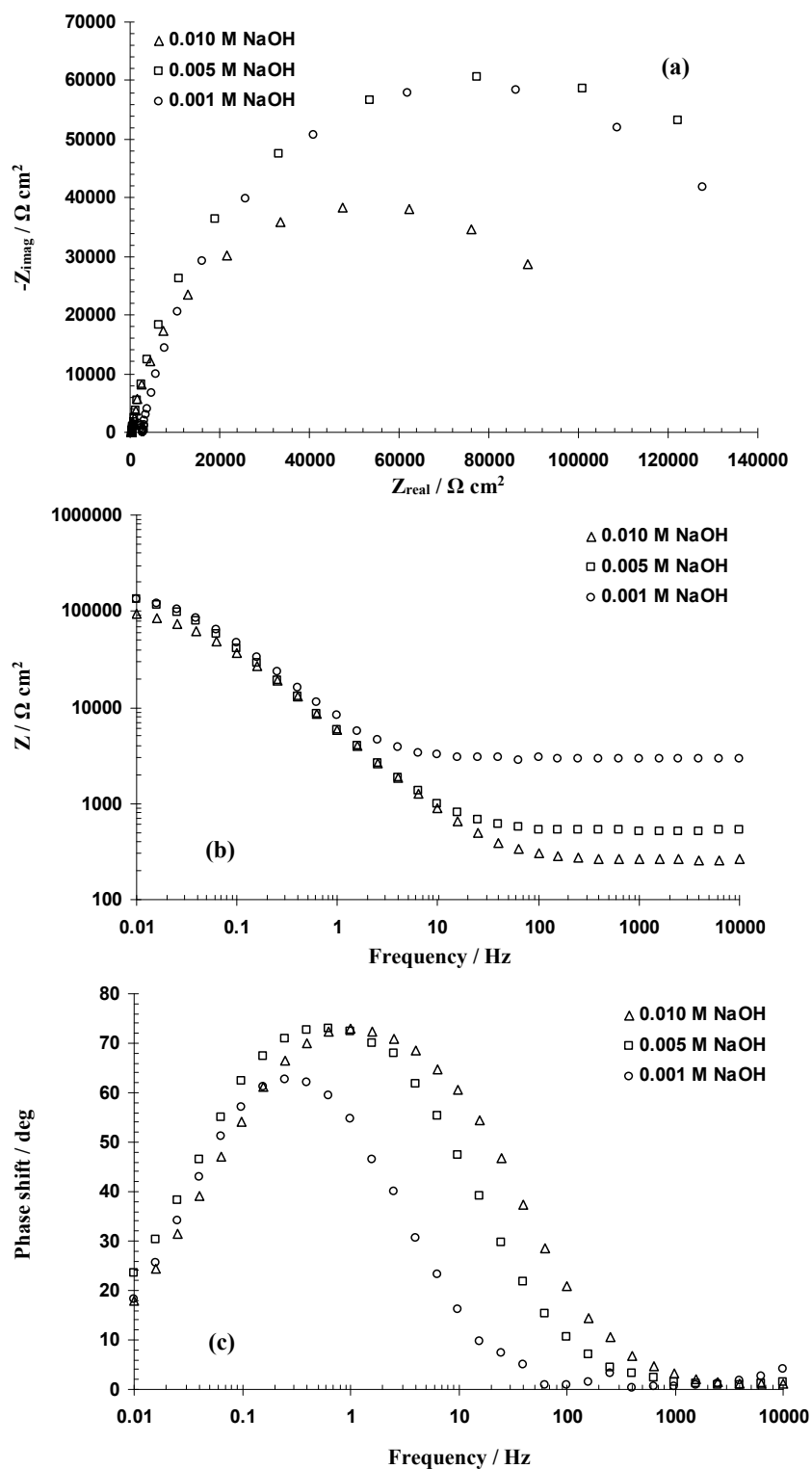


Fig. 5. Nyquist and Bode plots of alloy C in NaOH solutions

Based on these results, the equivalent circuit shown in Fig. 6 was used to simulate the measured impedance data of alloy C in NaOH solutions. This equivalent circuit is composed of: R_s – solution resistance; Q_{pf} – constant phase element corresponding to the capacitance of the passive film; R_{pf} – resistance of the passive film [2,3].

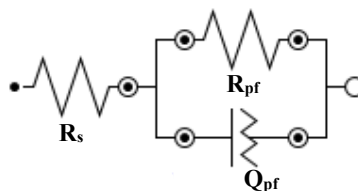


Fig. 6. The best equivalent circuit used to model the experimental EIS data [2,3]

Table 2 presents the best fitting parameters (with an average error of less than 3%) obtained for the impedance data of alloy C in NaOH solutions. As can be seen, R_{pf} increases with decrease in NaOH concentration while C decreases. This behavior indicates that grown passive film on alloy C surface is liable to dissolve in high NaOH concentration, since R_{pf} is inversely proportional to the corrosion current density.

Table 2. Best fitting parameters for the impedance spectra of alloy C in NaOH

NaOH Solution (M)	0.010	0.005	0.001
R_s ($k\Omega\text{ cm}^2$)	0.26	0.52	1.61
R_{pf} ($k\Omega\text{ cm}^2$)	99.61	149.63	151.6
C_{pf} ($\mu\text{F cm}^{-2}$)	34.75	34.21	29.25
n_{pf}	0.86	0.88	0.87

According to the equivalent circuit shown in Fig. 6, the passive film thickness (d) can be calculated using the Eq.(2) [2, 3]:

$$d = \frac{\varepsilon\varepsilon_0 A}{C} \quad (2)$$

where C is the total capacitance of the passive film, ε the relative permittivity of the passive film, ε_0 is the vacuum permittivity, and A the area in cm^2 . Generally, a change in the total capacitance of the passive film (C) can be used as an indicator for change in the passive film thickness (d). Therefore, the reciprocal capacitance of the passive film ($1/C$) is proportional to its thickness which increases with decreasing NaOH concentration. It is clear that dilute NaOH solutions give better conditions for forming the passive films with higher protection behavior, due to the growth of a much thicker and less defective passive films [2].

4. CONCLUSION

The electrochemical behavior of alloy C in NaOH solutions were investigated in the present work. Conclusions drawn from the study are as follows:

1. Potentiodynamic polarization curves suggested that alloy C showed outstanding passive behavior in NaOH solutions.
2. Mott–Schottky analysis indicated that the passive films displayed p-type semiconductive characteristics, where the Ni(II) vacancies (over oxygen vacancies and interstitials) preponderated.
3. Also, the Mott–Schottky analysis showed that the acceptor densities are in the order of 10^{20} cm^{-3} , which decrease with decreasing NaOH concentration.
4. EIS results showed that the reciprocal capacitance of the passive film is directly proportional to its thickness which increases with decreasing NaOH concentration.
5. Also, EIS results showed that dilute NaOH solutions offer better conditions for forming passive films with higher protection behavior, due to the growth of a much thicker and less defective films.

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