

Full Paper

Effect of Chloride Ions Concentration on the Semiconducting Behaviors of 1050 and 6061 Al Alloys

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Abstract- The effect of chloride ions concentration on the semiconducting behaviors of 1050 and 6061 Al alloys in 0.003 M NaOH has been investigated by using potentiodynamic polarization, cyclic potentiodynamic polarization and Mott-Schottky analysis. Potentiodynamic and cyclic potentiodynamic polarization curves indicate that chloride ions concentration narrowed passivation region for both Al alloys. Also, these polarization curves revealed that increasing chloride ions concentration leads to decrease the pitting potential of both Al alloys. Mott-Schottky analysis demonstrated that the passive films formed on both Al alloys in 0.003 M NaOH with and without NaCl addition show n-type semiconducting behaviors in nature. For both alloys, the passive films formed in chloride-free solution are most stable, and that formed in chloride-containing solution are unstable. Also, the Mott-Schottky results showed that the donor density evaluated from the Mott-Schottky plots increases with increasing chloride ions concentration.

Keywords- Al alloy, Chloride, Concentration, Passive film, Mott-Schottky

1. INTRODUCTION

Aluminum is a lightweight metal having good corrosion resistance to the atmosphere and many aqueous solutions [1-4]. It is assumed that the passive films formed on Al and its alloys are composed of Al oxide, which is estimated at about 2-10 nm in thickness. Indeed, this

passive layer forms an efficient barrier against the metal dissolution and undergoes a passivity breakdown under certain conditions. But, Al tends to pit in waters containing chloride ion, particularly at crevices or at stagnant areas where passivity breaks down through the action of differential aeration cells [5,6].

In the last decade, little studies investigated the electrochemical behavior of passive films formed on Al and its alloys. The passive films formed on Al and its alloys are known to exhibit semiconducting behaviors, because of their non-stoichiometric nature. Depending on the predominant defects present in the passive film, either p-type or n-type behaviors are observed. Mott–Schottky analysis indicated that the passive film formed on Al and its alloys, exhibit semiconducting behaviors, because of their non-stoichiometric nature [7-12].

Generally, 1050 and 6061 are two of the most widely used grades of Al alloys. They are good compromise between mechanical resistance and corrosion resistance. These alloys have a wide range of applications such as buildings, pipelines, sheet metal working, fins and tubes for heat exchangers, welded boiler work, and mechanics applications [13].

Although, some works published on the passivity of Al and its alloys, little information about the effect of chloride ions concentration on the semiconducting behavior of the passive film formed on these alloys was available. In this work, Mott–Schottky analysis of 1050 and 6061 Al alloys in 0.003 M NaOH solution with and without NaCl addition have been performed to determination of the semiconducting behavior and estimation of the dopant levels in the passive film, as well as the estimation of the dopant levels as a function of chloride ions concentration.

2. EXPERIMENTAL

Chemical composition of 1050 and 6061 Al alloys used in present investigation is shown in Table 1. All samples were ground to 2000 grit and cleaned by deionized water prior to tests. All the electrochemical measurements were performed in a conventional three-electrode flat cell under aerated conditions by using an Autolab potentiostat/galvanostat system. The counter electrode was a Pt plate, while the reference electrode was Ag/AgCl saturated in KCl. The solutions used in this study were 0.003 M NaOH with and without NaCl addition (0.0001 M, 0.0010 M and 0.0100 M NaCl).

Prior to the electrochemical measurements, working electrodes were immersed at open circuit potential to form a steady-state passive film. The potentiodynamic and cyclic potentiodynamic polarization curves were measured potentiodynamically at a scan rate of 1 mV/s. Mott–Schottky analyses were done by measuring the frequency response at 1 kHz during a 25 mV/s negative potential scan.

Table 1. Chemical compositions of 1050 and 6061 Al alloys

Elements	Mg	Si	Fe	Mn	Zn	Ti	V	Cu	Cr	Al
1050 Al alloy /wt%	0.02	0.04	0.35	0.01	0.01	0.01	0.01	-	-	Bal
6061 Al alloy /wt%	0.09	0.70	0.35	0.02	0.06	0.01	0.01	0.23	0.19	Bal

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic Polarization Measurements

Figs. 1 and 2 show the potentiodynamic polarization curves for 1050 and 6061 Al alloys in 0.003 M NaOH solution with and without NaCl addition.

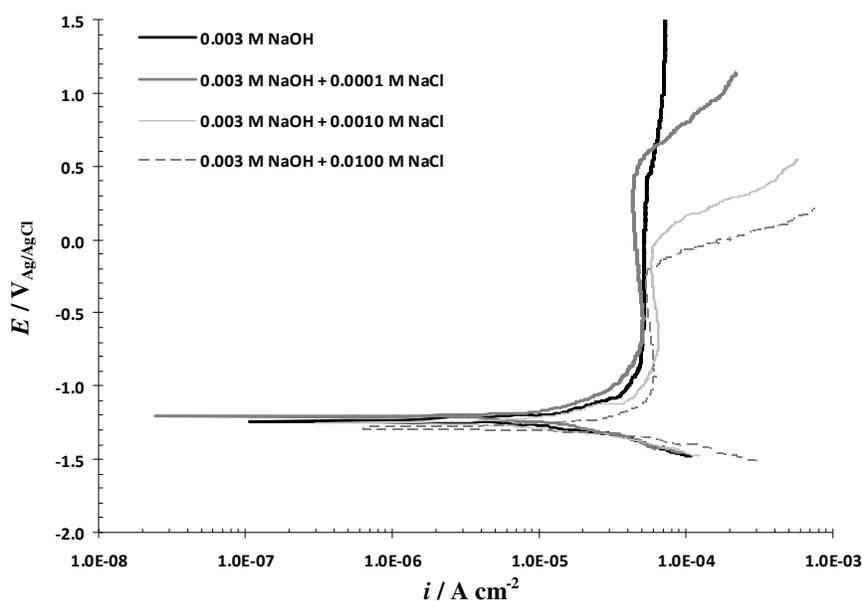


Fig. 1. Effect of chloride ions concentration on the potentiodynamic polarization curve of 1050 Al alloy in 0.003 M NaOH solution

For both alloys, the electrodes exhibit the same curve shapes similar to that reported previously [14], where the current changes smoothly and linearly around the rest potential manifesting cathodic and anodic Tafel behavior. Also, no active-passive transition peak can be observed in the anodic curve. As can be seen, for both alloys, in the absence of chloride ions, a nearly constant current density was observed in the anodic potential region. In contrast, in the presence of chloride ions, pitting occurred above the pitting potential at which the anodic current density increased remarkably with increasing applied anodic potential. It is

clear that the passive current density appeared to be approximately constant only below the pitting potential.

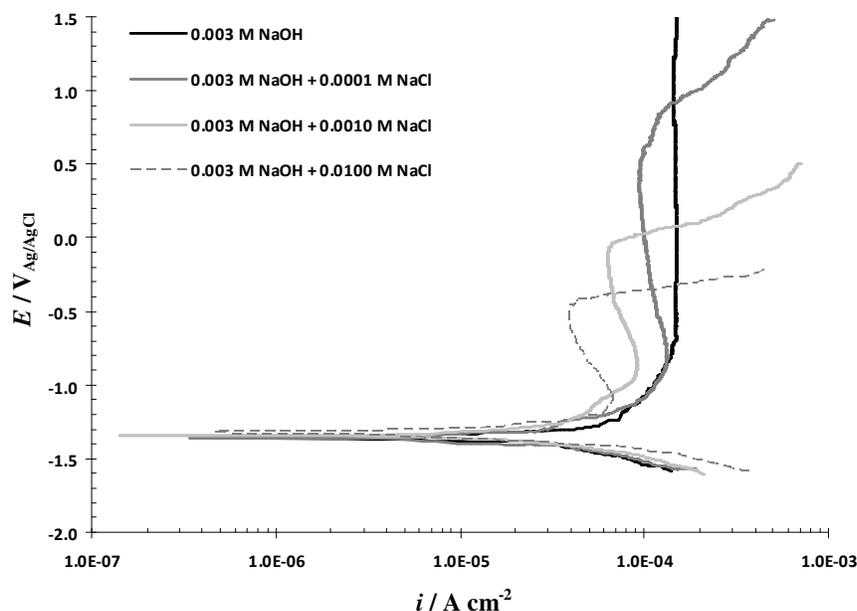


Fig. 2. Effect of chloride ions concentration on the potentiodynamic polarization curve of 6061 Al alloy in 0.003 M NaOH solution

The corrosion current density (i_{corr}) was calculated by Tafel extrapolation of the linear part for the cathodic branch back to the corrosion potential with accuracy of more than 95% for the points more negative to E_{corr} by 50 mV [15]. The variation of the corrosion current density of 1050 and 6061 Al alloys in 0.003 M NaOH solution with and without NaCl addition are illustrated in Fig. 3.

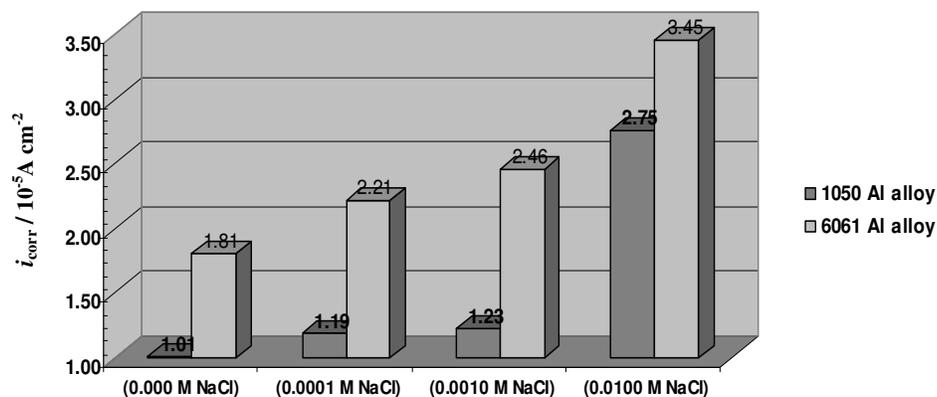


Fig. 3. Variations of the corrosion current density of both Al alloys in 0.003 M NaOH solution with and without NaCl addition

It is observed that the corrosion current density of both alloys increases with increase in the concentration of chloride ions. Also, the variations of the pitting potential of both Al alloys in 0.003 M NaOH solution with NaCl addition are shown in Fig. 4.

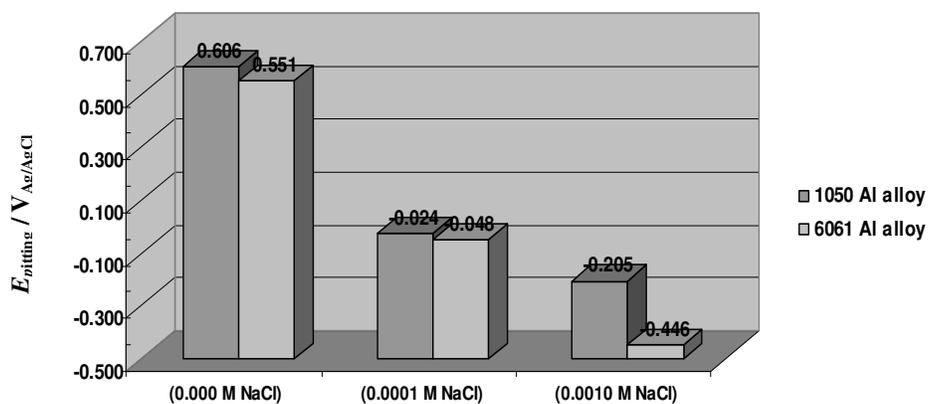


Fig. 4. Effect of chloride ions concentration on the pitting potential of 1050 and 6061 Al alloys in 0.003 M NaOH solution

As can be seen in this Fig. the pitting potential of both alloys increases with increase in the concentration of chloride ions.

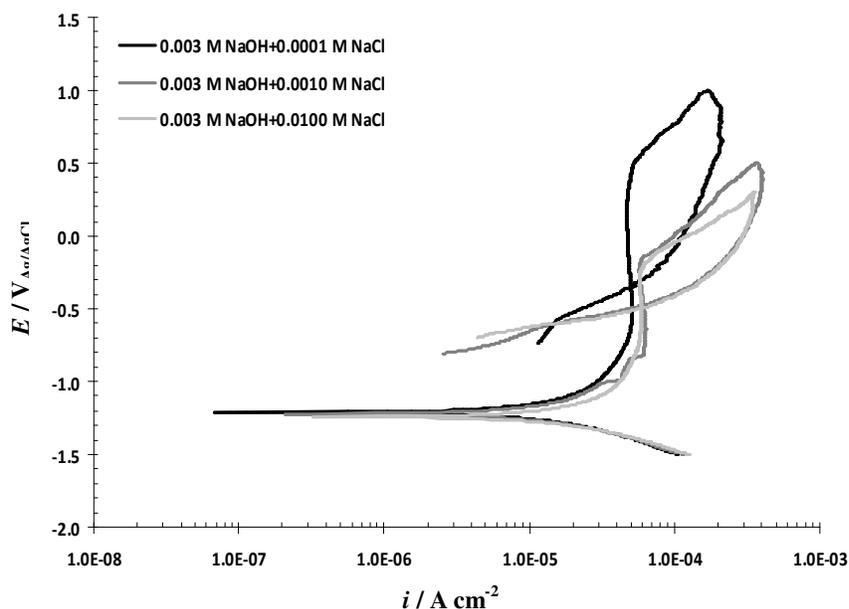


Fig. 5. Effect of chloride ions concentration on the cyclic potentiodynamic polarization curve of 1050 Al alloy in 0.003 M NaOH solution

3.2. Cyclic Potentiodynamic Polarization Measurements

Figs. 5 and 6 show the effect of chloride ions concentration on the cyclic potentiodynamic polarization curve of 1050 and 6061 Al alloys in 0.003 M NaOH solution. For both alloys, positive hysteresis loops is observed. As can be seen in these Figs. the pitting potential of both alloys increases with increase in the concentration of chloride ions.

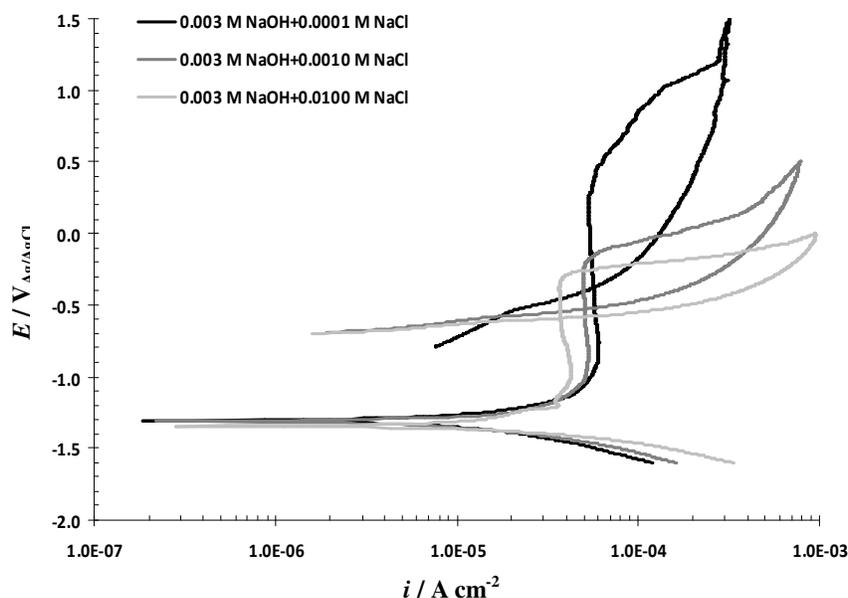


Fig. 6. Effect of chloride ions concentration on the cyclic potentiodynamic polarization curve of 6061 Al alloy in 0.003 M NaOH solution

3.3. Mott–Schottky Analysis

According to the Mott–Schottky analysis, the potential dependence of the space-charge layer capacitance (C_{sc}) given by the following the Mott–Schottky relationships assuming that the capacitance of the Helmholtz layer could be neglected [15,16]:

$$\frac{1}{C_{sc}^2} = \frac{2}{\epsilon\epsilon_0 e N_D} \left(E - E_{FB} - \frac{k_B T}{q} \right) \quad \text{For an n-type semiconductor:} \quad (1)$$

$$\frac{1}{C_{sc}^2} = \frac{-2}{\epsilon\epsilon_0 e N_A} \left(E - E_{FB} - \frac{k_B T}{q} \right) \quad \text{For a p-type semiconductor:} \quad (2)$$

where e is the electron charge, N_D is the donor density (cm^{-3}), N_A is the acceptor density (cm^{-3}), ϵ is the dielectric constant of the passive film ($\epsilon=10$), K_B is the Boltzmann constant, T is the absolute temperature and E_{FB} is the flat band potential. N_D and N_A can be determined

from the slope of the linear relationship between C_{sc}^{-2} and E . The slope is equal to $(\frac{2}{\epsilon\epsilon_0 e N_A})$.

The semiconductor type can be distinguished according to the positive or negative slope (positive slope indicates n-type, whereas the negative indicates p-type) [5,14-16].

Figs. 7 and 8 represents the Mott-Schottky plots for the passive films formed on 1050 and 6061 Al alloys in 0.003 M NaOH solution with and without NaCl addition. All plots show one region (with the positive slope) in which a linear relationship between C^{-2} and E could be observed. Therefore, this analysis demonstrated that the passive films formed on both Al alloys show n-type semiconducting behaviors, where the oxygen vacancies and interstitials (over the cation vacancies) preponderated [5,17-20].

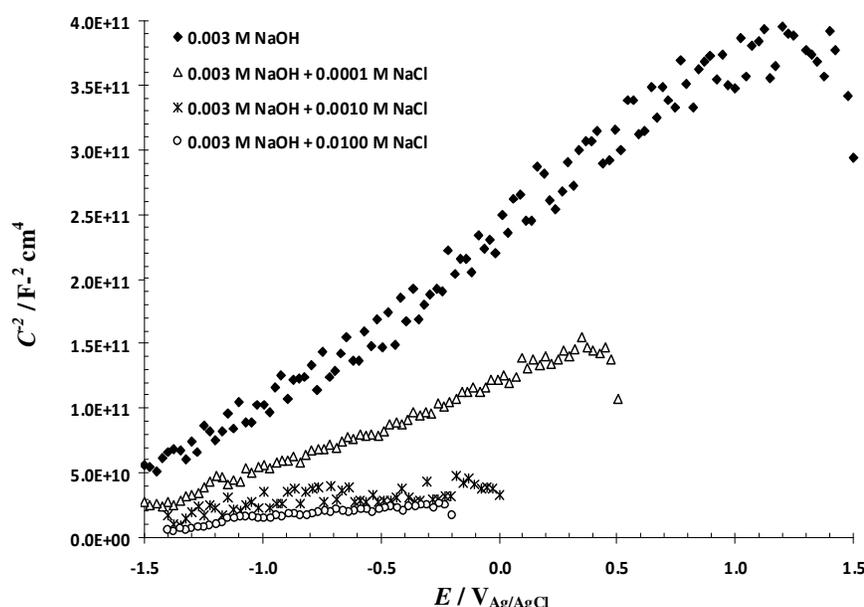


Fig. 7. Mott-Schottky plots of passive film formed on 1050 Al alloy in 0.003 M NaOH solution with and without NaCl addition

For both Al alloys, it should be noted that capacitances clearly increase with chloride ions concentration. The donor density calculated indicates the density close to the alloy/passive film interface, where the concentrations of oxygen vacancies and metal interstitials are predicted to be the highest.

Indeed, according to the point defect model (PDM) [17,18], the flux of oxygen vacancy through the passive film is essential to the film growth process, which supports the existence of oxygen vacancy in the film regardless of its concentration. In this concept, the dominant point defects in the passive film are considered to be oxygen vacancies and/or cation interstitials acting as electron donors [17,18]. Therefore, adsorption and permeation of chloride ions into passive film is usually the first step to cause pitting. It has been

demonstrated that passive film with a higher donor density is always associated with a lower resistance to pitting [16].

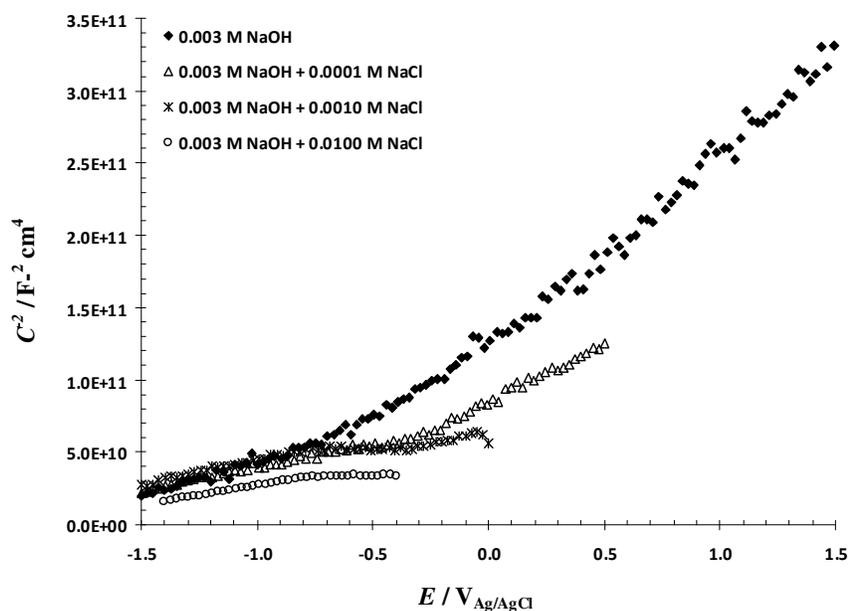


Fig. 8. Mott-Schottky plots of passive film formed on 6061 Al alloy in 0.003 M NaOH solution with and without NaCl addition

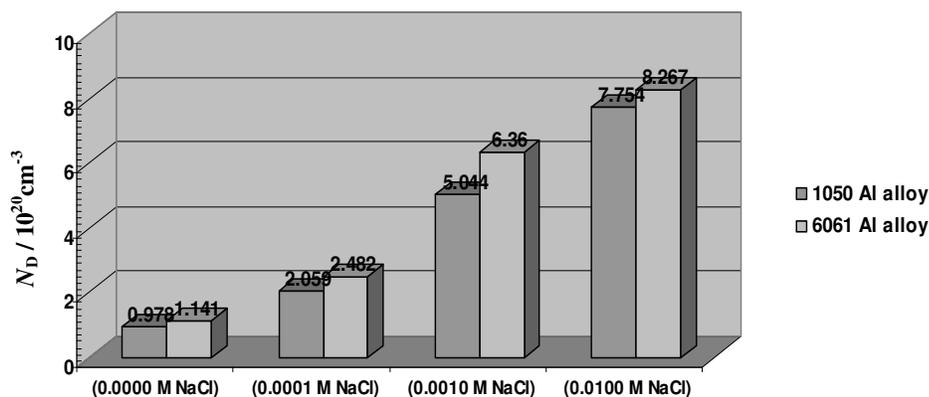


Fig. 9. Variations of the donor density of the passive films formed of 1050 and 6061 Al alloys in 0.003 M NaOH solution with and without NaCl addition

Fig. 9 displays the donor density of the passive films formed on 1050 and 6061 Al alloys in 0.003 M NaOH solution with and without NaCl addition. It could be observed that the donor density increases with increasing chloride ions concentration. The passive film formed

in solution with the highest NaCl concentration has the highest donor density and providing potential sites for chloride ions to occupy. Thus this passive film has the lowest resistance to pitting, as demonstrated by a lowest Epit [14-16]. Indeed, the addition of chloride ions to aqueous solution (0.003 M NaOH solution) increases the incorporation of chloride ions into the passive film by which the additional charge carriers are generated [16].

4. CONCLUSION

Semiconducting behaviors of 1050 and 6061 Al alloys in 0.003 M NaOH solution with and without NaCl addition was studied in the present work. Potentiodynamic and cyclic polarization curves indicated that increasing chloride ions concentration leads to increase the corrosion current density of both 1050 and 6061 Al alloys in 0.003 M NaOH solution. It is observed that the pitting potential of both alloys increases with increase in the concentration of chloride ions.

Mott–Schottky analysis demonstrated that the passive films formed on both Al alloys show n-type semiconducting behaviors, where the oxygen vacancies and interstitials (over the cation vacancies) preponderated. Also, the Mott–Schottky results showed that the donor densities evaluated from the Mott–Schottky plots are in the range of 10^{20} cm^{-3} and increased with increasing chloride ions concentration.

According to the variation of corrosion current density, pitting potential and donor density for both alloys, the passive films formed in chloride-free solution are most stable, and that formed in chloride-containing solution are unstable. Also, based on the variation of corrosion current density, pitting potential and donor density for both alloys, the passive film formed on 1050 Al alloy in 0.003 M NaOH solution with and without NaCl addition is more stable than the passive films formed on 6061 Al alloy.

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