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The Effect of Chloride Ions for Corrosion Resistance of C276 Material in NaCl Solution

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Abstract: Hastealloy-C276 is an austenitic nickel-molybdenum-chromium alloy with small amounts of tungsten added. This material is quite familiar and is used in various industrial components. However, this alloy, like other types, is very susceptible to corrosion due to the influence of chloride ions in solution. The corrosion resistance of steel alloy materials was investigated using electrochemical methods including open circuit potential (OCP), Anodic Potentiodyamic (AP) with and Tafel in NaCl solution media. The test parameters carried out were chloride concentration (0.001 M-1M) and pH (2, 7 and 10) values. The test results show that an increase in chloride ion concentration causes a decrease in the OCP value in a negative direction, which indicates a tendency for decreasing of the corrosion resistance for C276. The AP test results show that the pitting potential (E_{pit}) value slowly decreases as the chloride ion concentration increases up to 1 M. On the other hand, the role of pH is very important in changing the corrosion resistance performance. A decrease in pH to 2 causes an increase in the corrosion rate of the material, whereas an increase in pH causes this decrease.

Keywords: Hastealloy C276, Corrosion, chloride ion, electrochemical, Pitting Potential.

Abstrak: *Hastealloy-C276 merupakan paduan austenitik berbasis nikel-molibdenum-kromium yang ditambahkan sejumlah kecil unsur tungsten. Material ini cukup dikenal dan digunakan dalam berbagai komponen industri. Namun demikian, seperti jenis paduan lainnya, Hastealloy-C276 sangat rentan terhadap korosi akibat pengaruh ion klorida dalam larutan. Ketahanan korosi dari material paduan baja ini dianalisis menggunakan metode elektrokimia, meliputi Open Circuit Potential (OCP), Anodic Potentiodynamic (AP), dan Tafel dalam media larutan NaCl. Parameter pengujian yang digunakan adalah variasi konsentrasi ion klorida (0,001 M–1 M) dan nilai pH (2, 7, dan 10). Hasil pengujian menunjukkan bahwa peningkatan konsentrasi ion klorida menyebabkan penurunan nilai OCP ke arah negatif, yang mengindikasikan kecenderungan penurunan ketahanan korosi pada material C276. Hasil uji AP menunjukkan bahwa nilai pitting potential (Epit) menurun secara bertahap seiring dengan meningkatnya konsentrasi ion klorida hingga 1 M. Di sisi lain, peran pH sangat signifikan dalam memengaruhi performa ketahanan korosi. Penurunan pH hingga 2 menyebabkan peningkatan laju korosi material, sementara peningkatan pH menyebabkan penurunan laju korosi.*

Kata kunci: *Hastealloy C276, Korosi, Ion Klorida, Elektrokimia, Pitting Potential.*

INTRODUCTION

Corrosion is a phenomenon of the process of deterioration on metal surface caused by the surrounding environment electrochemically [1]. The corrosion process leads the conversion of a pure metal to other substances, more stable forms such as sulfides, oxides, hydroxides, and others in corrosive media [2]. Hastelloy-C276 is a nickel-chromium-molybdenum metal alloy with added tungsten elements. The advantage of this alloy is good corrosion resistance in corrosive environments. The high molybdenum content in Hastelloy-C276 material can increase corrosion and oxidation resistances, where the chromium element enhances metal stability and thermal resistance [3]. C276 material has the high corrosion resistance to the sensitization process due to the lower carbon content [4].

Furthermore, the presence of chloride ions is an important factor in metal corrosion in the marine environment. Those ions have a small radius and strong penetration, so they can damage the oxide passivation layer on the metal surface and accelerate the corrosion rate compared to without chloride ion [5]. In addition, the impact of chloride ions (Cl^-) relates to the anodic behavior of metal surfaces. When the chloride anion concentration is low, it has no or little effect on the passive mechanism. The higher chloride concentration leads oscillations in the anodic side oxygen evolution region [6]. For passivated metal alloy materials such as aluminum, stainless steel, nickel alloys and so on, the higher concentrations of chloride anions cause severe destruction to the passivation layer and initiation of pitting corrosion. Chloride ions can be easily adsorbed on the surface of the passive film, resulting in pitting [7]. Effect of chloride ions (Cl^-), pH value, and temperature on pitting corrosion of AIS 304L8 stainless steel [8].

Many researchers have investigated the corrosion properties of hastealloy-C276 materials, which are generally in high temperature salt environments [9]–[12]. Furthermore, investigating the corrosion resistance of hastealloy-C276 material, especially in sodium chloride media at room temperature, is still an interesting topic to be carried out. Therefore, the aim of this research is to determine the corrosion resistance of hastealloy-C276 material by considering the parameters of chloride ion concentration and variations in pH value at room temperature.

METHODS

Sample Preparation

Plate of samples were cut according to electrochemical testing procedures with dimensions of 1 cm x 1 cm. The minimum thickness of the samples to be cut is 1 mm. The sample are connected with a copper wire through a soldering process and molded in epoxy resin which is hardened with a hardener compound. Before the corrosion test was carried out, the test samples that had been mounted were sanded with silicon carbide paper from grit 120 to grit 800, then cleaned with distilled water and stored in a vacuum desiccator.

Electrochemical Test

The specimens were polished with silicon carbide paper up to 1000 grit and then rinsed with aquades water. The test solution is a neutral sodium chloride (NaCl) solution with various concentrations (0.001 M to 1 M), which is prepared with distilled water and high-grade chemical reagents. On the other hand, the pH value parameter is carried out by determining the concentration of NaCl solution at 0.5 M, then the process of reducing the pH value to 2 by adding hydrochloric acid (HCl) solution. The process of increasing the pH value to 10 is carried out by adding sodium hydroxide (NaOH) solution. Furthermore, all prepared specimens and solutions were applied to the following two types of experiments:

1. **Open Circuit Potential (OCP)**

   Open circuit potential, E_{corr} changes were measured against a standard saturated calomel electrode (SCE) placed in the same cell. This type of electrochemical experiment was carried out in a 300 ml round bottom cell using a potentiostat instrument (Gamry Instruments), connected to a computer. Potential changes were monitored using a saturated calomel electrode (SCE) as a reference electrode in accordance with ASTM G3-89. During OCP test, the samples soak up to 3600 seconds. The surface of the working electrode is covered with resin which hardens to show an effective area of 0.6 cm^2. The platinum wire serves as the counter electrode.

2. **Anodic Potentiodynamic (AP)**

   The potential value is measured using a saturated calomel electrode (SCE), thus all potential test values in this work refer to SCE. A platinum wire is installed as a counter electrode, where the working electrode is a hastealloy-C276 test specimen installed in a glass test cell. The anodic potentiodynamic test was carried out using a test solution medium with a volume of 300 mL containing various concentrations of NaCl from 0.001 M to 1 M at room temperature. Before testing begins, the test sample is soaked for 3600 seconds until it reaches a stable OCP value. In this work, the test potential range is between 0 V and 1.8 V where the scan rate is 1 mV/s. Each test is repeated at least 3 times. All tests were carried out in open air and room temperature.

Tafel

All tests of Tafel are the same as AP test which uses three electrodes in the test glass cell. The test solution medium is 0.5M NaCl solution with varying pH values of 2, neutral and pH 10 in open air and room temperature conditions. Before testing, the test sample is soaked for up to 3600 seconds until the OCP value stabilizes. In the Tafel test, the test potential range is between -0.7 V to 1 V to the OCP value, where the scan rate value is 1 mV/s.

RESULT AND DISCUSSION

Open Circuit Potential (OCP)

Open circuit potential (OCP) is a potential value where there is no external current or potential flowing through the test electrochemical cell. Figure 1 shows the OCP value curve as a function of exposure time for Hastealloy-C276 alloy with variations in chloride ion concentration at room temperature and open air conditions. On the basis of results, the tendency of increasing the chloride ion concentration to 1 M changes the OCP value of -220.5 mV (0.001 M) to become more negative at -239.7 mV (1 M). This indicates that the corrosion resistance of Hastelloy-C276 material tends to decrease slightly with increasing chloride ion concentration, which is the same behavior as SS 316L alloy [13]. Furthermore, up to an immersion time of 3600 seconds, the movement of all curves with variations in concentration is in the positive direction, indicating that the passivation process of the metal layer occurs over time1 [14]. Figure 1 denotes that the film depassivation process occurred in 540 seconds (0.001 M NaCl) then repassivated again, where concentrations of more than 0.001 M NaCl depassivated more quickly (300 seconds). Even though all NaCl concentration variants experience depassivation, the passive layer quickly forms again. However, the presence of chloride ion tends to interfere the passivation of material.

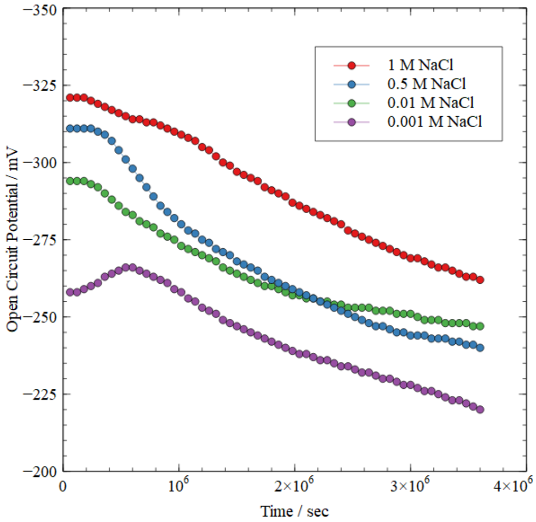

Figure 1. Open Circuit Potential value of Hastelloy C276 material with varying NaCl concentrations

Anodic Potentiodynamic

Figure 2 shows the anodic potentiodynamic curve of Hastealloy-C276 material with variations in chloride ion concentration. The current density value at the X coordinate is a linear value and not a logarithmic value. The current density value is very small at a certain potential value at anodic side, where that value is considered a passive current density. The anodic current density begins to increase rapidly with increasing potential values towards the oxygen evolution region. In Table 1, the pitting potential value (E_{pit}) can be calculated through the extrapolation method of the anodic current density curve which increases to the extreme by drawing a straight line on the curve until it intersects the Y line (intercept value). The sudden increase in current density values is led by the rapid formation of holes towards transpassivity region. Furthermore, the increase of the chloride ion concentration up to 1 M can decrease the E_{pit} value significantly. The phenomena of decrease in E_{pit} with increasing chloride concentration has been investigated in other nickel alloys [15], [16].

Table 1. Linear regression measurements of the anodic potentiodynamic curve for Hastealloy-C276 material

NaCl concentration (M)	Potential pitting/Epit (mV)	Slope vs Ref./A	Correlation coefficient (R)
0.001	959.1	249.4	0.99981
0.01	900.9	111.6	0.9977
0.5	862.1	19.76	0.94898
1	857.4	5.997	0.95343

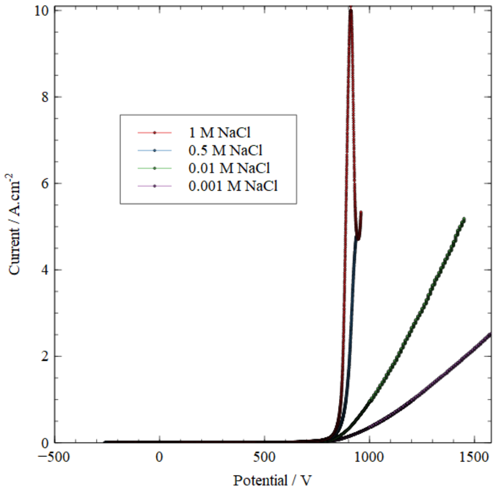

Figure 2. Anodic potentiodynamic curve of Hastealloy-C276 material with variations in chloride ion concentration

Relationship between pH value and corrosion rate

Table 2 shows the parameters of the Tafel plot curve analysis results through varying pH values of 2, 7 and 10 which represent acidic, neutral and alkaline conditions. Both the corrosion current and corrosion rate values increase with decreasing pH value, and vice versa. On the other hand, the increase in the corrosion rate value is close to 1 order. The decrease in the value of corrosion current and corrosion rate occurred as the pH value increased to 10, where the decrease was not significant compared to pH value of 7.

Table 2. Parameters of Tafel plot curve analysis results

pH	Beta A (V/decade)	Beta C (V/decade)	Corrosion Current /I_{corr} (µA)	Corrosion Potential /E_{corr} (mV)	Corrosion Rate (mm/year)
2	1.00E+15	7.76E-02	46.2	-356	3.06E-01
7	1.688	1.97E-01	5.78	-438	3.83E-02
10	1.401	3.00E-01	4.98	-457	3.30E-02

Figure 3 shows the Tafel curve for Hastealloy-C276 material with pH variations at a concentration of 0.5 M NaCl solution. In general, the decrease of pH value of the solution can reduce the cathodic and anodic current densities simultaneously. The range of the anodic passive region shortens as the pH decreases. The metal oxidation process is very dominant in the active or anodic area where the intensity of the process increases as the chloride ion concentration increases. The increase in intensity is marked by an increase in the active current density value which occurs at pH 2, whereas at pH 10 and neutral there is no active current density peak. The transpassive area clearly occurs in a pH 2 environment compared to pH 10 and is neutral where oxygen will come out of the passive layer (oxygen evolution). Oxygen will come out of the passive layer until a transpassive area is formed [17]. The transpassive area is the area where the passive layer dissolution process begins quickly [18]. Furthermore, in all pH ranges from 2 to 10, no fluctuations in passive current density were found in the passive area. The indication of a rapid increase in current density values is due to the formation and growth of stable pitting where the passivation speed of the passive layer is very low compared to the speed of rupture of the passive layer.

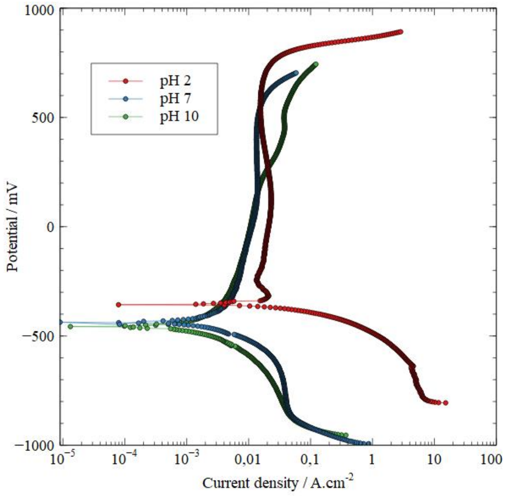

Figure 3. Tafel curve of Hastelloy-C276 material with pH variations at a concentration of 0.5 M NaCl solution

CONCLUSIONS

Present work on the effect of chloride ions on the corrosion resistance of Hastealloy-C276 alloy using electrochemical methods. The research results obtained can be concluded that increasing the concentration of chloride ions can reduce the open circuit potential (OCP), namely this potential value shifts to the active or negative area. The increase of the concentration of chloride ions can increase the current density value. The higher concentration of chloride ions can reduce the pitting potential value and shift it to the active area where a decrease in the E_{pit} value indicates lower pitting corrosion resistance. The reduction of pH value up to 2 can increase the corrosion rate of C276 alloy significantly.

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