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CORROSION BEHAVIOR OF BRASS IN NITRIC ACID

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Preliminary Note – Prethodno priopćenje

This research is a preliminary study of which purpose is to find some information about corrosion behavior of brass casted product in nitric acid. The corrosion rate test was conducted by polarization and Electrochemical Impedance Spectroscopy (EIS). This study was run with the variation of nitric acid of 0,5; 1; 1,5; 2 M. Optical Microscope (OM) were used to explain and to confirm polarization and EIS result. A mechanism for the reactions taking place at the electrode/electrolyte interface was explained.

Key words: corrosion, brass, EIS, nitric acid, polarization

INTRODUCTION

Copper and its compound are mostly used in the cooling system and as a good electric conductor because they have high thermal conductivity [1-2]. Brass is considered as compound copper with Cu and Zn as its main substance. There are more substances in it such as Pb, Sn, Ni, Mn, Al, Cr, P, S, and As which are influential in the addition of equivalent zinc content. Brass is usually used as condenser and heat exchanger [3-4]. Brass is usually made through a casting process. Brass cast products mostly are used as pumping parts, pads**,** gear and etc. The casted stuff usually has a rough surface which makes the corrosion rate higher.

In Indonesia, brass is usually used as art craft and ship propeller. The brass propeller is usually cast by a sand casting method. This product requires finishing to have a smooth surface and accurate dimensions. tools for die casting of brass are exposed to severe mechanical, thermal, and chemical conditions. The performance and quality surface of the die components are limited because of fracture, corrosion, and erosion [5]. The higher thesurface roughness of a material, the corrosion rate increases, causing pitting [6].

Various types of brass respond to corrosion effect in different ways in different environments [7]. Brass is a material which has good corrosion resistant characteristic but is sensitive to some media such as nitric acid and acetate acid. Among the corrosive media, nitric acid is strongly oxidized which causes more corrosion to brass. Corrosion mechanisms in nitric acid are affected by a number of factors, some of which include manufacturing processes, heat transfer, NOx gases, dissolved species, radiation, and solution boiling [8].The corrosion rate is dependent much on the solution concentration. The brass type used in this study was the brass which was produced through the casting process. Therefore, examination the parameter to produce a good brass plate with low surface roughness was concerned in this study.

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METHODS

Brass casting

Metal meltingwas done in a reverberatoryfurnace. Thefurnace is able to meltmetal up to 1000 ^{o}C of melting pointwith 6 to 9 kg of capacity. This process used a metal permanent mold. The process of making brass pattern was done by forming the casted product in shape of the plat with 1 cm thickness, 2 cm length, 1 cm width, and was added anti-drippaintwhich coats the specimen along1,2 cm.

Material

The chemical composition of the brass (in % of weight) which was used was <0, 01% Ag, 1,56 % Al,< 0,01% Cd, <0,01% Co, 0,006% Cr, 57,01% Cu, 0,56% Fe, 0,03% Mg, 0,08%Mn, <0,01 % Mo, 0,35 % Ni, 2,22 % Pb, 0,04 % Sb, 0,96 % Sn, < 0,01 % V, 35,51% Zn. The brass density was known to be 8,4 g/cm^3. The solution used was HNO_3. The solution concentration variant was 0,5; 1; 1,5; 2M. After casting process, the surface of brass was measured by Surface Roughness Tester SJ-210. The average surface roughness was 2,335μm.

Electrochemical measurement

The electrochemical measurement which was done in the study was polarization techniques and Electrochemical Impedance Spectroscopy (EIS). These techniques are very useful in the investigation of electrochemical processes occurring at the alloy/electrolyte

interface. Electrochemical measurements were performed through the electrochemical system on a conventional three-electrode cell where a brass specimen was used as working electrode, a platinum as an auxiliary electrode (AE), and Ag/AgCl (KCl 3 M) as the reference electrode (RE). The electrochemical test was run using the tool of Autolab PGSTAT 128N. Standart ASTM (American Standart and Testing) G31-72 was the standard used in this study [9]. One batch contained HNO_3 solution of 0,5; 1; 1,5; 2M. The three electrodes were soaked in batch for 1 hour. The polarization measurement at the change of -1 V to +1 V along the corrosion potential (OCP) with a scan rate of 0,001V/s.

EIS Measurement was conducted in the range frequency 10^4– 1 Hz. An excitation amplitude of 10 mV peak to peak was used. The impedance values were plotted on the Nyquist plot. All measurements were carried out at a constant room temperature of 298K.

RESULTS AND DISCUSSION

Polarization studies

The polarization curves obtained were extrapolated to calculate corrosion parameters such as I_{corr}, E_{corr}, βa,and βc [10]. The results of extrapolation of Tafel plots shown in Table 1.

Table 1 **The Corrosion Rate Measurement with Polarization Method**

Concentration HNO_3/M	Ba/ V/dec	Bc/ V/dec	E_{corr}/ V	I_{corr}/ μAcm^{-2}	CR/ mm/year
0,5	0,128	0,110	0,059	92,14	1,381
1	0,203	0,154	0,049	598,24	8,971
1,5	0,229	0,089	0,036	301,94	4,528
2	0,0884	0,077	0,028	237,82	3,566

Typical Tafel polarization of brass in variousHNO_3concentrationis presented in Figure 1. It was clear that the brass was relatively more corrosion resistant in 0,5 M HNO_3. The highest corrosion rate occurs in 1M HNO_3 solution. Polarization measurements do not show

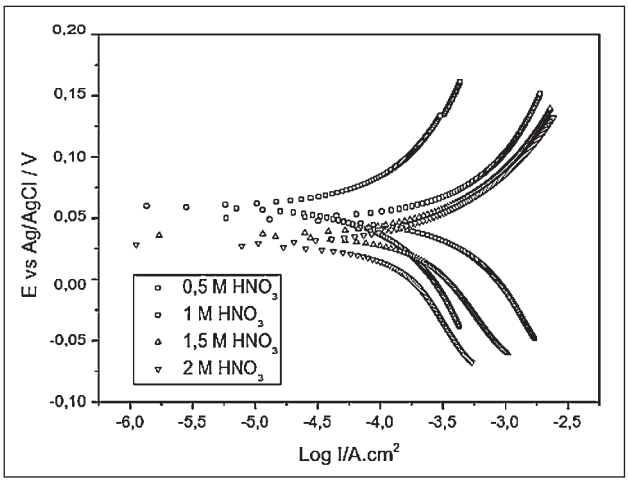

Figure 1 Tafel plots of brass polarization in HNO_3 concentration variant

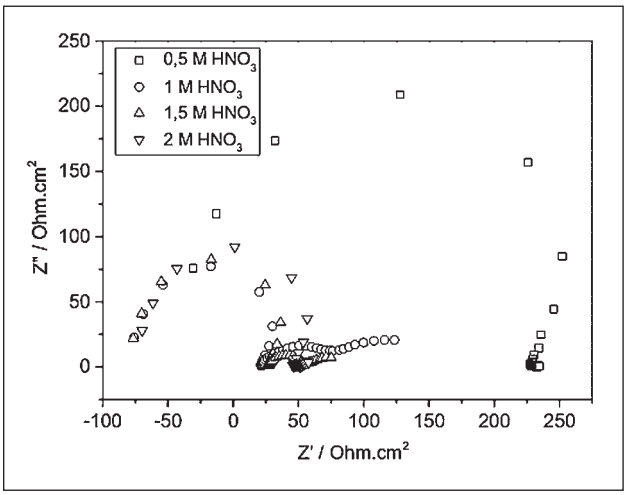

Figure 2 Nyquist plots of brass in HNO_3 concentration variant

that the more concentrated HNO3, the higher the corrosion rate. In low and high concentration solutions (0,5 and 2 M), the brass is less aggressive in terms of lower corrosion reactions. This is due to the vulnerability of corrosion to certain environments. Thus, it shows a reflection of the low acid concentration used comparatively. In the more concentrated acids (2M) decreases the oxidizing power thereby decreasing the electrode resistance to the corrosion reaction [7].

EIS studies

Table 2 **Electrochemical impedance parameters for corrosion brass in different concentration of HNO_3**

HNO_3/ M	Rs/ Ω	R1/ Ω	CPE1/ μF	R2/ Ω	CPE2/ μF
0,5 M	-4,2731	235,54	1,94919	3,0786	335,55
1 M	-66,544	89,032	5,2106	67,863	1303,2
1,5 M	-59,137	107,34	4,2579	8,3896	0,271
2 M	-67,11	95,398	4,9725	34,636	323,76

EIS measurements were in good agreement with the polarization techniques. Figure 2 presents Nyquist plots of the brass specimens in different HNO_3concentration. The semicircles of the Nyquist plots indicate the characteristic of roughness and inhomogeneity electrode surface [11]. Impedance data of the brass alloys were fitted to an equivalent-circuit model consisting of a parallel combination of two capacitors representing the electrode capacitance (CPE) and resistors representing small resistor (R_1 and R_2) in series with a solution resistance (Rs) representing the ohmdrop in the electrolyte (Figure 3).The electrochemical corrosion reaction behavior in low concentration is difficult to explain. In low concentration, caused dissociation of the $NO3^-$easier to initiate corrosion attack on the surface of brass [7]. The effect of nitrate ion is known to accelerate corrosion of brass at low acid concentration [12]. The ion adsorption of Zn of brass increased corrosion and the adsorption of Cu leads to inhibited corrosion rate. This makes the specific behavior of brass [7].

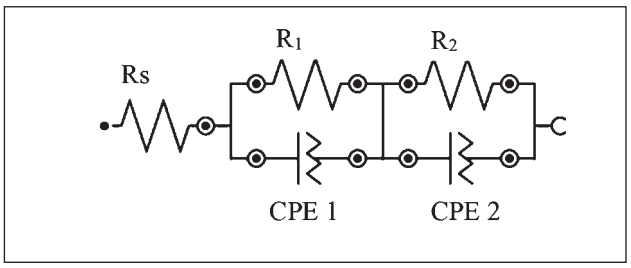

Figure 3 Equivalent electrical circuits of the experimental electrochemical impedance data

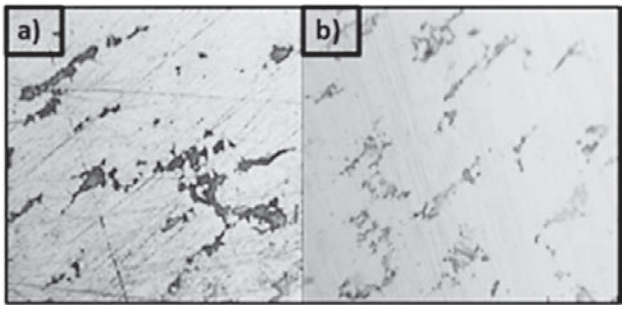

Figure 4 OM images of brass a) 1M HNO_3 solution, b) 0,5 M HNO_3 solution in 200 x zoom.

The corrosion mechanism clearly was that of the anodic dissolution of the tested metal alloys by the strong nitric acid solution used. This is because the hydrogen content got higher which made the brass oxidized. The dissolution anodic characteristic of the brass and nitrate acid is very complex. Generally, the anodic reaction for copper is considered to be as follows: [1, 13-15]:

$$Cu \rightarrow Cu(I)_{ads} + e- \text{ (fast)} \quad (1)$$

$$Cu(I)_{ads} \rightarrow Cu(II) + e- \text{ (slow)} \quad (2)$$

Where $Cu(I)_{ads}$are the specimen which is absorbed into the copper surface and not diffused into the solution. In another side, there is adsorption subtraction of copper ion Cu (II) on the surface because of some Zn. Thus, there was dissolution anodicof Zn based on the following equation [1]:

$$Zn \rightarrow Zn^{2+} + 2e- \quad (3)$$

There is no cathodic reaction in hydrogen evolution reaction because of corrosion potential in all HNO_3solution concentration variants on redox potential of hydrogen evolution [1]. The mechanism of cathodic reaction which may happen such as in the following equation [16]:

$$NO_3^- + 4H^+ + 3e- \rightarrow NO + 2H_2O \quad (4)$$

Besides that, there was oxygen loss in the acid media caused by the cathodic reaction. Based on equation (3.4) on the cathodic side, there is ion NO_3^-. Surface roughness gives rises to metal dissolution and also proposed cathodic reaction an area without coverage [1].

In this study, the brass used was produced through casting process and permanent molding. The permanent mold casting brass surface is relatively smooth compared to the brass from sand casting. However, finishing process or polishing or any surface treatment is needed to smoothen the surface.This is done to minimize the corrosion especially if the metal is in a corrosive environment.

The rough surface enables the micro reaction to happen which prompts the corrosive environment to produce corrosion on a rough surface and produces holes [17-19]. Smooth surface reduces the metastable holes production [20]. The rough surface has wider space between surfacesina corrosive environment which makes the surface roughness increases and increases the corrosion rate [17]. The metal surface roughness affects the corrosion potential which increases the holes forming on the metal surface [20]. The roughness on brass casted product surface also triggers the increase in corrosion rate.

Surface Analysis

The surface image of brass in 1 HNO_3 solution is shown in Fig 4a. Several black spotsappears on the surface of brass. The highest corrosion rate occurs in 1M HNO_3 solution. The surfacewas strongly damaged due to some pits which are the corrosion product. Figure 4b) shown the OM images of brass in 0.5HNO_3. The surface of brass in 0.5 HNO_3 looked brighter than in 1 M HNO_3 solution. Surface analysis by OM was in good agreement with the polarizationand EIS techniques.

CONCLUSION

The corrosion rate value of polarization and EIS method have the same trend The corrosion mechanism clearly was that of the anodic dissolution of the brass by the strong nitric acid solution used. The corrosion rate is also triggered by the surface roughness of non-finishing brass casted product surface.

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Note: The responsible translator for the English language is Ely Pratiwi – English-speaking translator at Bali, Indonesia