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CORROSION CHARACTERIZATION OF CU-BASED ALLOY IN DIFFERENT ENVIRONMENT

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Preliminary Note – Prethodno priopćenje

Corrosion behavior of copper as alloy base material had been investigated electrochemically in three different solutions. Solution of 1 M HNO_3, 3,5 % NaCl and 1M NaOH had been used as the corrosive medias for Cu alloys and Electrochemical Impedance Spectroscopy (EIS) method was used to study its corrosive characteristics. The result of the study revealed that bronze had corrosion resistance average which was higher compared to brass and copper in corrosive media of 1M HNO_3, 3,5 % NaCl and 1M NaOH. The most aggressive corrosive media attacked Cu and its alloys starting from 1M NaOH, HNO_3 and 3,5% NaCl.

Key words: corrosion, Cu alloys, HNO_3, NaCl, NaOH

INTRODUCTION

Copper is resistant to atmosphere influence and any chemical compound [1]. Copper and copper-based alloys (brass and bronze) form the big group of important construction material for outdoor application because of its interesting visual performance, required physical and mechanical characteristics and its resistance towards atmospheric corrosion [2]. Bronze is copper based alloy with lead (Cu-Sn). It possesses strength and good toughness and resistance to corrosion. Besides bronze, brass is also copper-based. Copper is mostly used in outer interior of buildings because of its good mechanical characteristics, corrosion resistance and electricconductivity which makes it the most important material in any industry field [3]. The copper material which is used in any industry field is always exposed to different environment, such as copper condenser pipe in a high temperature environment, sea water, etc. [4]. Even though they has high corrosion resistance in atmospheric condition, copper and the alloys are easy to give dissolution reaction in acidic or base environment [5,6].

The most identified compounds in material or structure which are indoor and outdoor bronze-based are polimorf and cuprite $Cu2(OH)_3Cl$. Because chloride compound is the most dangerous for copper-based structure, big attention is focused on characterization of copper and its special alloys, especially on polimorf identification $Cu_2(OH)_3Cl$ [7]. This study was aimed at investigating the corrosion behavior of Cu and the alloys (bronze and brass) in different corrosive medias which were 1M HNO_3, 3,5% NaCl and 1M NaOH. This study is very important because it is relevant with the condition of application of copper and the alloys in Indonesia.

METHODS

Material

Copper plate, brass and bronze with thickness of 0,4 cm, length of 5 cm, width of 1 cm and applied with nodrop covered the specimen with the length of 4 cm, so that the specimen corroded.

The chemical composition of the copper sample (wt.%) was: 0,007Si, 0,04 Ni, 0,06Fe, 0,006 Zn, 0,05Pb, 0,06 Sn, 0,01 S, 0,003 Bi and 99,701Cu. The copper density used in the study was 8,96 g/cm^3. The chemical composition of brass sample of corrosion test. The chemical composition of brass was (wt.%) 1,56 Al, 0,009 Co, 0,009 Ag, 0,006 Cr, 0,009 Cd, 0,03 Mg, 0,03Mn, 2,22Pb, 0,009 Mo, 0,35 Ni, 0,04 Sb, 0,009 V, 0,96 Sn, 35,51 Zn, 57,01 Cu. The brass density was 8,4 g/cm^3. The chemical composition of bronze (wt.%) was 99,1 Cu, 0,35 Sn, 0,01 Zn, 0,45 Ni, 0,09 Si The bronze density was 8,5 g/cm^3.

Three kinds of acid solution/aggressive corrosive media were prepared with analytic content dilution of 1M HNO_3, 1M NaOH, 3,5 % NaCl with aquades.

Electrochemical Measurements

The corrosion measurement of EIS method was performed by using AUTOLAB PG 128N, Software NOVA 11.1 was used to scan electrochemical impedance spectroscopy (EIS). The polarization measurement was performed at change of -1V to +1 V during corrosion potential (OCP) with scan rate of 0,001 v/s. The EIS measurement was conducted at the frequency range of 104 Hz - 1 Hz. The excitation amplitude of 10 mV from

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peak to peak was used. The impedance value was plotted at Nyquist plot.

RESULTS AND ANALYSIS

The potentiodynamic polarization test

Figure 1 explains the anodic and cathodic polarization curves of copper and the alloys in different corrosive medias 1M (HNO_3, 3,5 % NaCl and 1M NaOH). In Figures 1a, b and c, it is seen that anodic and cathodic position of copper and the alloys in 1M HNO_3 solution is the highest and in 3,5 % NaCl solution is the lowest.

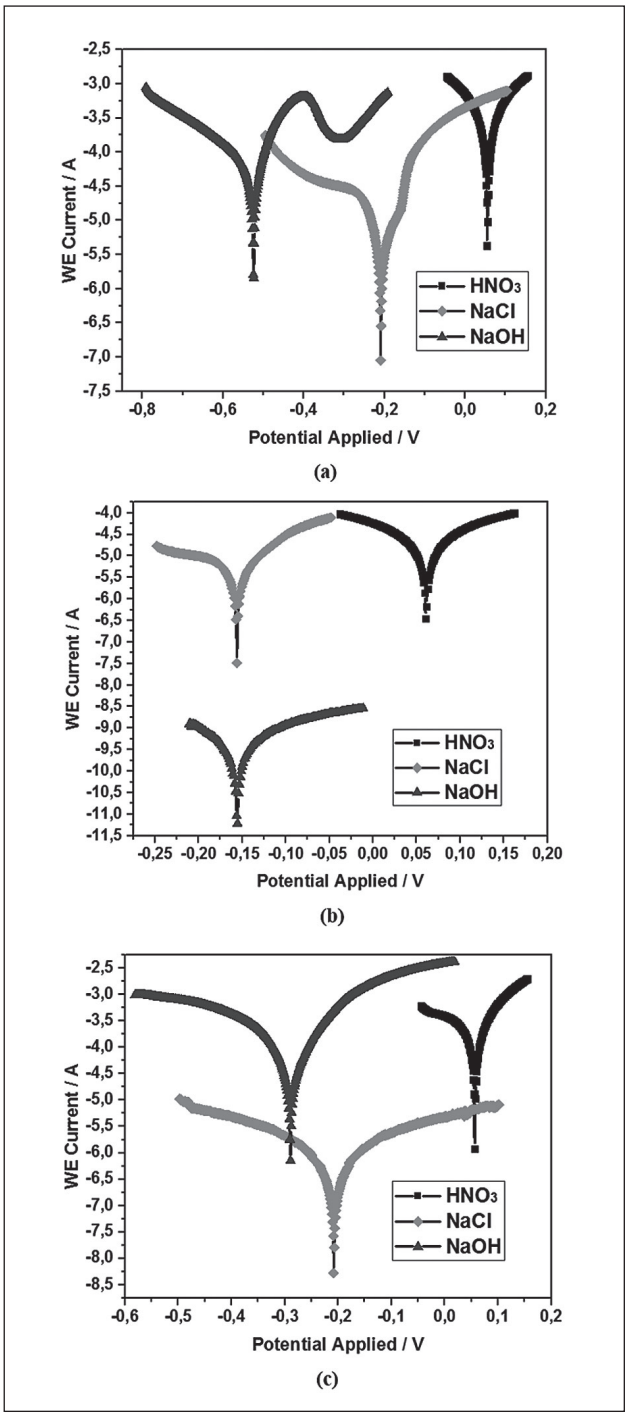

Figure 1 The polarization curve of Tafel anodic and cathodic; (a) brass, (b) bronze and (c)copper in corrosive media of HNO_3, NaCl and NaOH.

This means that HNO_3 solution has the most aggressive characteristics which attacks the material and causes the highest corrosion rate of copper and its alloys. This is aligned with what has been stated by Khaled that the shift from zero point to the right on cathodic curve explains that the corrosion rate is mostly accelerated by cathode reaction [8]. HNO_3 solution is a strong oxidator of copper and the alloys which is able to attack copper faster than NaCl and NaOH solution. From the extrapolarizationTafel in Figure 1, it can be seen corrosion parameters like in Table 1.

Table 1 **Polarization potentiodynamic parameters**

Material	Media	ba/V/dec	bc/V/dec	Ecorr/V	Icorr/A	Corrosion rate/mm/year
Brass	HNO3	0,18263	0,1655	0,0545	0,0005043	7,5623
	NaCl 3,5%	0,18118	-0,8029	-0,208	3,58E-05	0,53683
	NaOH 1 M	1,2347	0,1218	-0,522	0,0001383	2,0735
Bronze	HNO3	0,28892	0,2716	0,0608	5,83E-05	0,87426
	NaCl 3,5%	1,475	0,2251	-0,156	2,89E-05	0,43265
	NaOH 1 M	0,06902	0,0616	-0,156	3,00E-10	3,49E-06
Copper	HNO3	-1,299	0,159	0,0563	0,0008868	13,298
	NaCl 3,5%	0,23332	0,2181	-0,207	9,79E-07	0,014681
	NaOH 1 M	0,0607	0,0623	-0,289	3,26E-05	0,48895

Where βa is Anodic tafel slopes, V/dec, βc is Cathodic tafel slopes, V/dec, Ecorr is Corrosion potential, V. Figure 1 and Table 1 show that all alloys are Cu-based and they are not resistant to corrosion in 1M HNO_3 environment. With the addition of Zn (in brass) and Sn (in bronze) and another elements in Cu-based alloys, the corrosion rate decreases. The Tafel plot of brass and bronze seems to get more anodic. The highest corrosion rate of brass and bronze is in HNO_3 media [9].

Corrosion rate on pure copper is higher compared to on Cu alloys (bronze and brass). Bronze has the lowest corrosion rate in any environment. This because there is an addition of lead which is quite high in the alloys composition. In NaCl environment (sea water) it is possible that there is protecting layer formed in form of lead oxidation [10]. On bronze, the corrosion rate is higher than on bronze because Zinc tends to be easier to corrode in corrosive environment. On brass in chlorideenvironment, when ionization/sediment produces Cu-sponge metal, the neutral chloride solution creates some additional surface layer which contains zinc oxide and copper [11].

The result of Nyquist Plot of the test sample of copper, brass and bronze in corrosive medias of HNO_3, NaCl and NaOH. In Figure 1, it is seen that copper has more ordered Nyquistplot which forms half circle pattern. From half circle diameter of the three samples, sample in 3,5 % NaCl has bigger diameter. This indi-

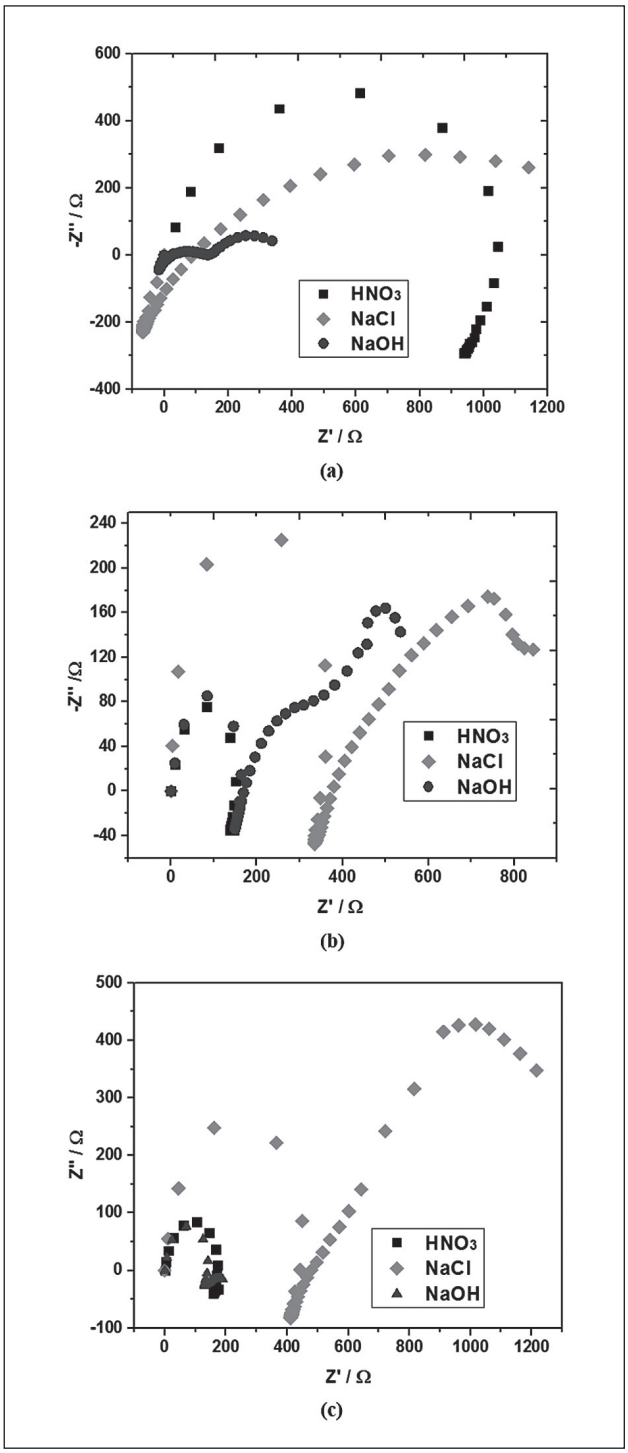

Figure 2 Nyquist plot for (a). Bronze, (b). Brass and (c). Copper in corrosive medias of HNO_3, NaCl and NaOH.

cates that corrosion rate caused by 3,5 % NaCl solution is not too aggressive or charge transfer resistance is bigger than the solution of 1M HNO_3 and 1M NaOH [12]. Tables 2-4 are the values of some corrosion parameters of EIS method of copper alloys in any corrosive solutions where higher value of charge transfer resistance means lower copper alloys electron release. Copper metal in 1M NaOH solution has lowest transfer resistance value (Rp) and bronze in 3,5 % NaCl has highest transfer resistance value which are 117,150 Ω and 1954,450 Ω, respectively.

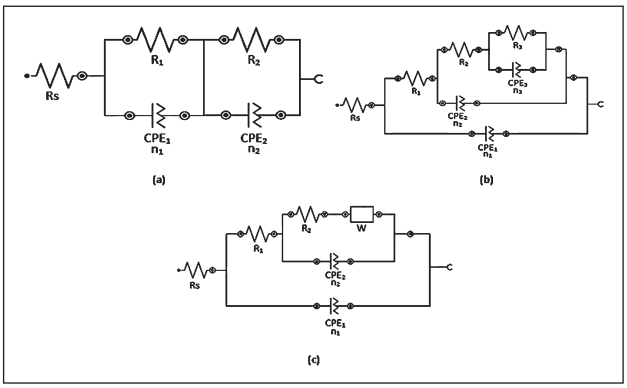

Figure 3 Equivalent electrical circuit of electrochemical impedance data measurement of copper alloys; (a) brass, (b)bronze and (c) copper.

Figure 2 displays the Nyquist plot of brass specimen in some different corrosive medias, where the Nyquist plot graph forms half circle showing that there is characteristics of roughness and non homogeneity on electrode surface [13]. Generally, the impedance loop of measurement result encounters half circle. This phenomenon is known as the effect of electron dissolution [8]. The value of impedance of the sample in 1M NaOH solution is the lowest and the value of impedance of the copper alloys in 3,5% NaCl is the highest. This shows from the three types of solution, 1M NaOH is the most aggressive which attacks copper alloys [4].

Figure 3 about equivalent electric circuit of data measurement of electrochemical impedance of copper alloys, constant phase element, it can be seen that CPE have been widely used to explain distortion caused by surface roughness. Rough electrode in resistance condition towards corrosion does not have perfect capacitive response [8]. CPE can explain unideal dielectric characteristic of electrode surface [4].

From Tables 2, 3, and 4, it is seen that the value of R in 3,5 % NaClof bronze material has the highest charge transfer resistance than the materials in the other solutions. This shows that the protecting passive film formed in corrosive solution is stronger. Tables 2, 3, and 4 show that brass in three corrosive solutions (HNO_3 1 M, 3,5 % NaClandNaOH 1 M) has value with average of 1.1 showing that there is weak conductivity passive film on the electrode (brass) surface. Copper and bronze in three corrosive medias have the value of n of 0-1,1. This indicates that there are pores/roughness with corrosion holes on the surface of copper and bronze (electrode) [6].

Table 2 **Parameters of electrochemical as the result of brass EIS measurement**

Material	Media	R_s/Ω	R_1/Ω	CPE_1/ nMho	N_1	R_2	CPE_1/ nMho	N_2
Brass	1M HNO_3	-74,7	75,7	1,28	1,1	75,7	1,28	1,1
	3,5 % NaCl	-73,1	84,1	1,28	1,1	84,1	1,28	1,1
	1M NaOH	-69	192	883	1,1	192	883	1,1

Table 3 **Parameters of electrochemical as the result of bronze EIS measurement**

Material	Media	R_s/Ω	R_1/Ω	CPE_1/ nMho	N_1	R_2/Ω	CPE_2/ nMho	N_2	R_3/Ω	CPE_3/ nMho	N_3
Bronze	1M HNO_3	-650	-1,1	404	0,06	-1,1	110	0	-1,1	110	0
	3,5 % NaCl	1,31	743	112	0,81	1005	295	0,59	209	6,77	0,97
	1M NaOH	278	766	1,17	0,4	310	2,95	0,05	-469	1,97	0

Table 4 **Parameters of electrochemical as the result of copper EIS measurement**

Material	Media	R_s/Ω	R_1/Ω	CPE_1/ nMho	N_1	R_2/Ω	CPE_2/ nMho	N_2	W/ TMho
Copper	1M HNO_3	-78,9	-1,10	3,54	0,06	-1,10	110	0	1,10
	3,5 % NaCl	-82,8	798	2,28	1,01	-652	1,58	1,1	58,2
	1M NaOH	-57,7	349	317	1,1	74,6	392	0	1,98

CONCLUSION

The results of corrosion test on copper, brass and bronze with EIS method in three corrosive medias show that NaOH 1 M (base oxide) produces the highest corrosion activity, followed by HNO3 (nitrate acid) and base/acid NaCl. In general form, the corrosion rate from the highest to the lowest of the three material (copper, bronze and brass) in corrosive solution is NaOH 1 M > HNO3 1 M >3,5 % NaCl.

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