Corrosion of copper alloys in KOH, NaOH, NaCl, and HCl electrolyte solutions and its impact to the mechanical properties

Ida Hamidah\textsuperscript{a}, Agus Solehudin\textsuperscript{a}, Aam Hamdani\textsuperscript{a}, Lilik Hasanah\textsuperscript{a}, Khairurrijal Khairurrijal\textsuperscript{b}, Tedi Kurniawan\textsuperscript{c}, Rizalman Mamat\textsuperscript{d}, Rina Maryanti\textsuperscript{a}, Asep Bayu Dani Nandiyanto\textsuperscript{a}, Belkheir Hammouti\textsuperscript{e}

\textsuperscript{a} Universitas Pendidikan Indonesia, Jl. Dr. Setiabudi no 229, Bandung 40154, Indonesia \\
\textsuperscript{b} Institut Teknologi Bandung, Jl. Ganesha no. 10, Bandung 40132, Indonesia \\
\textsuperscript{c} Community College of Qatar, Ad Dawhah, Doha, Qatar \\
\textsuperscript{d} Universiti Malaysia Pahang, Darul Makmur, 26600 Pekan, Malaysia \\
\textsuperscript{e} LCAE, Faculty of Science, University of Mohammed Premier Oujda, B.P. 4808, 60046 Oujda, Morocco

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Abstract Effects of electrolyte solution (i.e., KOH, NaOH, NaCl, and HCl) with various concentrations (from 0 to 0.71 M) on corrosion and mechanical properties of the copper alloys were investigated. Experimental results showed that the increases in the concentration of electrolytes allowed faster corrosion process. However, too high concentration of electrolytes has no further impacts on the corrosion profile due to the existence of the passivity phenomena on the surface of the material, preventing the material to get more corroded. Acidic (HCl) and salt (NaCl) electrolytes gave more impacts on the corrosion compared to the alkaline solution (i.e., NaOH and KOH) since the acidic and salt ions are able to destroy the formed passivation layer. The correlation of the corrosion rate and the mechanical properties was also presented, in which the increases in the corrosion rate were in line with the decreases in the mechanical properties (i.e., tensile and yield strength). During the corrosion, the atomic structure in the material received attacks from the electrolyte ions, making the structure inside the copper alloys to be less strong and easily fatigued. Understanding the corrosion process and mechanical properties is important for further applications of copper-related alloys in extreme and severe conditions.

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E-mail address: nandiyanto@upi.edu (A.B.D. Nandiyanto)

1. Introduction

Copper in its pure and alloyed components has been widely used in industries since it has excellent corrosion resistance,
high electrical conductivity, tensile strength, wear resistance, and attractive visual appearance (by varying alloying elements) [1]. Copper and its alloys are used in various uses from the electronic devices, the electrical wire, to the components in the transportation system.

The successful synthesis, characterizations, and application of copper-related components have been reported and well-documented [2,3]. However, researches on explaining in detail about the corrosion properties of copper and its alloys in electrolyte solutions are limited. In fact, this becomes one of the most important parameters in the material [4–6]. It relates to the long-term usage of material and it is a function of relative humidity, chloride ion activity, oxygen content, and the existence of trace metal on the corrosion rate of copper and its alloys [7]. In fact, copper and its alloys have been used for the application in extreme and severe conditions such as acidic and alkaline solutions [8,9].

Although many literature related to corrosion of copper alloys have been reported [10–14], they concerned on the corrosion only from various parameters. The impact of the corrosion itself on other properties of material such as mechanical properties was not reported yet. In fact, this information is important for further developments and applications of copper alloys.

Here, the objective of this study was to investigate corrosion and mechanical properties of copper alloys in various electrolyte solutions. Different from other reports that considered only on the corrosion rate, this study covered the effect of electrolytes on the corrosion and mechanical properties of the copper alloys. This becomes the main novelty in this study since the corrosion phenomena can change the atomic structure in the material that can alter other properties in the material.

Experiments were done by testing and dipping copper alloys on several electrolyte solutions (i.e., alkaline, salt, and acid solutions) with various concentrations (from 0 to 0.71 M). The corrosion test were done in solution containing hydrochloric acid (HCl) (as a model of acid electrolyte), sodium chloride (NaCl) (as a model of salt electrolyte), as well as sodium hydroxide (NaOH) and potassium hydroxide (KOH) (as models of basic electrolytes). To make sure the corrosion phenomena, two types of basic electrolytes were used. Although several types of copper alloys have been used [15–17] and are available in the market, this study used C70600 type (processed alloy) as a model of copper alloys since this type of copper has been well-known to be used in sea water.

To confirm the analysis of corrosion and mechanical properties of copper alloys, several characterizations were conducted, including electron microscope, elemental analysis (using energy dispersive X-ray spectroscopy (EDS) and Fourier transform infrared (FTIR; FTIR-4600, Jasco Corp., Japan)), weight loss measurements, as well as tensile (using electromechanical universal testing machine (EUTM) (Multi Ensayo Test Resources Ltd., USA)) and yield tests (Impact 300 (Galdabini Ltd., Italy)). Regarding the weight loss measurement, this study used the method according to ASTM G31 standard procedure, which was to determine the corrosion rate using following equation (1):

\[ CR = \frac{534 \times W}{D \times A \times t} \]

where \( CR \) is the rate of corrosion (mpy), \( W \) is the mass change (mg), \( D \) is the density of specimen (g/cm³), \( A \) is the surface area of specimen (in²), and \( t \) is the exposure time (h). Detailed information for the weight loss measurement is reported in our previous studies [18,19].

In addition, to ensure the precise measurements, all data were taken at least three times. Then, these data were then plotted to get curve.

3. Results and discussion

3.1. Physicochemical properties of specimen before and after the corrosion test

Fig. 2 shows the photograph images of specimen before and after the corrosion process. Initial specimen had red-brown color. Putting into the electrolyte solution, the color of speci-
men changed into dark color. The main reason for the change in color is due to the change in pH and potential that can cause corrosion phenomenon.

To confirm the visual observations in Fig. 2a, Fig. 3 depicts the SEM images of copper alloys specimens after corrosion test using 0.63 M solution of electrolytes. Fig. 3(a), (b), (c), and (d) are the SEM images of specimens under HCl, NaCl, NaOH, and KOH, respectively. As shown in the SEM analysis images, some cracks were observed clearly (as black area). To confirm the elemental composition of the corroded specimens, the EDS analysis on the pitting area (see red area in Fig. 3) was conducted. The results of EDS are presented in Table 1. In addition, the corrosion rate referred in this paper is not uniform corrosion but pitting corrosion. The corrosion rate was based on the weight loss calculation before and after immersion in the electrolyte solution.
Table 1 presents changes in the elemental compositions of corrosion product. The initial specimen contained majorly copper and oxygen, while some small amounts of elements were also identified such as silicon and iron, in which this is in line with the commercially available C70600 elemental composition [20]. Carbon was also detected in the measurement, however it should be from the impurities that can be neglected (since the copper alloys themselves must have no high amount of carbon component).

When analyzing corroded component in the corroded specimen, different elemental compositions were detected. The corroded component (see red area in Fig. 3) contained mostly copper and oxygen, informing that the main rust is copper oxide. The results of the analysis in Table 1 can be explained in the following:

(i) The interesting phenomena are the oxygen composition. Initial oxygen component existed due to the passivation layer in the originating specimen. The composition of oxygen decreased when applying corrosion test, informing the electrolytes attack and destroy the passivation layer. The composition of specimen corroded by basic electrolyte solution was almost the same, informing the healing and regeneration of passivation oxide layer on the specimen. The lowest composition of oxygen was found for specimen corroded with acid (HCl) and salt (NaCl), informing the destruction and less regeneration of passivation layer.

(ii) The composition of Cu element changes. The decreases in the oxygen elemental composition makes the composition calculation of Cu element higher.

(iii) Other interesting phenomena are the decreases in the elemental composition of iron, reaching one-tenth of its originated value. This indicates the corrosion process attacks severely on the iron element.

(iv) The composition of silica can be classified as almost identical. Since silica is relatively inert against pH condition.

FTIR analysis of the specimen corroded by electrolytes is presented in Fig. 4. FTIR peaks and patterns of initial specimen and dipped specimen on the alkaline solution are identical, informing the outer surface of specimen contained similar chemical structure. The initial specimen (prior to immersed into electrolyte solution) contains CuO layer, in which this is found in the copper alloys in alkaline solution. The higher intensities of peaks in the wavenumber of between 1400 and 1900, about 2300, and between 3500 and 400 cm⁻¹ correspondence to the carbon-related intensities [21]. These peaks decreased when specimen were dipped into electrolyte solutions, in which these are in a good agreement with the removal carbon element in the EDS analysis in Table 1. When specimen was dipped into either salt or acidic solution, changes in the FTIR peaks and patterns were identified (compared to the originated copper alloy specimen), informing the medication of the chemical structure on the surface of specimen, in which this is in line with the EDS analysis in Table 1. Most of the components in the HCl- and NaCl-dipped specimens are copper component, replying that these types of electrolytes destroyed the formation of passive CuO layer on the surface of specimen and convert metal elements into metal ions (i.e. Cu²⁺, Cu⁺, Fe²⁺, etc).

Based on the above analyses, the elemental compositions in the specimen changed during the corrosion process. The corrosion process converts copper metal into copper ions and copper oxide (CuO). Copper oxide is formed as a passive layer on the surface of specimen. Different from iron-related materials [22, 23], the formation of passive CuO layer on the metal surface retard further corrosion processes to the deeper position in the material [24].

The analysis found that iron as the impurities are also corroded during corrosion test (see iron composition deterioration in Table 1), which is in line with the literature [25]. When iron metal exists as the impurities in the alloys, the corrosion process possesses the conversion of iron elements to intermediate ions from the beginning. Then, the intermediate ions spread the corrosion phenomena to other metal elements, making the combination of electrolytes and intermediate ions more aggressive in making corrosion.

3.2. Effects of electrolyte concentrations on the corrosion process

Fig. 5 depicts the SEM images of specimen after 3-week corrosion test using various concentrations of KOH solution. Different types of corrosion holes were found, in which the number of corrosion holes increased with increasing amount of KOH in the electrolyte solution. The darker hole were observed, informing the creation of deeper corrosion holes. The results implied that the more additional electrolytes led to the more attacks to the material, resulting in the more corrosion experiences. In addition, to verify the localized corrosion of the specimen, cross-section morphology analysis is important, in which this will be done in our future work.

Fig. 6 shows the effects of types and concentrations of electrolytes on the corrosion rate. The experiments were done in
the 3-week dipping process. Experimental results showed that increases in the concentrations of electrolytes gave positive impacts on the corrosion rate. This is due to the fact that concentrations of electrolytes relate to the number of electrolytes available for attacking the material. The increases in the conductivity of the solution are also the reason for the corrosion, allowing the creation of high solubility of oxidant such as oxygen (O₂) [18,19].

Regarding the types of electrolytes, the results showed different corrosion profiles. Acidic solution shows the highest corrosion rate (3.3292 mpy), while alkaline solutions were the worst (0.2020 mpy). These results replied that copper alloys had better corrosion resistance in alkaline solution because of the presence of oxide film (CuO) as a passivation layer on the surface to protect further and deeper corrosion in the material [26]. However, when copper alloys meet hydrochloric acid, passivation layer cannot be formed completely. Chlorine ion can disturb and destroy the formed passivation layer (CuO) into copper ion (Cu²⁺). This is also found in the case of sodium chloride as the salt electrolyte.

**Fig. 4** The FTIR analysis results of specimen before and after dipped into electrolyte solutions.

**Fig. 5** The SEM images of specimen after 3-week dipping process in various concentrations of KOH: (a) 0.18; (b) 0.27; (c) 0.45; (d) 0.54; (e) 0.63; and (f) 0.71 M.
In addition, this study found that too high concentration of electrolyte has no impact to the further increases in the corrosion rate when using alkaline and salt electrolytes. The formation of passivation layer is the main reason for deterring the corrosion phenomena [27]. In the case of the hydrochloric acid, there is no limitations in the corrosion rate. The increases in the concentration of hydrochloric acid gave impacts to increases in corrosion rates exponentially. Different from other types of electrolytes (i.e. salt and alkaline solution) that have only one type of ion species for making corrosion, hydrochloric acid has two types of ion species that are actively attacking the metal elements. Hydrochloric acid have hydrogen ion (H+) and chlorine (Cl-) ions, making it to have higher corrosion rate compared to other types of electrolytes.

To confirm the corrosion rate, additional other techniques for the corrosion determination must be provided, such as potentiodynamic polarization test, impedance test, etc. Coupling technics used in this study with electrochemical methods are also necessary to illustrate the mode of copper corrosion (uniform and/or pitting corrosion) in different used medium. However, these will be done in our future work.

In the alkaline solution, increases in the solution concentration depend on the pH (see Fig. 7). The increases in pH are caused by the concentration of hydrogen ions in solution. And, pH is known as one of the factors affecting the corrosion rate. The changes in pH can either induce or modify electrochemical reactions [28], causing an increase in the rate of cathodic reaction as an effect of a significant decrease in pH [29]. The increases in pH relate to the increases in stability of the formed corrosion product, most likely as an oxide. These oxides can form protective films, slowing down anodic activity [30]. The formation of a protective film on copper alloys surface when it immersed in acidic or alkaline solution.

Fig. 8 depicts the Pourbaix diagram for copper alloys which was immersed in 0.63 M of KOH, NaOH, HCl, and NaCl solutions for 1–6 weeks. Based on this figure, copper alloys demonstrate a passive behavior in the potential range of pH conditions (from 7 to 13). Most of the copper alloys had a passive layer in KOH, NaOH, and NaCl solutions, and most copper alloys got corrosion in HCl solutions. In the passivity region, oxides in the surface of copper alloys could form a passive layer. And, one of the factors affecting the stability of the passive layer is the chemical composition of the corrosive solution. Hence, to study these parameters, EDS tests were carried out and the results are presented in Table 1.

In addition to the concentration of the electrolytes, the existence of dissolved oxygen (DO) is important. Thus, the analysis was also completed with DO measurement in the solution (near to the corroded specimen) (See Fig. 9). The changes in the concentration of the electrolytes can give impacts in the amount of oxygen inside the solution, while the dissolved oxygen content influences the corrosion rate of Cu specimen. This is confirmed that specimen in the solution with higher electrolyte concentration has faster decreases in the DO amount, informing the oxygen near to the corroded specimen was consumed during the corrosion process.

3.3. Effects of corrosion rates on the mechanical properties of specimen

Fig. 10 presents the effect of corrosion rate on the tensile strength of the material. To make easily understand, the plotted data were the mean results in every sampling measurement. Then, the plotted data were then normalized and linearized to obtain linear curve. The results showed that all data agree with the trend for increases in the reduction of tensile strength as an impact from increasing the corrosion rate. The corrosion process makes elemental conversion and atomic structural loss, decreasing the material to maintain its structure during the mechanical test [31]. Indeed, this hypothesis is supported by the results in Figs. 3–5, elemental structures in the material experience several attacks during the corrosion. The more corrosion rate has the more number of corroded points and the deeper corrosion holes (see Fig. 5). When applying mechanical tests using external forces, these corroded points and corrosion holes make the material having lower mechanical properties.

As shown in Fig. 10, different curves were obtained, depending on the type of electrolyte. The highest reduction
of tensile strength occurs in the specimen immersed into hydrochloric acid solution, informing that hydrochloric acid gave the worst destruction during the corrosion test (compared to specimen corroded by other electrolytes). This result was also confirmed by the fact that the copper alloys are more stable when corroding using alkaline solution. This is because the copper alloys themselves have experiences in making passive layer, protecting the material to have less cracks and pitting corrosions [17,32].

To confirm the tensile test, this study also tested using a yield strength measurement (Fig. 11). In line with the tensile test, increases in the corrosion rate have a positive correlation.

Fig. 8 Pourbaix diagram for copper alloys in 0.63 M of KOH, NaOH, HCl, and NaCl solutions.

Fig. 9 DO concentration of solution near to the corroded specimen as a function of NaCl electrolyte solution.
to the increases in the mean reduction in yield strength. However, the reduction can be minimized for the case of corrosion using alkaline solution.

4. Conclusion

Corrosion and mechanical properties of copper alloys after the addition of electrolyte solutions (i.e., KOH, NaOH, NaCl, and HCl) with various concentrations (from 0 to 0.71 M) have been successfully investigated. The experimental results showed several phenomena:

1. The addition of electrolytes with various concentrations influences the corrosion rate. The higher the electrolyte concentration added to the copper alloys results in the higher the corrosion rate.

2. Higher concentration of electrolytes has no further impacts on the corrosion profile due to the existence of the passivity phenomenon on the surface of the material, preventing the material to get excessive corrosion.

3. Acidic (HCl) and salt (NaCl) electrolytes give more impacts on the corrosion compared to the alkaline solutions (i.e., NaOH and KOH).

4. The corrosion rate influences the mechanical properties of the material (i.e., tensile and yield strength). The attacks from the electrolyte ions made the structure inside the copper alloys less strong and easily fatigued.

This study has demonstrated the correlation of corrosion process and mechanical properties, in which this is important for the further applications of copper-related alloys in extreme and severe conditions.

Declaration of Competing Interest

The authors declared that there is no conflict of interest.

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