Evaluating the effect of atmospheric conditions on the corrosion behavior of aluminum bronze

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Abstract: Given the widespread use of copper base alloys in the marine industry, this article attempts to determine the corrosion properties of one of the alloys are widely used in the industries. The desired alloy is considered in aluminum bronze group. It is used in the manufacture of the water propellers and other products which contact with different kind of water such as sea water due to the high volume of manganese in it. In this article, the corrosion of alloy C95700 in sea water, that is a 3.5% solution of sodium chloride in laboratory, was studiedparticularly. The potentiodynamic polarization test was investigated to study the anodic behavior of samples and comparing them with each other. Investigating its chemical composition in terms of type and the percentage of alloy or base elements and ensuring that their limitation are standard were done by quant meter. According to results, the effect of the rotation of samples was greater at higher temperatures and increased the corrosion speed more.

Key words: *Aluminum bronze; Corrosion behavior; Environmental conditions; Marine industry*

1. Introduction

Aluminum alloys are widely used in a variety structures, aviation and marine industries, transmission lines, transportation and due to their unique properties such as the ratio of strength to the high weight, good weldability, excellent ductility, high corrosion resistance (Vargel, 2004). It is important to discuss about the corrosion issues, because the industries work with corrosive materials and in difficult conditions of temperature and pressure. The corrosion threats the continued work in industries and on the other hand, the cost of inspection, identification, the repair or replacement of corroded parts leads to more damages such as shut down, plant upset and the reduction of production. According to the statistics and studies, the corrosion costs are billions of dollars in oil and gas industry and by regarding to this issue that the wells are made deeper and the operating conditions are changed to increase the production and utilization and this leads to the contact of metal with more corrosive environment, so, the cost of corrosion will increase by the day in case of failure to deal with that, so that, the total annual costs of floods, tornadoes, fires, lightning and earthquakes are less than the cost of corrosion.

In the first step to reduce the costs of corrosion and before any preventive action, the type and the mechanism of corrosion in the system should be identified. There are many variables in any system that influence on the corrosion of the environment and thus, using the result of a system cannot be generalized to other similar systems. Therefore, it should act by regarding to existing observations and experiences to conclude and offer a solution for a system. One of the actions that help to recognize the corrosion and find a proper way to control it is to understand the environment in which the metal is in contact with it. When the metal is in contact with the fluid, there will be a relative motion between the surface of metal and fluid. The hull moves in the water, in the condenser or water transfer equipment, the fluid moves on the wall of pipe, in all these states, there is forced convective in the environment certainly. On the other hand, there is little evidence for movement in static conditions in which the currents are caused by natural convection. The corrosion speed depends on the relative velocity of fluid, the type of metal and the analysis of transfer water. In the cases that the sediment of Chloride (for example in the coastal environment) or the sediment of SO_2 (for example in the industrial environment) is high, the speed of corrosion is commonly more (Zhenhua, 2012).

Given the widespread use of copper base alloys in the marine industry, this paper discusses the corrosion properties of the alloys are widely used in the marine industry, aluminum bronze alloy C95700, which is used in the manufacture of the water propellers and other products which contact with different kind of water such as sea water. Since the chemical composition, hardness, density and other properties of water greatly differ from each other, in this study, the corrosion of the alloy in seawater at the laboratory in 3.5% solution of sodium chloride has been investigated particularly. For this reason, the potentiodynamic polarization test was done by

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changing two main parameters: temperature and flow rate in the standard samples of aluminum bronze C95700 and after drawing the necessary graphs, its corrosion properties and the impact of these two parameters on the corrosion were investigated.

The rest of the paper is as follows: the first section is a brief review of the literature on the corrosion of metals in sea water. In the second part, the used materials and methods are explained. In 3rd part, the parameters are defined and explained and test results are given in Section IV.

2. Literature

Most of the corrosion of metals in aqueous solutions has the electrochemical nature and also two electro-chemical reactions which happen on the surface of metal and their result causes some metals or metal alloys become non-metal. More studies were done about the local corrosion of aluminum alloys in chloride solutions. For instance, in 2004, Sinyavskii and Kalinin studied the corrosion of aluminum alloys in seawater (Synyawskii, 2005). The Cl ion plays a central role in corrosion. The corrosive environmentis highly dependent on the concentration of Cl ion in the atmosphere (Vargel, 2004). The Cl ion causes the damage and perforation of the protective oxide layer. According to the research of Berukshtis and Klark (Berukshtis, 1966), the existence of this ion in the marine atmosphere cause that the corrosion speed of aluminum is 22 times more than the corrosion speed of rural atmosphere.

The susceptibility to corrosion is highly dependent on the structure formed during the alloying process, the forming and heat treatment. The intermetallic compositions play an important role in inter-granular corrosion. The chemical composition, size, distribution and the development of these compositions are influencing factors (Zhen-Yao, 2007). The experts have problems in determining the lifetime of aluminum structures because of the local corrosion such as vacuolar and inter-granular corrosion and also they cannot provide detailed reports. Unlike a lot of studies done over 80 years on the local corrosion of the aluminum, the corrosion is still not understood completely. As mentioned, investigating the inter-granular corrosion of aluminum alloys in different chloride environments was performed by immersing or electrochemical polarization, while it cannot express the actual environmental conditions in the atmosphere properly. Given the importance of protecting materials against corrosive environmental factors, the researches and experiments are ongoing to verify and find the properties and reactions of materials in different environments. Here, we investigated the corrosion of copper base alloys, particularly aluminum bronze.

Among the copper base alloys, nickel aluminum bronze group has high mechanical strength and low corrosion speed at high flow rates. These alloys are more resistant to vacuolar corrosion than other copper alloys. The resistant to vacuolar corrosion is basically a result of plastic deformation resulting from the low-defect energy in the accumulation. The erosion-corrosion resistance is related to the formation of protective layers. Nickel-aluminum bronzehas no problem in terms of the corrosion in seawater or turbulent flow (Schossler, 1993). North et al.(North, 1979) along with Bates et al. (Bates, 1975) reported that the main product of the corrosion of Cu-Ni alloys in a solution of sodium chloride is Cu_2O. The protective nature of the corrosion layer is due to composing and entering the Fe and Ni in the network of Cu_2Owhich increases the resistance of ionic and electronic layer. The researches show that the chloride is also effective in passivation process. Kato et al. (Kato ,1987) and Castle and Parvizi (Castle, 1985) suggested that the passivation is interior due to the thin layer of chlorine and a rich layer of copper and moveslike a barrier to the movement of electrons.Also, other researchers don't accept the electron transfer as the determinant of the rate and believe that the corrosion resistance of the Ni-Cu alloys in seawater is due to the electro-catalytic properties of the corrosion layer of oxygen reduction (SCn Iffpan, 1985) and (Kato, 1984). The decrease in the corrosion speed during the process of forming layer is done by reducing the anodic reaction within growing layer of Cu_2O and cathode reaction on its surface simultaneously.The aluminum plays a role in passivation due to its composition in the network of Cu_2O which reduces the rate of oxygen reduction on the surface of Cu_2O (Schossler, 1993).

3. Material and methods

In this study, the alloy C95700 was used. Its chemical composition was measured by quantometer in terms of the type and percentage of alloy and base elements and ensuring that they are within the standard range and shown in table 1. To test the corrosion, a solution with a known concentration of sodium chloride (3.5%) and once-deionized distilled water were provided.

The cell preparation for the test is as follows:

First step: Prepare the chloride sodium solution with desired concentration at least 30 min before starting each test. This is done to create the same aeration in all experiments. The used electrolyte is changed after each test and replaced with fresh and clean solution.

Second step: Wash the test chamber with distilled water.

Third step: The sample is attached to the rotating disk electrode and put in cell containing sodium chloride solution.

Forth step: The connection of sample is done by the cables connecting the rotating disk device and potentiostat.

Fifth step: Put the reference and auxiliary electrodes in the cell containing sodium chloride solution surround sample before switching on the

device. Each electrode is attached to device by cables. The reference and auxiliary electrodes are Ag/Ag cland Platinum which shown in Fig. 1. To investigate the results of corrosion tests and draw necessary charts and extract data, Iviumsoft and Excel are used.An area of the region exposed to corrosion is a circle with a diameter of 5 mm.

Fig. 1: The reference and auxiliary electrodes

4. Environmental parameters

The corrosive conditions such as high humid, salt in environment and industrial contaminants in atmosphere cause different corrosion in these environments. The parameters studied in this article are as follows:

4.1. Salinity and chlorinity

One of the main properties of seawater is its salinity. Salinity means the amount of mineral salt (gr) which is solution in 1Kg seawater when all bromide and iodideof it are replaced with the equivalent amount of chloride and all carbonate is replaced with the equivalent amount of oxide. The salinity is frequently assessed by measuring chlorinity or the electrical conduction of seawater. The salinity of seawater is usually 3.5% or in another word 35 in thousand. Chlorinity is the necessary amount of Ag (gr) to sediment halogen in 0.32852 Kg of seawater, this amount is equivalent the weight of Cl ion in seawater. Chlorinity and salinity are related to each other as follow:

Salinity=1.8065Cholorinity   (1)

where S and Cl are expressed by part in thousand. If the salinity of water is not 35 in thousand, the concentration of existing ions in seawater can be calculated by eq(2).

(x)in salinity S = (x) in salinity of 35 in thousand * $\frac{S}{0.035}$ (2)

Eq.(2) is not correct for very low salinity(with concentration less than 10 in thousand for HCO_3- and Ca^{+2}, less than 5 in thousand for other ions), it may be not correct in contaminated water (Carlton, 1994).

The main effects on corrosion caused by salinity, electrical conduction of seawater and also collapse and demolition of zinc layers are due to Cl ion (such as the corrosion of aluminum and steel).The higher the salinity, the Cl ions penetrate more easily into the protective layers and cause the germination of cavity. The alloys in which the corrosion happens uniformly, the change of corrosion speed due to the change of salinity is a little while the corrosion of

these alloy depends on the concentration of dissolved oxygen in water and temperature. The specific conduction of water depends on the temperature and salinity (Dexter, 1980).

The high electrical conduction causes that its electrical resistance has no more role in the reduction of corrosion reactions. Galvanic corrosion in sweet water due to the low electrical conduction is just limited to the environment of two metals' connection, while in seawater, the different metals which are near in a few meters form galvanic couple and the corrosion process will be activated between them. Also in vacuolar corrosion due to the high electrical conduction of seawater, more surface of metal participates in cathode reaction and therefore the speed of corrosion will be intensive in anodic small regions within cavity (Dexter, 1980).

4.2. Temperature

Considering other variables constant, the increase of temperature causes the increase of corrosion by seawater. If the concentration of dissolved oxygen in seawater is considered constant, the corrosion speed of low carbon steel increases 2 times per every increase of 30°C. The corrosion speed in surface warm water is usually more than deep cold water. The higher temperature increases the penetration of oxygen through cathode layer of protective oxide film. But the important note is that the solubility of dissolved oxygen in water is increased, while the caused effect on the corrosion process by the concentration of dissolved oxygen are more than the effect of temperature (Costlow, 1984) and (Smart, 1980). Fig. 2 shows the effect of temperature on corrosion. In a closed system in which oxygen cannot exit, the corrosion increases by increasing temperature and continues until all oxygen will be used. In an open system in which oxygen can exit, the corrosion increases by increasing temperature to 80°c. The more increase of temperature causes the reduction of corrosion significantly, because the solubility of oxygen in water in high temperature decrease more (LaQue, 1975).

4.3. Dissolved oxygen

In some corrosion process such as zinc solution of hydrochloric acid, hydrogen gas is released. Copper in NaCl solution, hydrogen is removed by a chemical reaction between hydrogen and chemical oxidizing agents such as oxygen to form water molecules. For this reason, oxidizing agents are the powerful factors accelerating corrosion. The concentration of dissolved oxygen in seawater is an important factor of the corrosion process and is influenced by factors such as the exchange between atmosphere and ocean and biochemical processes. Dissolved oxygen concentrations in surface waters will be close to saturation equilibrium with the oxygen in the atmosphere (in a certain temperature). The solubility of oxygen in seawater is reduced by

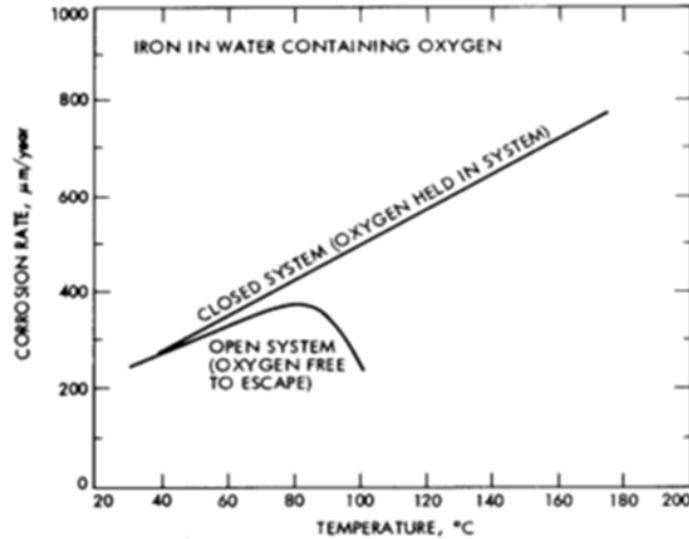increasing temperature and salinity but the influence of temperature on it is further.

Fig. 2: the effect of temperature on the corrosion speed (LaQue, 1975)

If the values of temperature (T) (in Kelvin) and salinity (S) (in the thousands) are given, the solubility of oxygen is obtained from eq. 3:

$$Ln\,[O_2] = A_1 + A_2 \left(\frac{100}{T}\right) + A_3 Ln\left(\frac{T}{100}\right) + A_4\left(\frac{T}{100}\right) + S(B_1 + B_2\left(\frac{T}{100}\right) + B_3(\frac{T}{100})^2) \quad (3)$$

Where the oxygen concentration is in millimeters per liter (mm / l) and salinity is in parts per thousand. The coefficients A1 to B3 in the above equation are presented in Table 1. Table 2 contains the oxygen saturation in millimeters per liter at different temperatures and salinities were calculated by using Eq. 3 and Table 2.

Table 1: The constants of eq. 21-2 (Kester, 1975)

Constants	Amount
A_1	-173.4292
A_2	249.6339
A_3	143.3483
A_4	-21.8492
B_1	-0.033096
B_2	-0.014259
B_3	-0.0017

Table 2: The solubility of oxygen at different temperatures and salinities (Charng, 1982)

Temperature		The solubility of oxygen(multi/litre) at different salinities					
0C	0F	0	8	16	24	31	36
0	32	10.22	9.7	9.19	8.7	8.27	7.99
5	41	8.93	8.49	8.05	7.64	7.28	7.04
10	50	7.89	7.52	7.14	6.79	6.48	6.28
15	60	7.05	6.72	6.4	6.1	5.83	5.65
20	70	6.35	6.07	5.79	5.52	5.29	5.14
25	75	5.77	5.52	5.27	5.04	4.48	4.7
30	85	5.28	5.06	4.84	4.63	4.45	4.33

The corrosion speed decreased with increasing depth and subsequently reducing the concentration of dissolved oxygen. This process would continue until the concentration of dissolved oxygen in seawater becomes the lowest. More in depth, despite the continuous decrease in temperature, the corrosion speed increases by increasing oxygen concentration (LaQue, 1975). The effect of oxygen concentration on the corrosion of carbon steel in distilled water at a low flow rate and room temperature is shown in Fig. 3. The corrosion speed is reduced by increasing the volume of oxygen from 12 to 25 ml per liter. This is due to the formation of the passivation of a protective oxide film or the chemical absorption of extra oxygen which is on the iron. But, the reduction of the corrosion speed will not occur with increasing the amount of oxygen in the presence of significant quantities of chloride (LaQue, 1975).
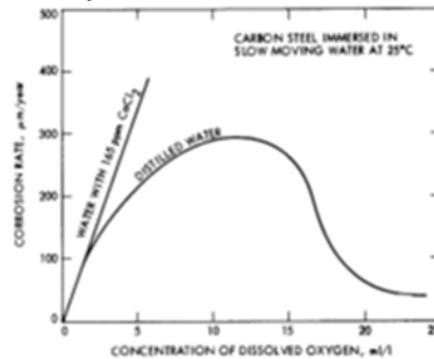

Fig. 3: The effect of oxygen concentration on the corrosion rate of carbon steel

In protective metals such as aluminum and stainless steel, the influence of dissolved oxygen concentration, shows a dual behavior. On the one hand, the high oxygen concentration in these alloys causes healing the protective layers, delaying the formation of cavities and on the other hand, intensifying the cathode reaction and therefore, the growth rate of the cavity increases (Smart, 1980; Charng, 1982; Harvey, 1996).

5. Results and discussion

After checking the chemical composition of the used alloy, the potential dynamic polarization corrosion tests conducted on samples at the different speeds of the rotation of electrode and at two different temperatures (room and 40 ° C) were investigated. The corrosion behavior of an alloy is a composed property of alloying- environmental conditions and thus a corrosion test that is efficient for all of the above conditions do not exist. In a corrosion test, the factors related with alloy and corrosive environment must be considered and if we want that the test condition is quite similar to the working conditions, these factors must be selected well and controlled properly. The results of corrosion tests can be used to develop an alloy so that it can be prepared cheaper, more effective and with better efficiency.

The potentiodynamic polarization test is investigated to study the anodic behavior of samples and compare them with each other. Fig. 4 shows the electrochemical polarization curves of sample C95700 in sodium chloride solution at different rate of the rotation of sample.

5.1. Potentiodynamic polarization test

Fig. 4 shows the electrochemical polarization curves of sample C95700 in sodium chloride solution at different rate of the rotation of sample. Regarding to this shape, the polarization curve of the inert solution is on the left side than the other curves, it means the density of flow shows the lower corrosion than the other curves. Increasing the speed of rotation, electrochemical polarization curves are moved to the right side.
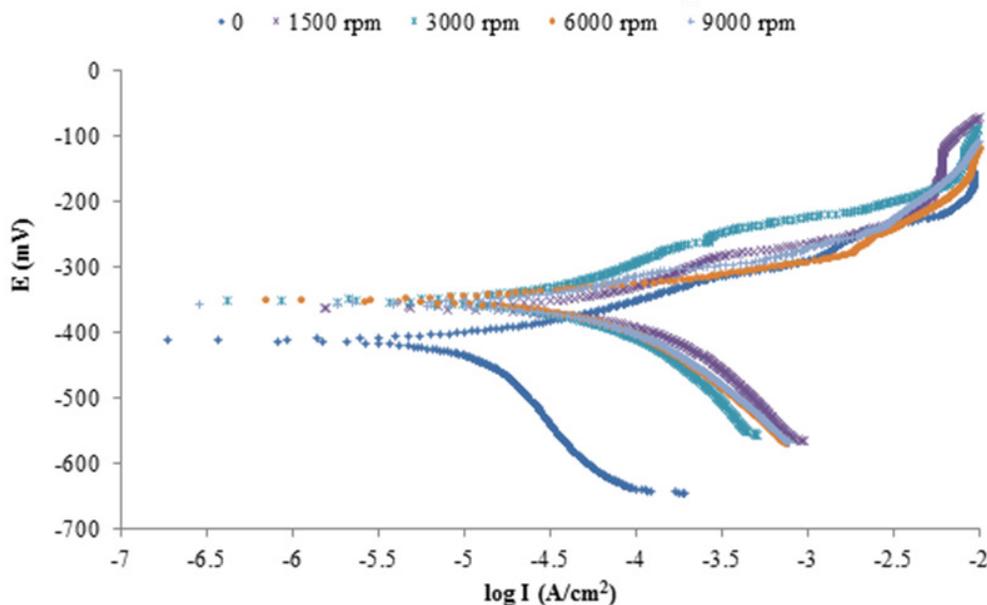
Fig. 4: The electrochemical polarization curves of alloy C95700 at different speed of the rotation of sample in solution 3.5% of NaCl at room temperature

The increase of the electrochemical polarization curves' solution rate means that the more positive potential was moved. It can be related to the creation of the oxide film of Cu2o on the surface. In order to study the electrochemical polarization curves, these curved were analyzed by Ivium soft. Table 3 shows the results of the analysis of the polarization curves. The polarization curves were investigated to study the anodic behavior of samples and compare them with each other.

The increase of potential is justified by forming the passive film on the surface. On the other hand, with the increase of the rotation speed, the density of corrosion increased from 12.6 A/cm$^2\mu$ to 57.8 A/cm$^2\mu$. The increase in corrosion speed suggests that the film formed on the surface is not protective and doesn't create a bulwark against the corrosive ions. When the corrosion potential is more positive and the density of corrosion decreases, the corrosion resistance will increase. Excellent corrosion resistance of aluminum bronze is due to forming a

thin film or strong bonding of aluminum oxide. This film has self-healing capability and once it forms, it prevents oxidation and therefore, it prevents flaking which usually occurs in ferrous alloys.

After forming this layer, for the continuation of corrosion, the oxygen should penetrate through this layer and reach the surface of the substrate alloy. The oxide film on the surface of copper is a mixture of CuO and Cu$_2$O.

If the aluminum is present in the composition of alloy, the formed film will be a mixture of two oxides of copper and aluminum. The visible light reduces the rate of the formation of copper's oxides greatly. This film is easily dissipated in turbulent water and is dissolved in the existing carbonic or organic acid in fresh water or soil and thus causes the increase of corrosion.

Table 3: The result of the electrochemical polarization curves of alloy C95700 at different speed of the rotation of sample in solution 3.5% of NaCl at room temperature

Rotating Rate(rpm)	E_{corr} (mV)	i ($\mu A/cm^2$)	$_a$(mV/dec)β	$_c$(mV/dec)β
0	-416	12.6	73	210
1500	-343	35.7	102	211
3000	-329	44.5	102	200
6000	-338	52.4	98	185
9000	-331	57.8		181

The dissolution of copper in sodium chloride occurs by the oxidation of copper to Cu^+:

$$Cu \rightarrow Cu^+ + e^-$$
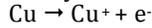
The produced copper ion reacts with the existing Cl ion as follow and creates copper chloride:

$$Cu^+ + Cl^- \rightarrow CuCl$$
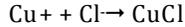
The produced copper chloride has a little adhesion to the surface and cannot protect the surface and converts to complex with the help of following reaction:

$$CuCl + Cl^- \rightarrow CuCl_2^-$$
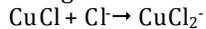
So $CaCl^{2-}$ is the main component created on a copper surface. On the other hand, the cathode reaction complementing the corrosion process on the surface in the sodium chloride environment of the oxygen reduction is as following:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
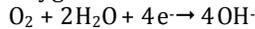
Thus, by increasing the corrosion process and oxygen reduction, the surface become alkali. Becoming alkaline along with the production of copper chloride complex and the production of copper oxide layer on the surface can cause a thin layer on the surface:

$$Cu_2O + Cl^- + 2H_2O \rightarrow Cu_2(OH)_3Cl + H^+ + 2e^-$$
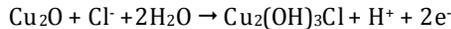
After the formation of this layer, for the continuation of corrosion, the oxygen should penetrate through this layer and reach the surface of the substrate alloy. The oxide film on the surface of copper is a mixture of CuO and Cu_2O. If the aluminum is present in the composition of alloy, the formed film will be a mixture of two oxides of copper and aluminum. The visible light reduces the rate of the formation of copper's oxides greatly. This film is easily dissipated in turbulent water and is dissolved in the existing carbonic or organic acid in fresh water or soil and thus causes the increase of corrosion.

According to the potentiodynamic polarization test, by increasing the rate of sample's rotation, different processes occur. On the one hand, by increasing the rotation of sample, the oxygen and corrosive ions reach the surface easily due to the increase of solution's turbulence. Easier accessibility of the oxygen to surface causes that the passive film form on the surface and the potential becomes more positive. On the other hand, by increasing the speed of rotation, the stress is created on the surface. This shear stress can separate the clung layers which have no high adhesion from the surface. Therefore, by increasing the speed of rotation, the accessibility of oxygen and corrosive ions to the surface increase and the product of corrosion and formed layers on the surface separate from the surface easier. The

potentiodynamic polarization test was performed at different rates of sample's rotation on this alloy in room temperature, 40℃.

6. Conclusion

The results show that the used method in this research is a proper method to study the corrosion in the atmospheric condition, because it prepares the atmospheric stepped-up condition. By regarding to the potentiodynamic polarization curves, the solution was placed on the left side than other curves. It means that the density of flow has a lower corrosion than other curves. By increasing the rotation speed, the electrochemical polarization curves were moved to right side. Also by increasing the rate of solution, the electrochemical polarization curves were transferred toward more positive potentials. This can be related to the creation of the oxide film of copper oxide on the surface.

In general, as expected, increasing temperature and the rotation speed of sample cause increasing the speed of corrosion. To investigate further, the corrosion behavior of this alloy can be investigated by other tests in atmospheric conditions or the corrosion behavior of this alloy can be studied by heat treatment on the samples and compared with the results of test without heat treatment.

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