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The Study of corrosion behavior of aluminum, bronze and nickel alloys on different speeds rotated samples

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Abstract: The purpose of this paper is to investigate of the corrosion behavior of aluminum, bronze and nickel alloys. In order to study the corrosion behavior of C95700 alloy, Polarization experiment was performed on the alloy on different speed of rotation sample in sodium chloride solution. The results show the corrosion potential enhanced by increasing the rotation speed from -416 mV to -330 mV. On the other hand, the density of corrosion rate increased from 12.6 A/cm2µ to 57.8 A/cm2µ by increasing rotation speed.

Key words: *Corrosion behavior; Speed of rotation; Polarization experiments; Aluminum, bronze; Nickel alloys*

1. Introduction

Because of aluminum bronze properties such as high strength and excellent corrosion resistance, especially under conditions of turbulent flows, those are applied in industries like chemical and marine industry and also in making pieces such as bushes, pumps, valves, small gears, bearings, and ship propellers (Tang et al, 2004). A proper selection of materials and good design are effective in reducing corrosion cost. Now, corrosion science and its importance become clearer. In polluted environments between sulfide influences of these ions to alloy surface increase corrosion rate (Dehghani, 1392).

Aluminum bronze is a group of copper-aluminum alloys, which has good corrosion resistance and stability and is extensively used in both states of casted and wrought. Aluminum bronzes has developed from a simple alloy of copper and aluminum to complex alloys with the addition of elements such as iron, nickel, manganese, silicon and other elements (Powell, 2012). Aluminum- nickel-manganese bronze (C95700) is known CMA1 in British standard is alloys, which widely used for the manufacture of large marine propellers. For the first time in 1950, this alloy developed in order to correcting common alloys which were used in propeller manufacturing like as elastic brass and aluminum-nickel bronze (Tang, 2004). C95700 alloy is formed of 75% (wt%) copper (Cu), 2% nickel (Ni), 3% iron (Fe), 8% aluminum (Al) and 12% manganese (Mn). Copper is one of the most important known useful metals for human and one of the first metals which have been used. Thermal conductivity of copper is very high and Due to made commercial product, there are about 400 different copper alloys, (Bissey-Breton, 2014).

This alloy has better mechanical properties than nickel bronze (NAB) and also its density is (7.45 gr/ cm^3 against 7.65gr / cm^3) lower. Its melting point is lower thus also its welding and casting properties are better. In contrast of aluminum- nickel bronze, this alloy doesn't have the brittleness problem in the temperature range 250- 400 ° C and therefore, Kargrm and its fixing is easier; However, it has less resistance versus to types of corrosion such as fatigue corrosion, stress corrosion and gap erosion-corrosion (Tang, 2004).

All of aluminum bronze has good resistance versus corrosion; however the amount of resistance to corrosion is different due to their metallurgical structure that is dependent on the chemical composition and production history in particular their heat treatment has been done on them. These alloys on the surface have thin films and adhesion of copper oxides and aluminum oxides which, if damaged or destroyed, spontaneously formed again. These alloys also have considerable resistance versus erosion, abrasion and fatigue corrosion (Tang, 2004), simple aluminum bronzes, which are only alloy of copper and aluminum to 8%, have single alpha phase structure. By increasing aluminum content to more than 8%, is formed beta-phase and is produced alpha-beta structure alloy. If Alpha Beta aluminum bronze is cooled slowly rate from high temperatures about 600 ° C Beta phase is converted to the gamma2 phase at about temperature 565 ° C. As a result, if this phase is formed continuously, is caused decreasing of resistance corrosion and increasing penetration rate of corrosion.

Research performed on aluminum alloys with 8.5 to 9.5% has shown that if the amount of aluminum in aluminum bronzes is less than 9.1 percent will not be formed gamma2 phase continuously. Alloys with the higher percentage of aluminum for lack of gamma phase must are cooled quickly e.g. by

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quenching in water from 600 ° C after casting or hot working (Schossler, 1993).

Obviously, the addition of other alloying elements will leads other changes in the metallurgical structure alloys and existing phases. The presence sufficient quantity of iron to prevent from formation of gamma2 phase and thereby is refined the grain structure alloy and if is formed gamma-2, which will be discontinuous. Nickel has the same effect with iron and prevents the formation of gamma 2 phase continuously and destructive. However, with this goal cannot be added to aluminum bronze, because iron can have the same effect with cheaper price. To adding manganese also prevent the breakdown beta phase to gamma 2 and alpha phases. Beta phase of Aluminum bronzes containing ten percent of aluminum with iron and nickel produce alpha and kappa phase, in the temperature range 950-750 ° C during the cooling. Kappa phase contains all the components of aluminum, iron, nickel and manganese; if there is manganese. Usually, corrosion resistance of aluminum bronze increases by increasing amounts of aluminum and other elements alloy (Powell, 2012) & (Schossler, 1993).

Although more than one hundred years, the research is ongoing better understand the actual mechanism of active corrosion and what happens in many corrosion processes is understandable, but the investigation isn't complete by no means; Many fields remain unexplored or are known little. In this part we survey some of the similar studies that assess different climate or environmental on materials.

Schussler and his colleague experiments showed in presence of sulfide contamination which corrosion rate increases due to changes in the structure of the passive layer caused by entering copper sulfide into structure. The amount of copper oxide and aluminum oxide are reduced in this case, which is corrosion inhibitors. As such the corrosion products are very porous and composed of copper sulfide. The sulfide accelerates the reaction of charge transfer for oxygen reduction that occurs on the surface of corrosion layer dramatically (Tang, 2006).

Tang and his colleagues seek to improve the corrosion resistance of these alloys in their research. These researchers used a laser surface melting (LSM) aluminum-nickel-manganese bronze and also laser surface alloying (LSA) by using of aluminum powder with combined 75.6% Mn, 10.8 wt% Cu, 7.8 wt% Al, 3.6 Fe and 2.2 wt % nickel. In first case, (LSM) was performed for surface melting and creating a resistant layer of depression - gap corrosion and the second case (LSA) with the aim of forming a new alloy layers. Resistance of erosion-gap corrosion was improved 5.8 times in solution contain 3.5% sodium chloride compared to the initial alloy (Kwok, 2000).

Results of Tang and his colleagues' survey showed an approximate thickness of 1 mm alloy layer without cracks and pore is formed on the substrate using laser surface alloying method and aluminum powder. The single- beta phase layer with BCC structure has an aluminum amount greater than the substrate and also its rigidity was measured two times than the substrate. Depression - gap corrosion resistance this layer was about 30 times better than initial alloy because of the formation of single-phase layer with high hardness. Also the samples due to higher hardness and lower grain boundaries were better than surface melting samples by laser (Kwok, 2000). Kwak and his colleagues were studied Simultaneous effects depression and corrosion of engineering alloys in solution with 3.5% NaCl.

2. Materials and Methods

The purpose of this paper is to study the corrosion behavior of base copper alloy, which is C95700 standard number. The sample alloy prepared from engineering company and study of the type and amount alloy elements of the chemical composition and basement and ensure from their range in the standard range was performed by quantimeter. After determining test method (potential, flows and other variables) by computer, enter the control system into it and test is performed. Rotating disk electrode rotates samples according to different speed in a cell. To study the effects of rotation speed of disk was performed at different periods of 0, 1500, 3000, 6000 and 9000 rpm. The effect of temperature was studied by examining and testing on the ambient temperature and the temperature of 40 ° C.

Way of increasing the tasting temperature at 40 ° C was performed as putting the samples into a beaker which is connected to rotating disk electrode machine and is placed on hot plate and its temperature is held stationary at 40 ° C by circulating water. The corrosion tests carried out on samples included of electrochemical impedance spectroscopy, potentiodynamic polarization and linear polarization. To perform the corrosion test is prepared solution with a known concentration of commercial sodium chloride (3.5%) and distilled water which it is distilled one time. Cell preparation process for the test is as follows:

First step: Preparation of sodium chloride solution with the specified concentration of at least 30 minutes, before the start of each test, this was performed in order to create same aeration in all the experiments. The electrolyte is replaced by fresh and clean solution after each test.

Second step: washing test chamber by distilled water.

Third step: the sample was attached to the rotating disk electrode and was placed into the cell containing brine.

Fourth step: manner of connecting the sample between the rotating disk electrode and Potentiostat is performed by the connecting cable.

Fifth step: The time and manner putting the reference and auxiliary electrode before turning machine on and within the cell containing brine around the sample that each of the electrodes is connected to the machine by cables. For the preparation of the samples is polished the sample before performing each test at each speed of rotation. The polishing was performed by silicon carbide sandpaper with numbers 600, 1000 and 2000 respectively. Water was used as a lubricant during the polishing process. The samples were rotated 90 degrees between successive steps to be removed scrape the previous steps. Next step was polished by an electric polisher. After polishing, oil, grease and probable pollution are relieved on the surface of sample by alcohol and then were dried in Dryer, and samples have been kept in the desiccator until tests to ensure remaining without pollution and contact with other materials or components. To evaluate the results of corrosion tests and plotting the necessary diagrams and data extraction were used Ivium soft and Excel software. Cross section area exposed to corrosion was a circle with a diameter of 5 mm.

3. Corrosion test results at room temperature and at 40 ° C with changing speed of rotation of the sample

3.1. Study of C95700 alloy behavior for linear polarization test

In order to study the corrosion behavior of C95700 alloy, linear polarization tests were performed at different speeds of sample rotation it into sodium chloride solution. Fig. 1 show curves obtained from the linear polarization tests.

Based on this Fig., a line has been transferred to up by increasing the speed of sample rotation of the linear polarization which it represents the surface alloy has became more decent. Accurate analyses of these curves were performed by the Iviumstat software. In order to calculate the polarization resistance tests based on linear polarization is needed to equivalent weight and sample density. In order to calculate the equivalent weight of studied alloy samples were used ASTM-G 102 standard. Based on this standard, weight of alloy sample is calculated as follows:

$$EW = \frac{1}{\sum \frac{n_i f_i}{W_i}} \quad (1)$$

In this equation) f_i: weight percentage of i element, W_i: atomic weight of i element, n_i: number of valence electron of i element.

Due to this equation and quantimeter analysis of the tasting sample, equivalent weight of studying sample was obtained 9.25 gr.

Furthermore, sample density was obtained according to the ASTM-G102 standard and the following formula:

$$D = \frac{1}{\sum \frac{f_i}{D_i}} \quad (2)$$

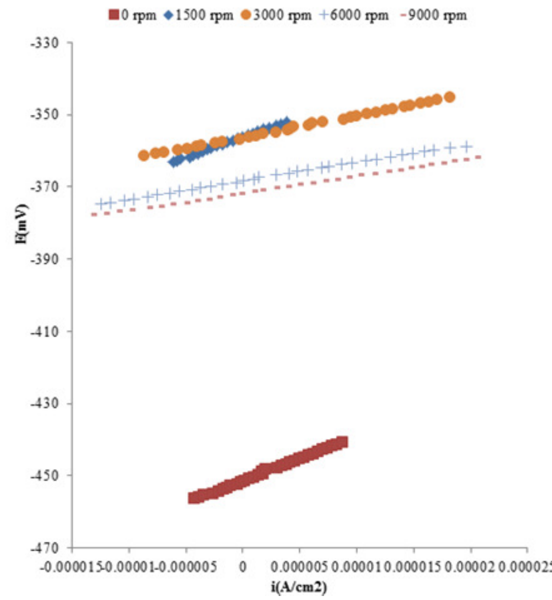

Fig. 1: the curves obtained from linear polarization tests C95700 alloy for different speeds of rotation samples in 3.5% sodium chloride solution at room temperature.

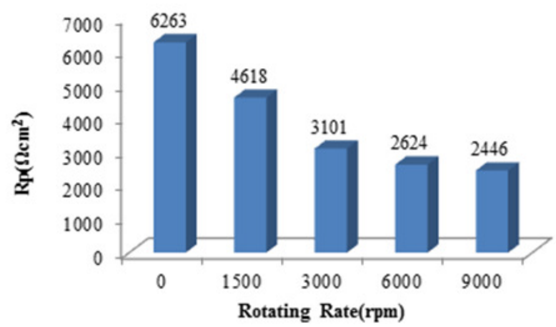

Fig. 2: the changes polarization resistance of the C95700 sample in sodium chloride solution or different speeds of rotation samples in 3.5% sodium chloride solution based on linear polarization testing at room temperature.

Fig. 2 shows the changes polarization resistance of the C95700 sample at different speeds of rotation samples in 3.5% sodium chloride solution on the basis of linear polarization testing at room temperature. As it is seen in this Fig., polarization resistance was 6263 Ωcm^2 in static solution it and has been reduced to 4618Ωcm^2 by increasing rotation speeds to 1500 rpm;. By further increasing the rotation speed, polarization resistance reduced more, and it is reduced to 2446 Ωcm^2 in the 9000 rpm.

3.2. Study of C95700 alloy behavior in potentiodynamic polarization tests

Polarization curves were investigated in order to study anodic behaviors of the samples and comparing them with each other. Fig. 3 shows the electrochemical polarization curves of C95700 sample in sodium chloride solution at different speed of the sample rotation.

According to this Fig., the polarization curve of the static solution is on the left side than the other curves. It means; its corrosion rate density is lower than the other curves. By increasing rotation speed, electrochemical polarization curves are transferred to the right. Furthermore by increasing the solution speed, electrochemical polarization curves have been shifted upwards, more positive potentials. This may is related to making an oxide film on the surface of copper oxide. In order to evaluate more accurate of electrochemical polarization curves, these curves analyses by Ivium soft. Table 1 shows the analysis results of the polarization curves.

Table 1: The results of electrochemical polarization curves of C95700 alloy at different rotation speeds of samples in solution of 3.5% sodium chloride at room temperature

Rotating Rate(rpm)	E_{corr} (mV)	i (μA/cm^2)	β_a(mV/dec)	β_c(mV/dec)
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

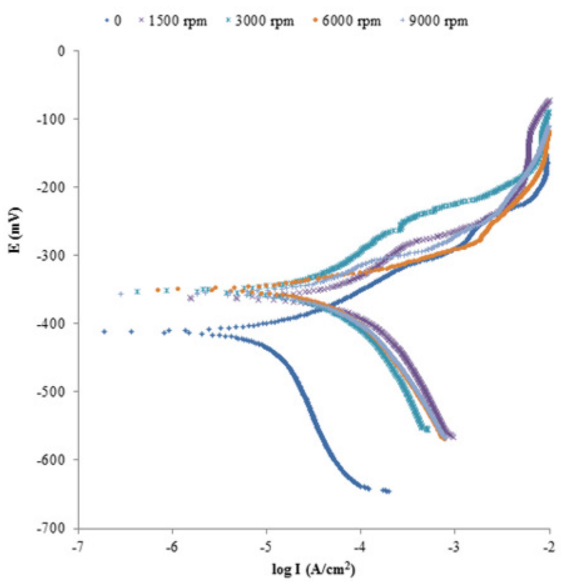

Fig. 3: The electrochemical polarization curves at different rotation speeds of C95700 alloy sample in a solution of 3.5% sodium chloride at room temperature

According to Table 1, the corrosion potential enhanced with increasing the rotation speed from -416 mV to about-.330 mV. This potential enhance is justified by forming passive film on the surface. On the other hand, the corrosion rate density enhanced from 12.6 μ A / cm^2 to 57.8 μ A / cm^2 by increasing the rotation speed. This corrosion rate enhancement represents that formed film on the surface is not protective and does not make a barrier versus corrosive ions. When corrosion potential is more positive and when corrosion rate density decreases, corrosion resistance increases. Excellent corrosion resistance of aluminum bronze is because of forming an inherent and thin film connecting or adhesive is stronger than aluminum oxide. The film has self-healing capabilities, and as soon as it forms, it prevents the further oxidation and thus prevents to flake, which usually occurs in ferrous alloys.

After this layer is formed, in order to continue corrosion, oxygen should penetrate through this layer to reach the surface of the substrate alloy. Oxide film on the copper surface is a mixture of Cu_2O and CuO oxide. When aluminum also is present in the alloy composition, the formed film is a mixture of copper and aluminum oxide. Visible light extremely reduces the formation rate of copper oxides. This film is easily exterminated in the turbulent water easily and dissolves in carbonic acid or organic acids which are present in fresh water or soil, and dissolving increases the rate of corrosion.

With increasing rotation speed of sample is done various processes. With increasing the rotation speed, because of enhanced turbulence of solution, oxygen and corrosive ions reach to surface easier. Easier access of oxygen to surface causes passive film is formed on the surface, and potential becomes more positive. On the other hand, with increasing the rotation speed, stress is created on the surface. This shear stress can separate linked layer to surface which don't have high adhesive to surface. So by increasing the rotation speed, the access of oxygen and corrosive ions to the surface increases and the corrosion products and formed layer on surface separate from the surface more easily.

3.4. Study of C95700 alloy behavior in electrochemical impedance test

Impedance test (3.5 wt% sodium chloride solution) was performed on the samples in the same environment. Nyquist curves obtained from experimental data are plotted in Fig. 4. Nyquist diagrams (imaginary part of the impedance on the Y-axis and real part of the impedance on-axis X) by using different equivalent circuit models are described and interpreted.

It is seen that the curves are not perfect semicircle. Quasi-semicircle diameter is related to charging transfer resistance; this value is equal to the polarization resistance if there isn't quasi-induced behavior. The distance between the source and the semicircle represents solution resistance, which there is between the reference electrode and the working electrode.

All curves have the same shape of the semicircle but with different sizes. This indicates that the main reaction is the same for all the electrode rotation speeds but for each of them to be, effective covering area is different versus corrosion. As it is observed in the Nyquist graphs, the graphs have a crush which represents are not ideal capacitive loop. Thus for analysis of curves, capacitor has been simulated by using a constant phase element (CPE) as mathematically. CPE values were calculated using the following equation:

$$CPE = Y_0 (\omega)^{n-1} \quad (3)$$

Where Yo is constant ω, CPE is angular frequency in maximum imaginary impedance condition and n is power of CPE which if the value of n is close to 1, it represents more capacitive behavior of CPE element.

Fig..4. the electrochemical Nyquist curves of C95700 alloy at different rotation speeds of sample in 3.5% sodium chloride solution at room temperature.

As it is evident in this the Fig., electrochemical impedance curve formed from a semicircle, which represent the corrosion process is influenced by charge transfer. By increasing rotation speed does not make any difference in the appearance of curves, and curves remain in a semicircle. Fixing shape curves shows by increasing rotation speed, corrosion processes and its ruling mechanisms are fixed and not changed. According to these curves, clearly by increasing rotation speed of the sample, electrochemical Nyquist curves diameter has been reduced.

For the electrochemical impedance curves, analyzing is used circuit equal Sel Randles circuit. These curves were analyzed by using the Iviumsoft software. Table 2 shows the results of the analysis of these curves.

Table 2: The results of the analysis of electrochemical impedance curve at room temperature

Rpm	R_p(Ωcm²)	CPE(μF/cm²)	N
0	6416	6.1	0.7
1500	3853	6.9	0.68
3000	2991	7	0.69
6000	2255	6.5	0.77
9000	2000	7.2	0.78

According to this table, polarization resistance of samples is 6416 ohm/cm² in residing solution. While by increasing rotation speed of sample to 1500 rpm, the polarization resistance decrease strongly and is reached to 3853 ohm/ cm². By increasing solution speed, polarization resistance decreased less and in rotation speed 9000 rpm, polarization resistance has been reduced to 2000.

3.4. Corrosion test results by varying the speed rotation of the sample at 40 ° C

It can be said that almost the temperature increases the rate of all chemical reactions. Sometimes temperature increasing has Akspvnansyly and strong effect from the beginning and another time hasn't been significant effect and then became strong. Temperature increasing in acidic environment enhances oxidation power.

In order to study more accurate corrosion mechanism and the effect of simultaneously temperature and rotation on the corrosion process of the C95700alloy in 3.5 wt% NaCl solution, all of tests were performed at room temperature (Linear polarization, potentiodynamic polarization and electrochemical impedance) and 40 ° C at different rotation speeds of the alloy samples. Fig. 5 shows the linear polarization curves at 40 ° C on C95700alloy.

Based on this Fig., by increasing the rotation speed of the sample, potential slope is reduced due to rate and thereby resistance is reduced to corrosion. Accurate analysis of these curves was performed based on the Iviumstat curve software. Values of equivalent weight and alloy density were considered according to previous calculations. Fig. 6 shows the variation of polarization resistance obtained from analyzed linear polarization tests at different rotation speed of the samples.

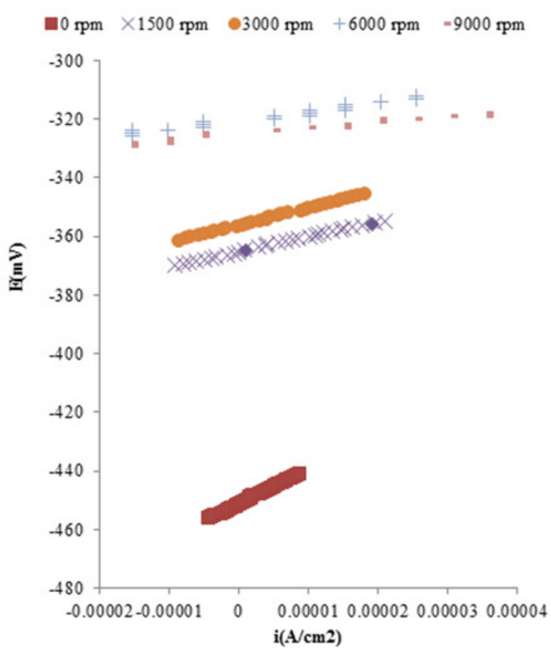

Fig. 5: The curves obtained from linear polarization tests of C95700 alloy at different rotation speed of the sample in 3.5% sodium chloride solution at 40 ° C

As you can see in this Fig., the polarization resistance is greatly reduced by increasing rotation speed of the sample. As previously mentioned, this is related to easier achievig corrosive particles to surface.

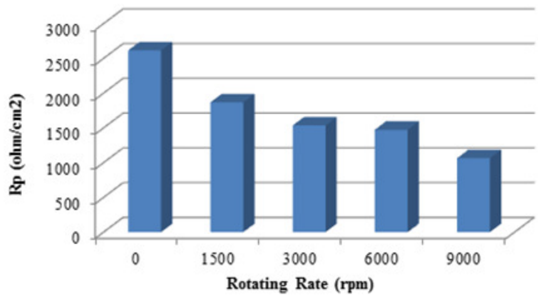

Fig. 6: The variation polarization resistance of C95700 alloy at the different rotation speed at 40 ° C

For Continuing work (or after that), electrochemical polarization tests were performed at different rotation speeds of samples at 40 ° C. Fig. 7 shows the curves obtained from these experiments. According to this electrochemical polarization, curves were shifted to the right and above by increasing the rotation speed of the sample. Shifting curves to the right represents an increasing in the corrosion rate. Table 3 shows the analysis of the polarization curves.

Table 3: The results of electrochemical polarization curve analyzing at 40 ° C at different rotation speeds.

Rotating Rate(rpm)	E_{corr} (mV)	i (µA/cm²)	β_a(mV/dec)	β_c(mV/dec)
0	456	13.18	62	181
1500	289	61.39	13	251
3000	299	134.2	56	244
6000	415	524.7	211	199
9000	425	716.3	260	185

Based on the results obtained, values of corrosion rate density enhanced by increasing the rotation speed and increased from 13.1 µA / cm² to 716 µA / cm². Corrosion rate density ehanced at room temperature by increasing rotation speed, but it has increased sharply at 40 ° C. This indicates that the effect of sample rotation was greater at higher temperatures and has increased corrosion rate more. The values of anodic tafel slope enhanced greatly by increasing rotation speed. On the one hand, this increasing is related to increasing environment temperature and the other hand, to easier distribution of anions at solution.

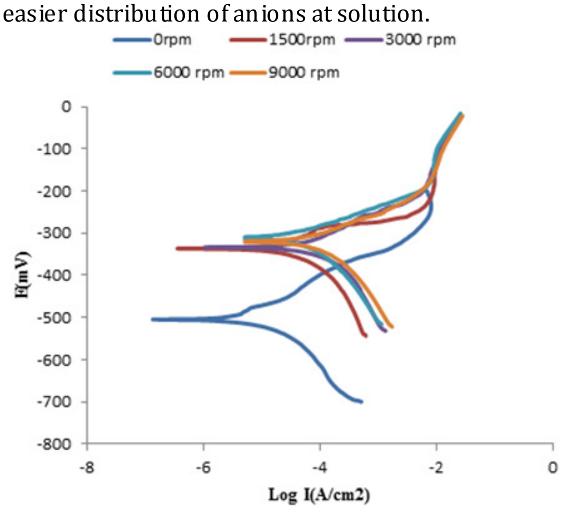

Fig. 7: The electrochemical polarization curves at different rotation speeds of the samples in 3.5% sodium chloride solution at 40 ° C

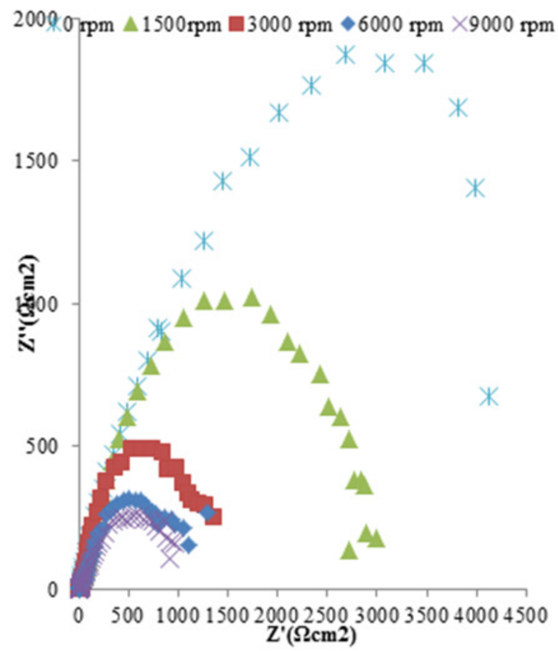

Fig.8: The electrochemical Nyquist curves of C95700alloy at different rotation speeds of the sample in 3.5% sodium chloride solution at room temperature.

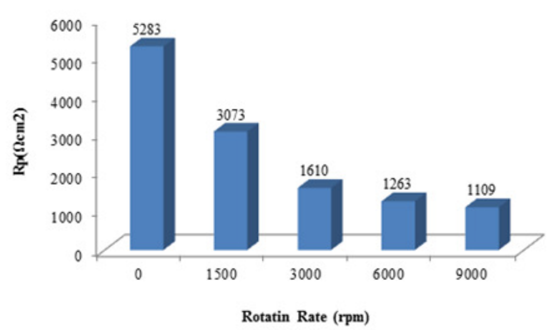

Fig.9: The changing polarization resistance at different rotation speed at 40 ° C

For continuing work (after that), Electrochemical impedance tests were performed at different rotation speeds of sample at 40 ° C that is shown in Fig. 8.

Based on this Fig., the diameter of electrochemical Nyquists curves has been reduced by increasing rotation speed so that, by further increasing rotation speed of the sample, percentage changing of polarization resistance has been reduced. These curves analyzed by appropriate equivalent circuit and Fig. 9 shows the polarization resistance changes at different rotation speeds at 40 ° C.

As you can see in this Fig., polarization resistance was decreased by increasing rotation speed. Notable thing in this Fig. compared with the results in table 3 is, in addition to polarization resistance changing to rotation speed, polarization resistance changing to temperature. Polarization resistance values were decreased by increasing temperature. This was observed in values of obtained from corrosion speed and its increasing. In general, corrosion rate is related to temperature according to Arrhenius equation and is enhanced by increasing temperature.

4. Conclusion

In this paper, from all of tests performed on C95700 alloy have been received the following results generally. Surface of alloy becomes nobler by increasing rotation speed of the sample at room temperature. Corrosion enhanced from -416 mV to about - 330mV by increasing rotation speed.

This increasing potential is justified with formed passive film on the surface. On the other hand, corrosion rate density is enhanced from 12.6μA/cm^2 to 57.8μA/cm^2 by increasing rotation speed. This corrosion rate increasing represents the formed film on the surface isn't protective and does not create a barrier versus corrosive ions. By increasing rotation speed, values of corrosion rate density enhanced greatly and increased from 13.1μA/cm^2 to 716μA/cm^2. Corrosion rate density increased by increasing rotation speed at room temperature, but increased sharply at 40 ° C. This indicates that the effect of sample rotation was greater at higher temperatures and was increased corrosion rate more.

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