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KOROZYON BİLİMİ VE MÜHENDİSLİĞİ
CORROSION SCIENCE AND ENGINEERING

THE INFLUENCE OF TEMPERATURE, pH AND PHOSPHATE ION (PO_4^{-3}) ON DISSOLUTION AND PASSIVATION OF BRASS

Güray KILINÇÇEKER*
Mehmet ERBİL

ABSTRACT

The influence of temperature (293 K, 313 K, 333 K and 353 K), pH (2.1, 7.2 and 12.3) and phosphate ions ($H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}) on dissolution and passivation of brass was studied in the sulphate solution. The electrochemical-three electrode-technique was employed. The cathodic and anodic current-potential curves were obtained by starting from the corrosion potential measured against SCE and polarizing it first in cathodic and then in anodic direction. According to the experimental results, the passivation of brass is succeeded at pH of 7.2 and 12.3, in medium containing SO_4^{2-} + PO_4^{3-} at all temperature. It should be expected that brass surface at pH = 12.3 are covered with ZnO, $Zn(OH)_2$, $Zn_3(PO_4)_2$ and small amount of Cu_2O, $Cu(OH)_2$, $Cu_3(PO_4)_2$ compounds. The anodic polarization curves of brass in the solution containing sulphate and sulphate + phosphate ions at pH=2.1 exhibit a broad potential region where Zn(II) soluble species are produced in the range from 293 K to 353 K. Brass was found not to be able to passivate when the medium contains only SO_4^{2-} ions, however it corrodes readily at pH=2.1, with and without PO_4^{3-} ions.

PİRİNÇ'İN PASİVASYONUNA VE ÇÖZÜNMESİNE SICAKLIK, pH VE FOSFAT İYONUNUN (PO_4^{3-}) ETKİSİ

Pirinç'in sülfatlı ortamlardaki pasivasyon ve çözünmesi üzerine, fosfat iyonlarının ($H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}) etkileri farklı sıcaklık (293 K, 313 K, 333 K ve 353 K) ve pH'larda (pH=2,1; 7,2 ve 12,3) araştırıldı. Çalışmalarda elektrokimyasal üç elektrot tekniği uygulandı. Pirinç, standart kalomel elektroda (SCE) karşı ölçülen korozyon potansiyelinden itibaren önce katodik sonra da anodik yönde polarizlenerek akım-potansiyel eğrileri elde edildi. Deneysel sonuçlara göre; pirinç, pH'ın 7,2 ve 12,3 olduğu SO_4^{2-} + PO_4^{3-} iyonlarını içeren ortamlarda tüm sıcaklıklarda pasifleşmektedir. pH'ın 12,3 olduğu koşullarda; pirinç yüzeyi, ZnO, $Zn(OH)_2$, $Zn_3(PO_4)_2$ ve küçük miktarlarda oluşan Cu_2O, $Cu(OH)_2$, $Cu_3(PO_4)_2$ bileşikleri ile örtülmektedir. Pirinç'in anodik polarizasyon eğrilerinden; pH=2,1'de, her iki ortamda da sıcaklık arttıkça (293 K→353 K)Zn(II) iyonları artmaktadır. Pirinç'in pH'ın 2,1 koşullarda, sade SO_4^{2-} iyonu içeren ortamlarda pasifleşmediği bulundu. Bununla birlikte, pirinç pH=2,1'de hem SO_4^{2-} hem de SO_4^{2-} + PO_4^{3-} iyonlarını içeren ortamlarda kolayca korozyona uğramaktadır.

1. INTRODUCTION

The electrochemical behaviour of copper and/or zinc has been studied extensively in alkaline and slightly alkaline solution[1-2]. It is well known that passive films formed on pure copper generally consist of duplex structure; an inner Cu_2O and an outer CuO layer, or hydrated copper oxide layer. The composition of these phases are dependent on the solution composition and polarization conditions[3-7].

Most of the studies conducted on the electrochemical behaviour of Cu-Zn alloys have centred on stress corrosion cracking and dezincification[8-10]. However, it has also been shown, that the passive layers formation on CuZn alloy in neutral and alkaline solutions consist of a complex combination of $ZnO \cdot xH_2O$ and CuO_2/CuO phases by using electrochemical and surface analysis techniques[11-12].

There have been reported that the heat exchange of the passive films formed on Cu-Zn alloys causes change in the passive behaviour of the electrodes[13-21]. For example, Dennis[14] showed that, Cu_2O formed on the copper surface and it reduces the passivation rate of the metal. The weight loss of copper in H_2SO_4 solutions has been measured by Deslouis et al.[15] and found that the weight loss of copper was high. In the same conditions Cordeiro[16], has also done the impedance measurments of bulk Cu_2O, showed that the charge transfer resistance is decreased considerably. In another reports, it has been shown that the passive layer on Cu-Zn alloys become more resistant [17, 18].

In the case of pure zinc, it

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has been shown that leads to an increase of the corrosion rate in sulphate + chloride containing solution[19-21] and in alkaline solution also[22-27]. In general, passivity breakdown depends strongly on the composition of the alloy, the aggressive environment and temperature. However, in contrast to other metals and alloys, little is known about the influence of temperature on the passivation and corrosion of brass[26-57].

The objective of the present work was to analyze the influence of temperature on dissolution and passivation of brass in the solution 0.1 M Na_2SO_4 as supporting electrolyte without/and with 0.1 M Na_3PO_4 addition, at different pH (2.1, 7.2 and 12.3), at the temperature range from 293 K to 353 K and to postulate an appropriate metal dissolution mechanism.

2. EXPERIMENTAL

Electrochemical behaviour of brass was investigated in solutions containing 0.1 M Na_2SO_4 as support electrolytes added with 0.1 M Na_3PO_4, at different temperatures (293 K, 313 K, 333 K and 353 K) and at different pH values (2.1, 7.2 and 12.3). To adjust pH values of the solutions H_2SO_4 and NaOH were used. Chemicals used to prepare solution in the experiments are of analytic purity (Merck), and freshly solution have been used in all experiment. Temperature adjustment of the mediums in question was accomplished with a thermostat type Nuve BM 101.

Electrodes used in the experiment were a brass bar (67 % Cu, 33 % Zn) with effective area of 1.15 cm^2 built in polyester, used as the working electrode, a Pt plate (1 cm^2) as auxiliary electrode and a standard calomel electrode (SCE) as the reference electrode. Polarization curves were obtained with the help of three – electrode technique (Potentiostat type Prt 10-0.5 Tacussel). Prior to each measurement, the surface area of working electrode have been subjected to finishing on a metal grinder with 400, 600, 800 and 1000 grade emery paper respectively (Dap-8 Struers) and were washed with distilled water and dried. Throughout the experiment, the solution was stirred with a magnetic stirrer at a constant speed and the pH value was monitored with pH meter (Edt Gp 353 Act pH). It took 2.5 hours before the system reached stable mix potential. From the moment that the stable potential was measured against the calomel electrode, the brass electrode was polarized with a scan rate of 6 mV/min, first in cathodic then in anodic direction upon which the current potential curves were drawn (ranging between –1.8V - +1.8V). Then the semilogarithmic polarization curves have been drawn, and the anodic and cathodic polarization slopes (respectively β_a and β_c) have been obtained.

3. RESULTS AND DISCUSSION

The experimental results are given in Figure 1–3 and in Table 1 and 2. Figure1 to 3 illustrate the curves obtained in mediums at pH 2.1, 7.2 and 12.3 respectively. In these figures working conditions are illustrated in alphabetical order (a) for 293 K, (b) for 313 K, (c) for 333 K and (d) for 353 K. Marked on each figure are symbols ▲ and • for solutions containing SO_4^{2-} and $SO_4^{2-} + PO_4^{3-}$ respectively.

The corrosion potentials of brass, measured in 0.1 M Na_2SO_4, 0.1 M Na_2SO_4 + 0.1 M Na_3PO_4 solution and the polarization slopes depending on the medium, temperatures and pH values are given in Table 1. The current density values measured at –1.000 V and at + 0.500 V are also given in Table 2.

3.1. Solution of pH=2.1

As it can be seen in Figure 1 a-d corrosion potentials which are in the range between –0.083 and –0.123 V in 0.1 M Na_2SO_4 solution change to –0.043 and –0.068 V after phosphate addition. The appearance of the polarization curves at such temperatures as respect 293 K, 313 K, 333 K and 353 K, being independent of phosphate contained in the medium, are quite close to each other.

After the values obtained from Figure 1 a-d and given in Tables 1 and 2 were compared with each other, the value $(\partial E_{cor}/\partial T)_{pH,c}$ was determined as $\cong -0.8\times10^{-3}$ V/K. Polarization slopes ranged between 0.059 and 0.127 V/dec in mediums containing only SO_4^{2-} ions whereas between 0.068 and 0.136 V/dec in $SO_4^{2-} + PO_4^{3-}$ solutions. No systematic variation exists in polarization slopes depending on temperature (Table 1).

The current densities chosen at a given anodic (+ 0.500 V) and a cathodic (-1.000 V) potential in mediums containing SO_4^{2-} ions at pH = 2.1 and 293 K were respectively 28 mA/cm^2 and –10 mA/cm^2, whereas the current values at increased temperature at –1.000 V went down to 17 mA/cm^2. The temperature dependency of current value is not systematic (Table 2).

Jinturkar et al.[17] pointed out that surface adsorption of sulphate ions at acidic mediums (pH = 0-3), being relatively low energy producing, does not inhibit conductance of anodic currents. Rebak and Galvele[18] point out that brass when polarized in anodic direction, in solutions containing phosphate

at relatively low acidic mediums (pH = 5), rather a poor coating is formed on the surface by phosphate ions; such coating is reported to be caused by $Zn_3(PO_4)_2$ compound. Moreira et al.[20] also points out that copper under influence of anodic polarization tends to dissolve in parallel with temperature increase in mediums with sulphate ions whereas sulphate adsorbtion ratio decreases. This conclusion is also supported by experimental results from our working conditions.

The composition of brass, which was used as the working electrode, was 67 % copper and 33 % zinc. Equilibrium potential of copper according to the Nernst equation is taken as: $E = E^o + RT/2F \ln a_{Cu}^{2+}$. In this equation E^o is 0.340 V and supposing Cu^{2+} ion concentration is about $\sim 10^{-6}$M, then E ≅ 0.163 V is obtained. Similarly for zinc, E ≅ -0.940 V can be obtained. Under these conditions, potential variation per unit temperature can be calculated as $(\partial E/\partial T)_{ai} = -5.95 \times 10^{-4}$ V/K theoretically. Then the corrosion potential deviation will be -0.012 V per 20°C. Experimental value of this potential deviation was determined as -0.016 V. Comparing the standard reduction potentials of copper and zinc with the corrosion potential of the alloy which was used as working electrode, it is concluded that the zinc composite corrodes selectively and the brass was found to exhibit the characteristic behaviour of copper[21]. Hence, in solutions of pH = 2.1, (Figure 1 a-d) brass is polarized to a more negative potential with respect to the theoretical equilibrium potential of copper and zinc, then the surface activity is enhanced. This outcome supports the idea that SO_4^{2-} and PO_4^{3-} ions being adsorbed poorly in 0.1 M Na_2SO_4 and 0.1 M Na_2SO_4 + 0.1 M Na_3PO_4 solutions, can not protect the surface[16, 22].

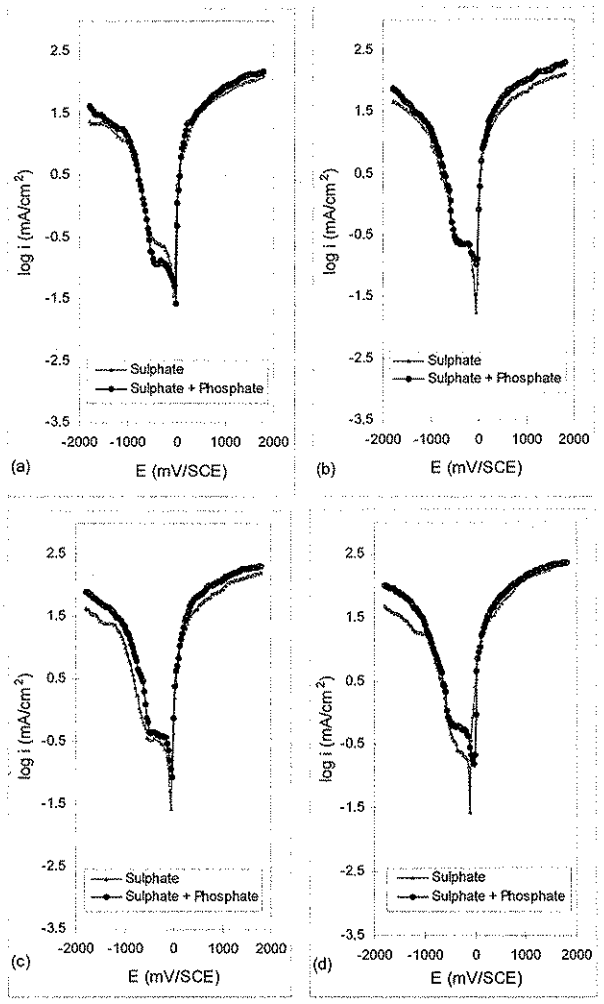


Figure 1. The Current Density-Potential Curves of Brass (67%Cu, 33%Zn) in 0.1 M Na_2SO_4 and 0.1 M Na_2SO_4 + 0.1 M Na_3PO_4 Solutions at pH=2.1 (a; 293 K, b; 313 K, c; 333 K and d; 353 K).
Şekil 1. *Pirinç'in, 0,1 M Na_2SO_4 ve 0,1 M Na_2SO_4 + 0,1 M Na_3PO_4 İçeren Ortamlarda pH=2,1'de Elde Edilen Akım-Potansiyel Eğrileri (a; 293K, b; 313 K, c; 333 K, d; 353 K).*

The following equations is written in the solution respectively,

$$[H_2PO_4^-] = K_1 \cdot [H_3PO_4] / [H^+] \; ; \; K_1 = 7.52 \times 10^{-3}$$
$$[HPO_4^{2-}] = K_2 \cdot [H_2PO_4^-] / [H^+] \; ; \; K_2 = 6.23 \times 10^{-8}$$
$$[PO_4^{3-}] = K_3 \cdot [HPO_4^{2-}] / [H^+] \; ; \; K_3 = 5.01 \times 10^{-13}$$

and the phosphate concentration with dependence of pH can be calculated with the equations as follows[23].

$$[PO_4^{3-}] = K_1 \cdot K_2 \cdot K_3 \cdot [H_3PO_4] / [H^+]^3$$
$$\log [PO_4^{3-}] = -22.63 + 3 \; pH \qquad (1)$$

PO_4^{3-} concentration in pH = 2.1 mediums was calculated as 5.53×10^{-17} mol/L by the equation 1. Since the theoretically calculated PO_4^{3-} ion concentration is very small the coverage by phosphate compounds is not expected.

The anodic polarization curves of brass in the solution containing sulphate and sulphate + phosphate ions at pH=2.1 (Figure 1) exhibit a broad potential region where Zn(II) soluble species are produced through a thin $ZnO \cdot xH_2O$ layer in the range from 293 K to 353 K. At constant temperature, this potential region moves positively as the zinc content in the alloy decreases[24], whereas the electrodissolution current increases with temperature (Table 2).

It can be concluded that the anodic layer formed at anodic potentials consist of copper oxides and

$ZnO \cdot xH_2O$. It should be noted that value of x determining the water content of the zinc oxide layer decreases as temperature is increased, as the $Zn(OH)_2$ species is easily dehydrated approaching the ZnO stoichiometry. The contribution of the electroformation of Cu_2O species to the anodic layer can be observed when the applied potential exceeds +0.250 V, whereas the electro-oxidation of Cu_2O to CuO takes place at E > +0.250 V[25].

Recently various mechanism of brass dissolution and passivation in aqueous solutions have been presented in the literature[10-13, 22, 24, 26, 36-57]. In these mechanisms, the effect multistep valance (Zn^I, Zn^{II}, Cu^I and Cu^{II}), the existence of several adsorbed intermediates (zinc oxides and copper oxides) and the formation of mixed zinc oxides and copper oxides are considered.

The copper ratio is higher than zinc in brass (67/33) but due to selective dissolution of zinc, at the surface copper enrichment take place more and more but the solution side of the metal/solution interface zinc ion enrichment occurs. Taking into consideration polarization slopes which we determined experimentally, at pH = 2.1, the dissolution mechanism of brass given below is suggested by us.

$$Zn_{(s)} + H_2O \rightleftharpoons (ZnOH)_{ads} + H^+ + e^- \quad (2)$$
$$(ZnOH)_{ads} \xrightarrow{r.d.s} ZnOH^+ + e^- \quad (3)$$
$$ZnOH^+ + H^+ \rightleftharpoons Zn^{2+}_{(aq)} + H_2O \quad (4)$$

$$Zn_{(s)} + (n)H_2O \rightleftharpoons Zn^{2+}_{(aq)} + 2e^-$$

Considering that reaction step 3 is rds and it controlls the dissolution of brass with reaction 2:

$$Zn_{(s)} + H_2O \rightleftharpoons (ZnOH)_{ads} + H^+ + e^- \quad (2)$$
$$(ZnOH)_{ads} \xrightarrow{r.d.s} ZnOH^+ + e^- \quad (3)$$

$$Zn_{(s)} + H_2O \rightleftharpoons ZnOH^+ + H^+ + 2e^- \quad (5)$$

According to the reaction 5 it is true that

$$\beta_a = (\partial\eta/\partial\log i_a)_{ai} = 2.303\ RT/2\alpha_5F \quad (6)$$
$$\beta_c = (\partial\eta/\partial\log i_c)_{ai} = -2.303\ RT/2(1-\alpha_5)F \quad (7)$$

If α_5 = 0.5, F = 96496 C, R = 8.314 J/mol K, T = 298, it is calculated that β_a and β_c = 0.059 V/dec. Considering that reaction rate can only be controlled by the reaction 3 it follows that

$$\beta_a = (\partial\eta/\partial\log i_a)_{ai} = 2.303\ RT/\alpha_6F = 0.118\ V/dec, \quad (8)$$
$$\beta_c = (\partial\eta/\partial\log i_c)_{ai} = -2.303\ RT/(1-\alpha_6)F = 0.118\ V/dec. \quad (9)$$

Table 1. Corrosion potentials (E_{cor}), cathodic (βc) and anodic (βa) polarization slopes of brass determined in different mediums, pH values and temperatures.
Çizelge 1. *Pirinç'in, Farklı Ortam, pH ve Sıcaklıklarda Belirlenen; Korozyon Potansiyelleri (E_{cor}), Katodik (βc) ve Anodik (βa) Polarizasyon Eğimleri.*

pH	Medium	Temperature (T/K)	E_{cor} (V/SCE)	β_c (V.dec^{-1})	β_a (V.dec^{-1})
2.1	SO_4^{2-}	293	-0.083	0.098	0.086
		313	-0.100	0.104	0.107
		333	-0.113	0.127	0.122
		353	-0.123	0.059	0.068
	$SO_4^{2-} + PO_4^{3-}$	293	-0.043	0.102	0.078
		313	-0.049	0.126	0.093
		333	-0.056	0.136	0.102
		353	-0.068	0.068	0.070
7.2	SO_4^{2-}	293	-0.065	0.050	0.081
		313	-0.124	0.111	0.112
		333	-0.133	0.095	0.096
		353	-0.191	0.060	0.067
	$SO_4^{2-} + PO_4^{3-}$	293	-0.057	0.112	*
		313	-0.105	0.118	*
		333	-0.118	0.121	*
		353	-0.168	0.058	*
12.3	SO_4^{2-}	293	-0.256	0.118	*
		313	-0.271	0.102	*
		333	-0.282	0.125	*
		353	-0.297	0.052	*
	$SO_4^{2-} + PO_4^{3-}$	293	-0.243	0.115	*
		313	-0.252	0.108	*
		333	-0.266	0.123	*
		353	-0.271	0.061	*

When we compare the variation range of polarization slopes experimentally determined by us namely (0.059 – 0.136 V/dec) with those theoretically estimated above, it appears that at pH = 2.1, the dissolution mechanism of brass is in accord with the reaction 3 and/or 2 and 3 timely. In the event that the surface is bare, the rate should only be controlled by reaction 2 and 3. As to the case where the reaction is controlled by reaction 3, this proves the presence of a coating layer, though thin, on the surface, which is most likely to be $Zn_3(PO_4)_2$ compound poorly soluble at pH = 2.1. In other words, the fact that anodic as well as cathodic polarization slopes determined at pH = 2.1 conditions are approximately 0.060 V/dec proves that dissolution rate of brass is controlled by reaction 5 while with polarization slopes appearing around 0.120 V/dec shows that the dissolution rate is controlled by reaction 3. As to the case where polarization slopes range between 0.060 and 0.120 V/dec, it follows that the mechanism is not controlled by only one step of reaction, which can be traced to the unstable coating layer on the surface.

3.2 Solutions of pH=7.2 and 12.3

Figure 2 (pH=7.2) and 3 (pH=12.3) show the polarization curves of brass in 0.1 M Na_2SO_4 and with 0.1 M Na_3PO_4. The presence of phosphate has a more profound effect on the rate of the anodic than the cathodic reaction. The anodic reaction is supported by the selective dissolution of zinc and subsequently the simultaneous dissolution of zinc and copper. The results show that at a certain anodic current, the potential increases (in the posi-

Table 1. Corrosion potentials (E_{cor}), cathodic (βc) and anodic (βa) polarization slopes of brass determined in different mediums, pH values and temperatures.
Çizelge 1. *Pirinç'in, Farklı Ortam, pH ve Sıcaklıklarda Belirlenen; Korozyon Potansiyelleri (E_{cor}), Katodik (βc) ve Anodik (βa) Polarizasyon Eğimleri.*

pH	Medium	Temperature (T/K)	- 1.000 V (mA/cm²)	+0.500 V (mA/cm²)
2.1	SO_4^{2-}	293	-10.698	28.521
		313	-10.959	36.352
		333	-12.003	42.512
		353	-16.956	51.743
	SO_4^{2-} + PO_4^{3-}	293	-12.956	37.833
		313	-15.739	53.655
		333	-22.435	65.392
		353	-24.000	67.484
7.2	SO_4^{2-}	293	-0.286	20.622
		313	-0.408	44.172
		333	-0.417	49.312
		353	-0.486	50.611
	SO_4^{2-} + PO_4^{3-}	293	-1.721	24.783
		313	-1.026	21.394
		333	-1.782	36.352
		353	-4.695	40.431
12.3	SO_4^{2-}	293	-0.347	10.000
		313	-0.365	10.872
		333	-0.478	17.301
		353	-0.486	31.222
	SO_4^{2-} + PO_4^{3-}	293	-0.173	0.213
		313	-0.208	0.262
		333	-0.539	0.412
		353	-0.721	0.682

tive direction) in the medium containing phosphate ions.

For example, when brass is polarized in the anodic direction (~0.000 V - ~ + 0.500 V) from corrosion potential, current densities grow bigger for both pH values in medium containing only SO_4^{2-} ions, while these current densities grow smaller in SO_4^{2-} + PO_4^{3-} solutions at both pH values. As seen in Table 2, in solutions with pH = 12.3 the current densities measured show an increase from 0.213 mA/cm² to 0.682 mA/cm² at conditions where temperature is increased from 293 K to 353 K. These current density values in solutions with pH = 7.2 are close to each other.

After making a comparison among the values given Figure 2 and 3 as well as in Tables 1 and 2, we found that $(\partial E_{cor}/\partial T)_{pH,c}$ variation of brass in solutions with pH=7.2 as ~ -2.0x10^{-3} V/K, while in solutions with pH=12.3 as ~ -0.8.0x10^{-3} V/K. As to anodic polarization slopes, there could be determined in mediums containing only SO_4^{2-} ions (0.081 – 0.112 V/dec). In polarization curves obtained as a result of anodic polarization of brass in SO_4^{2-} + PO_4^{3-} solutions no linear zone could be obtained. The change of those polarization slopes depending on the temperature is not of systematic character (Table 1).

It is stated by Kabasakaloğlu and et al.[41] that anodic polarization behaviour of brass in nearly neutral and alkali solutions (pH=7.2 – 9.8) containing SO_4^{2-} ions, vary depending on SO_4^{2-} ion concentration (0.05–1M) as well as on pH value of the medium. It is concluded that, the zinc ions resulting

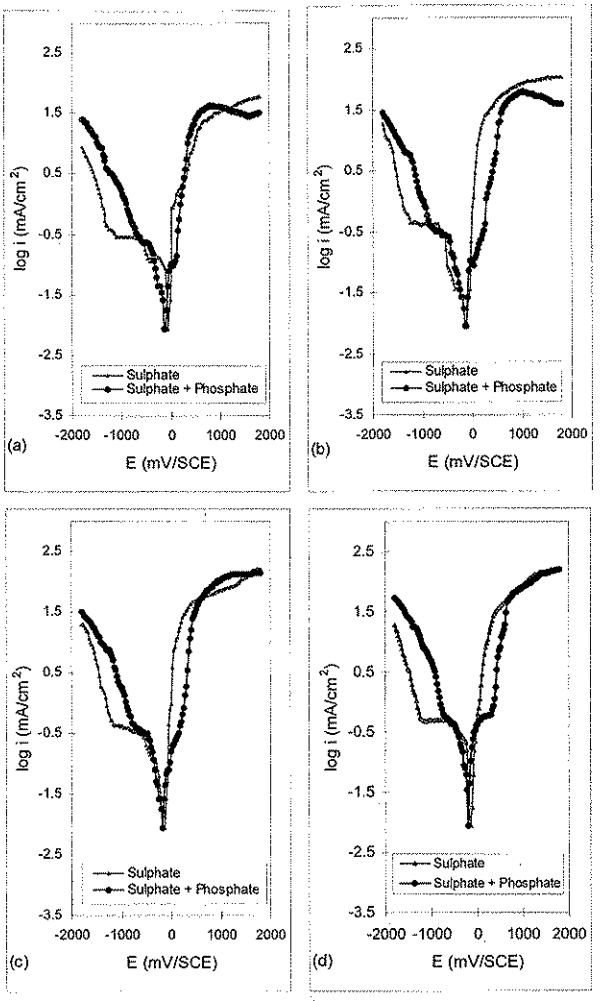


Figure 2. The Current Density-Potential Curves of Brass (67%Cu, 33%Zn) in 0.1 M Na2SO4 and 0.1 M Na2SO4 + 0.1 M Na3PO4 Solutions at pH=7.2 (a; 293 K, b; 313 K, c; 333 K and d; 353 K).
Şekil 2. *Pirinç'in, 0,1 M Na2SO4 ve 0,1 M Na2SO4 + 0,1 M Na3PO4 İçeren Ortamlarda pH=7,2'de Elde Edilen Akım-Potansiyel Eğrileri (a; 293K, b; 313 K, c; 333 K, d; 353 K).*

from selective corrosion of the zinc composite in the alloy react with the adsorbed SO_4^{2-} ions, on the surface, to form $ZnSO_4 \cdot 3Zn(OH)_2$ compound which covers the surface partly. This compound is also said to be seperated due to a dissolution–precipitation mechanism. However, taking into consideration polarization slopes and the polarization curves experimentally determined by us at pH=7.2 and 12.3 in mediums containing only SO_4^{2-} ions, it is clear that brass, even at these pH values, dissolves according to 2 – 5 mechanism (Figure 2, 3, Table 1, 2).

On the other hand, it is pointed out in the literature that in solutions with PO_4^{3-} ions OH^-, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} ions in the medium form ZnO, $Zn(OH)_2$, $Zn_3(PO_4)_2$, Cu_2O, $Cu(OH)_2$ and $Cu_3(PO_4)_2$

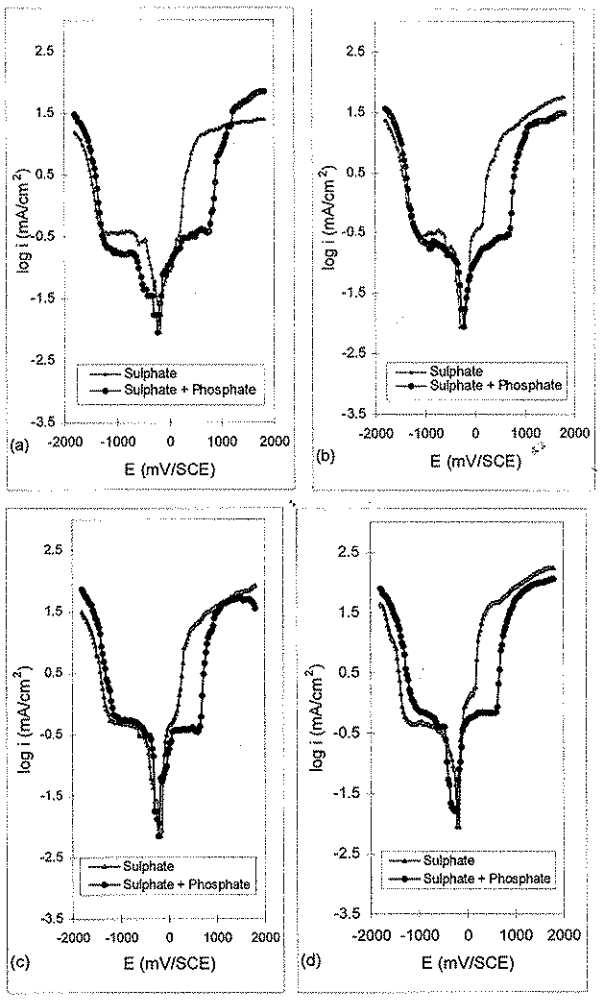


Figure 3. The Current Density-Potential Curves of Brass (67%Cu, 33%Zn) in 0.1 M Na2SO4 and 0.1 M Na2SO4 + 0.1 M Na3PO4 Solutions at pH=12.3 (a; 293 K, b; 313 K, c; 333 K and d; 353 K).
Şekil 3. *Pirinç'in, 0,1 M Na2SO4 ve 0,1 M Na2SO4 + 0,1 M Na3PO4 İçeren Ortamlarda pH=12,3'de Elde Edilen Akım-Potansiyel Eğrileri (a; 293K, b; 313 K, c; 333 K, d; 353 K).*

compounds of low dissolution characteristic on the surface and thus covering the surface, partially passivate the brass[10, 14, 19, 20, 24]. In the case of brass, the presence of zinc phosphate on the alloy surface is possible, for reasons related to the selective dezincification of brass and the highly insoluble nature of zinc phosphate[31-36].

Using the equation 1, the phosphate concentration at pH=12.3 is calculated theoretically as 0.1 mol/L, where the concentration, at pH = 7.2 should be 9.71×10^{-2} mol/L. It can be deduced that at pH = 12.3 PO_4^{3-} ion concentration suffices a complete passivation of brass while it does not at pH = 7.2 conditions. According to the experimental results, the potential shift at pH=12.3 is –0.016 V as the shift value is –0.040 V for pH=7.2, the temperature was identical for both pH's, 20°C (Figure 2, 3, Table 1 and 2). Since such potential deviation enhances the tendency for metal dissolution, sulphate and phosphate adsorption decreases, thus enhances dissolution of $Zn_3(PO_4)_2$ compound covering the surface of the metal, which accounts for partial passivation of brass at pH = 7.2 . PO_4^{3-} ions in sufficient numbers at pH = 12.3 medium even helps with passivation of brass. Moreover, this view is supported by a decrease in the deviation of corrosion potential to negative values depending on increased pH values. Hence it should be expected that a brass surface at pH = 12.3 is covered with ZnO, $Zn(OH)_2$, $Zn_3(PO_4)_2$ and a small amount of Cu_2O, $Cu(OH)_2$, $Cu_3(PO_4)_2$ compounds.

3.3. Cathodic Reactions

According to the literature, when a cathodic potential is applied to a system the expected cathodic reactions are oxygen ($O_{2(g)} + 4H^+ + 4e^- \rightleftharpoons 2H_2O$) and/or proton ($2H^+ + 2e^- \rightleftharpoons H_2$) reduction. Since the reversible electrode potentials (at 298 K, 1 atm) for these events are $E_{O_2/H_2O} = 1.228 - 0.0591$ pH and $E_{H^+/H_2} = 0.000 - 0.0591$ pH, O_2 reduction occurs at a 1.23 V more inert potentials than in the case with hydrogen. Reversible electrode potentials at possible cathodic events (O_2 and/or H^+) depending on pH value of the medium are respectively as follows :

1) For pH=2.1 $E_{O_2/H_2O} = 1.104$ V and $E_{H^+/H_2} = -0.124$ V
2) For pH=12.3 $E_{O_2/H_2O} = 0.501$ V and $E_{H^+/H_2} = -0.727$ V

With a view to explain polarization characteristics of copper basic polarization curves given in the form of Evans Diagrams were handled with a different approach put forward by Erbil[31] and are illustrated in Figure 4. Significance of each zone shown in Figure 4 is expressed as follows: Zones A and B shows possible corrosion potentials for copper, C and D shows possible corrosion potentials for zinc. Anodic reaction in points A and B illustrates dissolution of copper, on the other hand a cathodic reaction denotes a reduction of O_2 followed by hydrogen reduction. Anodic reaction in points C and D illustrates dissolution of zinc, on the other hand a cathodic reaction in point C reduction of hydrogen and point D illustrates reduction of oxygen followed by hydrogen reduction. When copper and zinc polarized in cathodic direction from corrosion potential, cathodic reaction rate shows a dissimilarities depending on the pH value of the medium.

The most remarkable difference is the slope β_c of cathodic polarization curves. When pH is

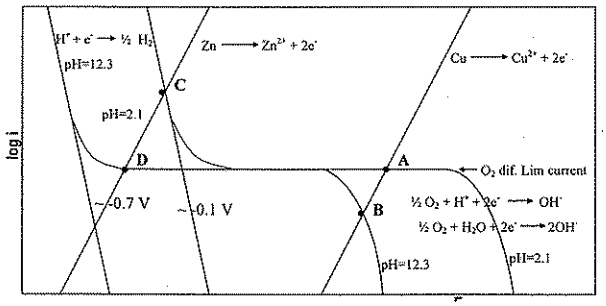


Figure 4. Principal Evans diagrams for copper and zinc.
Şekil 4. *Bakır ve Çinkonun Evans Diagramı.*

dropped from 12.3 to 2.1, it is possible that β_c may have any value ranging from ~ 0.120 V/dec to ∞. It should also be kept in mind that a cathodic reaction incorporates various mechanism depending on the values that β_c could gain. Regardless of the type of mechanism controlling the cathodic reaction, the dissolution rate of copper at pH = 2.1 always exceeds that of the dissolution at pH = 12.3 is about the same magnitude as diffusion limit current and the dissolution rate of zinc at pH = 2.1 always exceedes that of the dissolution at pH = 12.3 is greater than diffusion limit current. Furthermore, type of the metal particularly effects the rate of cathodic reaction. On the copper surface under cathodic polarization, oxygen reduction at pH = 2.1 occurs very rapidly followed by reduction of H^+ ions, where as oxygen reduction at pH = 12.3 develops very slowly after which reduction of H^+ ions can be started when a limit current is reached (Figure 4). In other words it should be acknowledged that, contrary to conventional belief, H^+ ions can be effective on cathodic reaction at higher pH values, while oxygen ions at lower pH values.

An increase in the limiting current considered as oxygen diffusion limiting current in paralle, during waiting period cannot originate from the oxygen itself. Thus an increased current may only be originating from dissolution of the film layer on the surface. It is expected that ZnO or $Zn(OH)_2$ ($pK_{Zn(OH)2}$ =16.7) film layer from according to the Rebak et al.[18]. But according to the Pech-Canul et al., $Zn_3(PO_4)_2$ ($pK_{Zn3(PO4)2}$ <<16.7) forms with formation of ZnO or $Zn(OH)_2$[14, 24, 26, 36-57].

Then the following possible mechanisms must account for the development of current potential curve in cathodic direction. Taking into consideration the polarization slopes experimentally determined by us at pH = 7.2 and 12.3, we suggest that zinc may be reduced according to possible mechanisms given below:

According to mechanism A:

$$Zn^{2+}_{(aq)} + H_2O \rightleftharpoons ZnOH^+ + H^+ \quad (2)$$

$$ZnOH^+ + e^- \xrightarrow{r.d.s} (ZnOH)_{ads} \quad (10)$$

$$(ZnOH)_{ads} + H^+ + e^- \rightleftharpoons Zn_{(s)} + H_2O \quad (11)$$

$$\beta_{c,A} = (\partial\eta/\partial\log|i_{,Zn2+}|) = -2.303RT/(1-\alpha_{10})F \cong 0.118V/dec \quad (12)$$

According to mechanism B:

$$Zn^{2+}_{(aq)} + H_2O \rightleftharpoons ZnOH^+ + H^+ \quad (2)$$

$$[Zn(ZnOH)] + ZnOH^+ + 2e^- \xrightarrow{r.d.s} [Zn(ZnOH)] + Zn_{(s)} + OH^- \quad (13)$$

$$Zn_{(s)} + ZnOH^+ + e^- \rightleftharpoons [Zn(ZnOH)] \quad (14)$$

$$\beta_{c,B} = (\partial\eta/\partial\log|i_{,Zn2+}|) = -2.303RT/2(1-\alpha_{13})F \cong 0.059\ V/dec \quad (15)$$

When the range of variation of polarization slopes experimentally determined (Table 1) is compared with above estimated values, it appears that at pH = 12.3 during reduction of zinc, the mechanism is under time controlling by reaction 10, at times by 13. Participation of reaction 10 in controlling the action denotes the presence of a covering layer on the surface, which must be $Zn_3(PO_4)_2$ compound having low solubility at pH = 12.3 conditions.

4. CONCLUSIONS

According to the results, it was found that both anodic and cathodic polarization characteristics vary depending on the composition of the alloy, pH value and the temperature. Findings can be summarized as follows:

- Brass is passivated in solutions SO_4^{2-} with and without PO_4^{3-} and pH=7.2 and 12.3, primarly, with the ZnO, $Zn(OH)_2$ and $Zn_3(PO_4)_2$ compounds formation following the corrosion of zinc composite in brass and then with the contribution of CuO and $Cu(OH)_2$ formation. It is concluded that in the absence of phosphate ions (for both pH values), the passivation is very difficult and the produced passive film. Also, the increasing temperature (293 K, 313 K, 333 K and 353 K) and lowering the pH (pH=2.1), brass is found to corrode readily, especially the zinc component of the alloy.
- Cathodic current at the whole pH range meets reduction of all corrosion products which do not dissolve on the surface particularly including oxygen. Taking into account the compound of the medium and the metal, though contrary to conventional belief, it should be considered that H^+ ions at higher pH values and oxygen at lower pH values can be effective on cathodic reactions.

- Comparing the theoretical equilibrium potentials of copper and zinc with the corrosion potential of brass, the zinc composite corrodes primarily and Zn^{2+} ions are formed. Probably, the resulting zinc ions form ZnO, $(ZnOH)_2$ and $Zn_3(PO_4)_2$ compounds reacting with OH^- and PO_4^{3-} ions present in the solution. It is estimated that these compounds are decomposed because of potential shift and then the reduction of the zinc ions present in the surface layer, an increases the limit current.
- It is suggested that protection processes of copper and its alloys for heating – cooling systems with orthophosphates (Na_3PO_4) be made at lower temperatures (293 K) and at higher pH values ($7.2 < pH < 12.3$). It is necessary to turn to other inhibitors in common with or without phosphates for protection applications of heating–cooling systems at higher temperatures.

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