ANODIC AND CATHODIC POLARIZATION IN A COPPER PYROPHOSPHATE ELECTROLYTE

(UDC 621.357.7)

B. L. Reizin and V. I. Lainer

Institute of Steels and Alloys

Translated from Zashchita Metallov, Vol. 2, No. 3,
pp. 339-343, May-June, 1966.
Original article submitted June 18, 1965

Pyrophosphate electrolytes have been investigated recently [1-4] in view of their replacing the poisonous and unstable cyanide electrolyte. These new electrolytes have a high scattering capacity and are economical.

The deposition of copper from pyrophosphate electrolytes has been studied by many investigators [5-8], but there is no agreement on the mechanism of the deposition of copper or the nature of cathodic polarization in these electrolytes. It should be noted that most of these investigations were made with electrolytes consisting essentially of $CuSO_4$ and $Na_4P_2O_7$ [5-7]. In our study we used, instead of $Na_4P_2O_7$, the more soluble and more conductive $K_4P_2O_7$, which allowed us to decrease the voltage on the bath, prevent the deposition of salt in the precathode space (which is enriched in P_2O_7 ions during the discharge of complex anions), and also use more concentrated electrolytes, thus increasing the rate of the process.

We investigated the influence of pH, temperature, $P_2O_7^{4-}$ concentration, and the influence of different additional elements on the passivation of the anode and on the cathodic process.

Anodic Process. The passivation of anodes is one of the disadvantages of pyrophosphate electrolytes for copper plating. The following equation is valid for the passivation of copper under the conditions investigated as well as for many cases of anodic passivation [9]:

$$(i - i_{cr})\tau^n = K, \quad (1)$$

where i_{cr} is the limit current density below which passivation does not occur; τ is the time of passivation at $i > i_{cr}$; K is a constant; and n can take different values between 0.5 and 3 [10].

To determine i_{cr} by Eq. (1) one must draw a straight line in i and $1/\tau^n$ coordinates and extrapolate it to $1/\tau^n = 0$. For an electrolyte composed of $[Cu^{2+}] = 1$ N and $[P_2O_7^{4-}]_{free} = 1$ N with the pH = 8.5 and t = 60°C the relationship is linear when n = 1. Then $i_{cr} = 2.25$ A/dm^2 and K = 3.71 if τ is expressed in minutes and i in A/dm^2.

The values of i_{cr} given above are slightly too high because they were obtained from nonsteady galvanostatic polarization curves (the samples were kept at each current density for 5 min).

A decrease of pH from 8.5 to 6 decreases the value of i_{cr} from 3 to 0.6 A/dm^2 because the concentration of $[CuP_2O_7]^{2-}$ increases with decreasing pH and copper pyrophosphate crystallizes at the anode:

$$[CuP_2O_7]^{2-} + Cu^{2+} \rightleftarrows Cu_2P_2O_7. \quad (2)$$

When the concentration of $P_2O_7^{4-}$ free is increased from 0.1 N to 1 N then i_{cr} increases from 2.1 3 A/dm^2. Further increase in the concentration of $P_2O_7^{4-}$ free has no significant influence on the value of i_{cr}.

An increase in the temperature from 20 to 80°C favors the removal of the products of the anodic reaction from the electrode and this increases i_{cr} from 0.8 to 3.5 A/dm^2 (Fig. 1).

In Fig. 1 the overvoltage measured with respect to a copper reference electrode is drawn along the x axis. The reversibility of this electrode was confirmed by special experiments and also in [7]. Figure 1 shows that in the electrolyte composed of $[Cu^{2+}] = 1$ N and $[P_2O_7^{4-}]_{free}^{2-} = 1$ N with the pH = 8.5 about the same value of overvoltage corresponds to the critical passivation current independently of

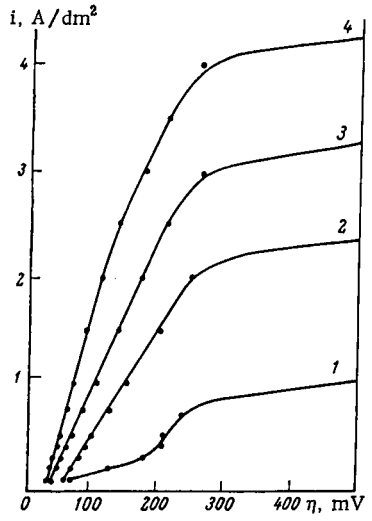

Fig. 1. Anodic polarization curves of copper in the following electrolyte: $[Cu^{2+}] = 1$ N, $[P_2O_7^{4-}]_{free} = 1$ N, with pH = 8.5. The temperature (°C) was: 1) 20; 2) 40; 3) 60; 4) 80.

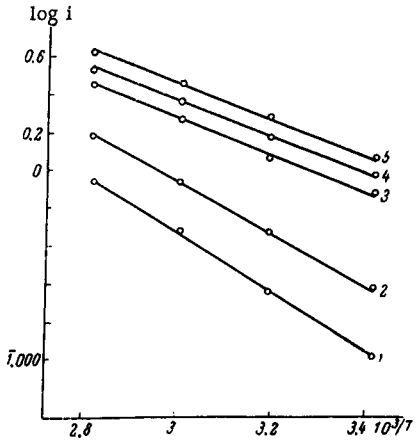

Fig. 2. Dependence of the logarithm of anodic current density of the reciprocal of the temperature of the electrolyte composed of $[Cu^{2+}] = 1$ N and $[P_2O_7^{4-}] = 1$ N with pH = 8.5 at different overvoltages (V): 1) 0.7; 2) 0.10; 3) 0.16; 4) 0.20; 5) 0.25.

the temperature. This makes it possible to determine the activation energy of the dissolution of copper at critical current densities from the slope of log $i_{cr} = f(1/T)$ curves. The activation energy turns out to be equal to 4900 cal/mole. Figure 2 shows the log $i = f(1/T)$ curves obtained at different overvoltages. At low overvoltages the effective activation energy is equal to 6820 cal/mole, which indicates the presence of both chemical and concentration polarization. An increase in overvoltage decreases the activation energy to 4900 cal/mole, and this corresponds to predominantly concentration polarization.

We used electrolytes containing $[Cu^{2+}] = 1$ N and $[P_2O_7^{4-}]_{free} = 1$ N with pH = 8.5 and t = 60°C to investigate the influence of additional elements commonly recommended as anodic depassivators (potassium oxalate, Rochelle salt, ammonium citrate). Beyond a certain concentration (usually about 20 g/liter) these additional elements induce a considerable decrease of i_{cr}. The most effective element was the oxalate ion. When the concentration of the oxalate ion is 50 g/liter then $i_{cr} = 5$ A/dm². The positive effect of these additional elements on the anodic process can be explained by the occurrence of additional substances capable of decreasing the activity of Cu^{2+} ions in the preanode layer, and this makes it difficult to reach the solubility product of $Cu_2P_2O_7$. The solubility of copper salts containing the anions of the additional elements mentioned above is higher than the solubility of $Cu_2P_2O_7$. It should be noted that the stability of the oxalate complex is lower than the stability of the pyrophosphate complex, and therefore the $[C_2O_4]^{2-}$: $[P_2O_7]^{4-}$ ratio in the preanode layer may turn out to be higher as compared to the volume of the solution.

Cathodic Process. Figure 3 shows that an increase in the concentration of $P_2O_7^{4-}$ ions in the electrolyte increases the cathode overvoltage considerably. Apparently, the rate of discharge of the hexavalent ion $[Cu(P_2O_7)_2]^{6-}$ is very low because of the presence of strong repulsion forces (the cathodic process occurs when the surface is negatively charged). Probably partial decomposition of the complex occurs under the influence of the double layer and this decomposition leads to the loss of one coordination group:

$$[Cu(P_2O_7)_2]^{6-} \rightleftarrows [CuP_2O_7]^{2-} + P_2O_7^{4-}. \quad (3)$$

The doubly charged anion can approach the surface of the electrode much more easily. The role of the value of the charge of the discharging ion was indicated in [11]. It was noted in this publication that when $S_2O_8^{2-}$ is discharged on mercury the dependence of the limit current on the potential ψ_1 obeys the equation for univalent and not divalent ions, and this is due to the fact that the $S_2O_8^{2-}$ ions can reach the surface of the electrode only by forming a univalent complex because of the rather large negative charge.

With increasing concentrations of $P_2O_7^{4-}$ anions (3) is displaced to the left, and as the result the

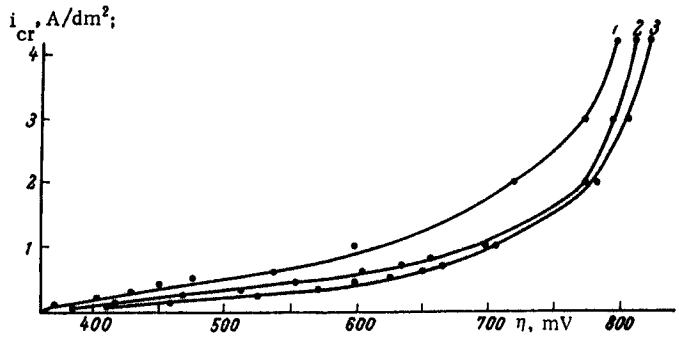

Fig. 3. Cathodic polarization curves in the electrolyte containing $[Cu^{2+}] = 1$ N with pH = 8.5 and t = 60°C and the following concentrations of $[P_2O_7^{4-}]_{free}$: 1) 0.1 N; 2) 1 N; 3) 5 N.

overvoltage increases. This increase is particularly great at low current densities. When i = 0.2-0.3 A/dm² the difference in the overvoltages in the electrolytes with concentrations of $P_2O_7^{4-}$ equal to 1 N and 5 N is 113-117 mV, while at i = 4 A/dm² this difference is 23 mV, i.e., the influence of the concentration of $P_2O_7^{4-}$ is manifestly stronger under conditions of significant chemical polarization. We shall discuss this point below.

An increase in the temperature from 20 to 80°C accelerates the deposition of copper within the whole range of current densities and this is probably due to the acceleration of the diffusion of complex anions toward the cathode and also to the facilitation of their discharge.

In the investigation of the influence of pH the desired values of pH (6-10) were obtained by adding KOH to pyrophosphoric acid which was obtained by prolonged heating of H_3PO_4 at 250-300°C. At pH = 6 the deposition occurs simultaneously with the precipitation in the electrolyte. A decrease of the pH below 8 induces the displacement of the polarization curve toward positive values. It was noted earlier that the concentration of the $Cu(P_2O_7)^{2-}$ ion increases with decreasing pH of the solution as the result of the reaction [12]:

$$[Cu(P_2O_7)_2]^{6-} + 2H^+ \rightleftharpoons [CuP_2O_7]^{2-} + H_2P_2O_7^{2-} \quad (4)$$

The $[CuP_2O_7]^{2-}$ ion is less stable and has a lower charge (this latter factor facilitates its entering the dense part of the double layer) than the $[Cu(P_2O_7)_2]^{6-}$ ion, and the deposition of copper is facilitated as the result. When pH = 8-10 the $[Cu(P_2O_7)_2]^{6-}$ ions are the essential constituents of the electrolyte, and therefore the variation of pH within this range of values has no effect on the deposition potential of copper. The electrolyte with $[Cu]^{2+} = 1$ N and $[P_2O_7]^{4-}_{free} = 1$ N with the pH = 8.5 was used to determine the activation energy (Fig. 4). The yield at the cathode at 20-80°C at current densities of 0.5-2 A/dm² is close to 100%. Therefore, we may, without committing any significant error, relate the whole overvoltage to the deposition of copper and introduce a correction only for hydrogen. At low overvoltages (0.3-0.35 V) the activation energy is 7770-6800 cal/mole; at high overvoltages (0.45-0.75 V) it is 5900 cal/mole This indicates a gradual transformation from mixed (concentration and chemical) polarization to concentration polarization. The predominance of concentration polarization is indicated also by the parallelism of the straight lines at high overvoltages.

We investigated the influence of additional elements used as depassivators on the cathodic process.

The addition of up to 20 g/liter of $C_2O_4^{2-}$ does not affect the magnitude of cathodic polarization. As the concentration of this ion is increased to 50 g/liter a considerable cathodic depolarization occurs up to i = A/dm² (at i = 1 A/dm² we have 116 mV). When the concentration of the oxalate ion is 100 g/liter then depolarization remains up to i = 4 A/dm². The decrease of polarization is due to the lower stability and the lower charge of the $[Cu(C_2O_4)_2]^{2-}$ anion as compared to the $[Cu(P_2O_7)_2]^{6-}$ anion.

A decrease in the concentration of Rochelle salt from 10 to 20 g/liter has no effect on the cathodic polarization. This is probably due to the fact that the instability of the tartrate copper complex is close to that of the $[Cu(P_2O_7)_2]^{6-}$ complex and the charges are similar. If we assume the presence of the

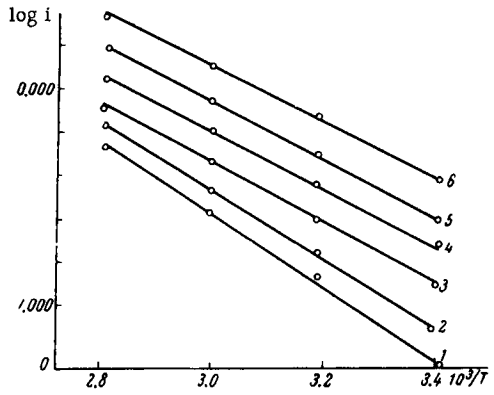

Fig. 4. Dependence of the logarithm of cathodic current density on the reciprocal of the temperature of the electrolyte consisting of [Cu] = 1 N and $[P_2O_7^{4-}]_{free}$ = 1 N with pH = 8.5 at different overvoltages (V): 1) 0.30; 2) 0.35; 3) 0.45; 4) 0.55; 5) 0.65; 6) 0.75.

$[Cu(OH)_2tart]^{2-}$ complex in the electrolyte then, since its instability constant is seven orders lower than that of the pyrophosphate complex, the deposition of copper is more difficult in spite of the smaller charge of this complex.

Ammonium citrate has a depolarizing effect on the cathodic process when its concentration is as low as 10 g/liter. This depolarization effect is the same as that resulting from the addition of the corresponding amount of ammonia, which indicates the participation of ammonia complexes in the discharge process. Ammonia complexes are less stable than the pyrophosphate complexes or citrate complexes and have a positive charge which considerably facilitates their reaching the surface of the cathode. Therefore, in spite of the small concentration of these complexes in the electrolyte they have a significant influence on the cathodic process.

CONCLUSIONS

1. The maximum acceptable anodic current density (i_{cr}) depends on the composition of the electrolyte, its pH, and its temperature. The optimum value of the pH is 8-9. With increasing temperatures from 20 to 80°C the value of i_{cr} increases from 0.8 to 3.5 A/dm^2.

2. With increasing concentrations of $P_2O_7^{4-}$ the anodic polarization decreases and the cathodic polarization increases.

3. At low overvoltages the cathodic polarization is mixed; at high overvoltages it is concentration polarization only.

4. Among the different anode depassivators, the most effective is the oxalate.

LITERATURE CITED

1. Rama Char, J. Scient. and Industr. Res., A19, 6, 265, (1960).
2. V.I. Lainer and B.L. Reizin, Zinc Plating from Pyrophosphate Electrolytes [in Russian], TsITÉIN, Moscow, (1965).
3. V.P. Persiantseva and P.S. Titov, Nauchn. dokl. vyssh. shk., Khimiya i khimicheskaya tekhnologiya 3, 584 (1958)
4. N.Ya. Fedotova, Candidate's dissertation [in Russian], Mos. in-t stali i splavov, Moscow, (1962).
5. S.V. Gorbachev and A.V. Izmailov, Zh. fiz. khimii, 26, 8, 399, (1952); 25, 1385, (1951).
6. A.L. Levin and E.A. Ukshe, Zh. fiz. khimii, 27, 1309, (1953).
7. A.T. Vagramyan and É.K. Yastrebova, Zh. fiz. khimii, 38, 2503 (1964); 38, 1551, (1964).
8. V.I. Lainer and N.A. Bardina, Izv. vyssh. shk., Tsvetn. metallurgiya, 3, 154, (1962)..
9. T.R. Hoar, in Coll: New Problems of Modern Electrochemistry, Edited by D. Bokris [Russian translation], IL, Moscow, (1962).
10. K. Schwabe and G. Diebz, Elektrochem., 62, 751, (1958).
11. V.G. Levich, Dokl. AN SSSR, LXVII, 2, 309, (1949).
12. J. Watte and A. Aaron, J. Chem, Soc., 75, 611, (1953).