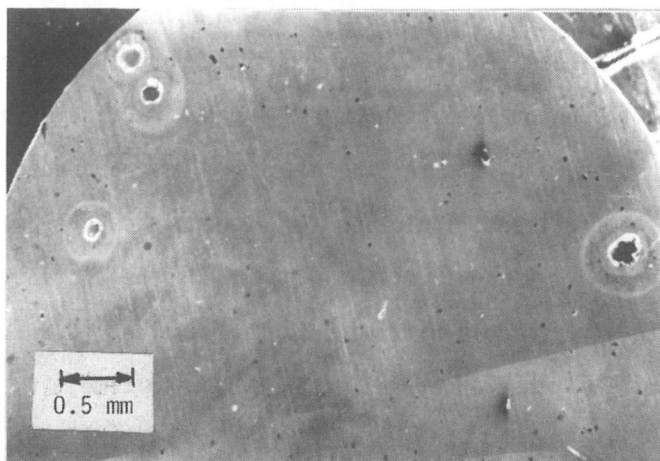


The value of pitting potentials and induction times decreases in presence of "Pseudomonas aeruginosa", therefore, the localized corrosion process are favored in presence of this one. This fact is possibility due at the formation of a biofilm in the passive layer containing.

b) Surface observations.-

Optical examinations of the specimens used in the anodic polarizations show a small number of macroscopical pits and a great number of microscopical pits (fig.2). SEM microphotograph exhibit a non hemispherical pits structures.



(Fig.2)

REFERENCES

- 1.- F. Mansfield and B. Litte; Corros. Science, 32, 247, (1991).
- 2.- C.C. Gaylarde and I.B. Beech; in Microbial Corrosion (Ed. C.A. Sequeira and A. K. Tiller), Elsevier Applied Science, 1988.

The corrosion and passivity of copper in aqueous solutions containing sodium perchlorate.

R.M.Souto, M.Pérez Sánchez, M.Barrera and S.González.
Departamento de Química Física. Universidad de La Laguna.
TENERIFE. ESPAÑA.
R.C.Salvarezza and A.J.Arvia.
Inifta. Universidad Nacional de La Plata. ARGENTINA.

1. INTRODUCTION

The electrochemical behaviour of copper in alkaline aqueous solutions was the matter of a number of studies which reveal the complex nature of the processes taking place in different potential ranges and how those processes are influenced by the solution composition. In general, the anodisation of Cu in aqueous solutions produces different copper oxides and hydroxides, and Cu(I) and Cu(II) soluble species. The onset of the passivity of Cu has been related to the formation of a duplex layer made of an inner Cu_2O layer and outer CuO layer. Depending on the nature of the anions present in the solution insoluble salts precipitate upon the passive layer, sometimes being also capable for blocking the growth of pits at the Cu surface. Conversely more soluble salts result in a more extensive attack including pitting corrosion of Cu.

The comparative electrochemical behaviour of Cu in alkaline solutions containing perchlorate, and carbonate and bicarbonate anions showed that the former behaves as an aggressive anion for Cu pitting, a fact which is not surprising after the great solubility of $\text{Cu}(\text{ClO}_4)_2$ in aqueous solutions.

2. RESULTS AND DISCUSSION

2.1. Voltammetric data.

Voltammograms run with 0.1M NaClO_4 at pH 9.1 exhibit on the potential going scan a well defined peak at -0.24V.(peak Ia) which is related to the Cu_2O electroformation. At potentials more positive than 0.02V. a remarkable current increase is observed. The negative scan shows a considerable hysteresis in the anodic current preceding a broad peak, X, at 0.0V. which partially masks other contributions. Thus, when the potential is reversed at values slightly more negative than 0.02V. (dash line), the small cathodic current peak . IIc can be

detected at -0.15V. and, simultaneously, peak X disappears. SEM observations of the electrode surface reveal that the large anodic current and the corresponding hysteresis is due to the nucleation and growth of pits on the Cu surface, whereas peak X is related to the electroreduction of soluble Cu(II)-species produced during the electrodisolution. Peaks II_c and I_c can be attributed to the electroreduction of CuO-Cu(OH)₂ to Cu₂O, and to the electroreduction of Cu₂O to Cu, respectively [1].

The voltammograms run at pH 11 show, in principle, the same features. However, Cu pitting occurs now at potentials more positive than 0.2V. Accordingly, the broad peak II_a related to the CuO-Cu(OH)₂ electroformation can be observed and the passive region becomes broader. Likewise, by setting the potential within the pitting potential region, the subsequent negative potential going scan comprises a relatively large electroreduction charge (peak X) which can also be attributed to the electroreduction of soluble species.

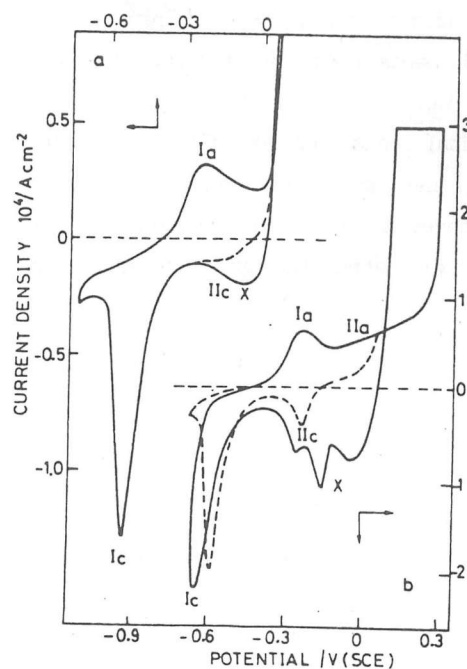


Fig. 1. Stabilized voltammograms of copper in 0.1 M NaClO₄ at 0.01 Vs⁻¹: (a) pH 9.1; (b) pH 11.0; 25°C.

The potentials of peaks I and II shift to more negative values with increasing pH in agreement with the thermodynamic predictions of the different Cu(0)/Cu(I) and Cu(0)/Cu(II) electrode reactions. It should also be noted that the protective characteristics of the passive layer at pH 11 are better than at lower pH. Furthermore, the reverse scan also shows a considerable hysteresis of the anodic current related to Cu electrodisolution.

2.2 SEM data.

SEM micrographs of the anodized electropolished Cu electrodes in the passive region show no differences with those of the blank (i.e. rounded copper grains with hemispherical micropits formed during the electropolishing procedure). By setting the potential in the pitting region cristallographic and hemispherical pits with a broad pit size distribution are seen on the metal surface. Corrosion products are formed around the pits, and at the highest positive potential these products are also observed inside the pits at pH 11.

The spacial distribution of pits formed on the Cu surface gives information about the character of the location of pits on the electrode surface. Assuming that pits are randomly distributed on the metal surface and considering that the probability P_m of finding the number of pits m in an arbitrary surface elements ΔS is given by the Poisson equation [2], data of Figure 2 are obtained,

$$P_m = N^m \cdot \exp(-N)/m! \quad (1)$$

where N is the average number of pits in the area ΔS . P_m is obtained by dividing the number of surface elements containing m pits by the total number of elements randomly distributed within the sample surface.

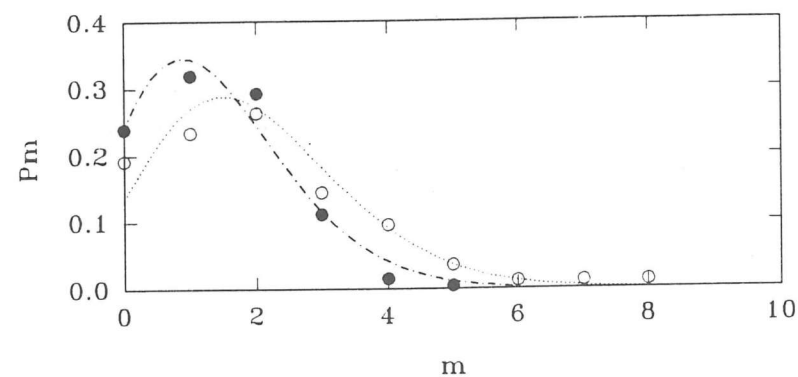


Fig.2. P_m vs m plot for (O) $E_s = 0.37$ V, pH 11.2; (●) $E_s = 0.18$ V, pH 8.6.

The circles in the figure denote the experimental probabilities and the solid line illustrates the theoretical distribution obtained by

using the equation. The good agreement between the theory and the experiment confirms the assumption of a random distribution of pits in the experimental systems. No marked influence of a pit on the nucleation of other pits is produced.

2.3. Potentiostatic current transients.

Potentiostatic current transients can be described in terms of a model comprising several currents contributions: the current density associated with the double layer charging, j_{dl} , the current density related to the passive film growth, j_p , the current density related to the base metal dissolution through the passive layer, j_d , and that related to the pitting process, j_c ,

$$j_t = j_d + j_p + j_c + j_{dl} \quad (2)$$

Double layer charging components quickly drops to zero in time, thus in the time domain of our study this contribution is negligible.

a) Passive region ($E_s < E_b$).

The growth of the passive layer can be regarded as the formation of a new face following an instantaneous nucleation and circular bidimensional growth mechanism under diffusion control. In this case, considering that the passive layer growth and the corrosion current are independent and separate processes occurring on the whole electrode surface, the rate equation is [3],

$$j_p = P_1 \cdot \exp(-P_2 t) \quad (3)$$

On the other hand, the rate of metal corrosion through the passive layer appears as the dissolution of tridimensional nuclei under diffusion control [4],

$$j_c = P_3 \cdot [1 - \exp(-P_4 t)] / t^{1/2} \quad (4)$$

b) Pitting region ($E_s > E_b$).

By prepassivating the electrodes for 100 s., j_p can be neglected, so

$$j_t = j_d + j_c \quad (5)$$

The base metal electrodisolution process can be modeled as the diffusion of Cu cations through the passive film. Assuming linear

diffusion:

$$j_d = P_1 \cdot t^{-1/2} \quad (6)$$

On the other hand, j_c can be assigned to the instantaneous nucleation and 3D conical growth of pits under charge transfer control [5],

$$j_c = P_2 \cdot [1 - \exp(-P_3 t^2)] \quad (7)$$

The present model applies to pits growing free of corrosion products exhibiting cristallographic feature. However, as the dissolution proceeds inside the pits, Cu salts can precipitate. These process should result in a change from a charge transfer control to a diffusional control for the pit growth. The precipitation of corrosion products inside the pits at the highest pH and potential values. In addition, a transition from hemispherical to cristallographic pits can be observed. Thus, when the precipitation occurs, the model precedingly described for j_c is not longer valid, then pit growth can be better described as a 3D growth under diffusion control [4].

$$j_c = P_4 \cdot [1 - \exp(-P_5 t)] / t^{1/2} \quad (8)$$

REFERENCES.

1. M.Pérez Sánchez, M.Barrera, S.González, R.M.Souto, R.C.Salvarezza and A.J.Arvia, *Electrochim.Acta*, 35(1990)1337.
2. R.C.Salvarezza, A.J.Arvia and A.Milchev, *Electrochim. Acta*, 35(1990)289.
3. W.Davison and J.A.Harrison, *J.Electroanal.Chem.*, 44(1973)213
4. B.Scharifker and G.Hills, *Electrochim.Acta*, 28(1983)879
5. M.I.Abyaneh and M.Fleischmann, *Electrochim.Acta*, 27(1982)1513