

Table 4 - The pitting potentials, E_p , for Al-W-Ta implanted alloys in 0.1M NaCl solution, without (A) and with (B) pre-exposure to an acid sulphate solution of pH 0.5.

Material	E_p / V (SCE) (A)	E_p / V (SCE) (B)
Al-W-Ta (40 KeV)	-0.101	+1.025
Al-W-Ta (150 KeV)	-0.325	-0.225

This seems to support the idea that some Ta is lost in acid media by dissolution through the film, which is probably a mixture of Ta_2O_5 and Al_2O_3 in proportions that would depend on potential amongst other factors.

Conclusions

- i) - In acid media, passivation of Al-W-Ta alloys produced by ion implantation yields a film containing presumably a mixture of Ta_2O_5 and Al_2O_3 .
The alloy behaviour depends on the solution pH: For pH 0.5, the sample reveals a stronger passivating tendency than for pH 3.
- ii) - Passivation in Al-W-Ta alloys seems to agree with the solute rich interphase model which requires that the solute forms a more protective passivating species than Al under conditions within occluded cells. I
It is thought that the role of Tantalum is two fold:
- contributes to the enrichment of the film in Ta_2O_5 ;
- acts as a reservoir of solute to be oxidized under occluded cell conditions, role thought also to be played by W.

Acknowledgments

To the British Council, UMIST and INETI for granting the means for the completion of this work. Also to CPCNM, Portugal, for ion implantations.

References

- [1] - M.Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, Second English Edition, NACE, Texas, 1974;
[2] - G.D. Davis, B.A. Shaw, B.G. Rees, M.Ferry, J. Electrochem. Soc., **140**, 951, (1993);
[3] - G.S Frankel, R.C.Newman, C.V.Jahnes, M.A. Russak, J. Electrochem. Soc., **140**, 2192 (1993);

LOCALIZED CORROSION OF COPPER IN NEAR-NEUTRAL SODIUM PERCHLORATE SOLUTIONS

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ABSTRACT

The effect of perchlorate ions on the electrochemical behaviour of copper in near neutral solutions was studied using cyclic voltammetry. Results showed that perchlorate ions do not interfere with the formation of the duplex oxide film on copper in the potential range before breakdown. In fact, results seem to be in agreement with the passivation model for Cu in mild alkaline solutions. There is a solubilization of the film that gives place to Cu (I) soluble species, that are collected at $-0.875 V$ (SCE). Solubilization of the film acidifies the interface and precedes breakdown with nucleation and growth of pits. Soluble species of Cu (I) and Cu (II), related to breakdown, were detected in the cathodic cycle.

INTRODUCTION

The anodic oxidation of copper has been the subject of numerous investigations, particularly in alkaline solution [1-23]. Oxidizing states have been identified by in-situ techniques such as rotating split ring-disc technique, ellipsometry, electron reflectance, photoacoustic spectroscopy, photocurrent, as well as by ex-situ spectroscopic methods such as XPS, ESCA, ion-scattering spectroscopy, etc. [10-13]. The oxidation cycle is been amply studied with the second oxidation stage involving the electroformation of a mixtures of copper oxides in the +1 and +2 oxidation states. Regarding the reduction cycle, the kinetics and mechanism is complex and still a matter of discussion. Some authors consider that the mechanism of the reaction involves the electroreduction of Cu (II) oxide to Cu (I) oxide prior to the electroreduction of Cu (I) to Cu^0 , whereas others claim that the electroreduction of Cu (II) oxide to Cu^0 occurs at more negative potentials that those where the former takes place. The participation of ageing of Cu (I) oxide and chemical reactions yielding new phase formation have been also suggested [10].

The potentials at which copper (I) and (II) are reduced depend on the thickness of the oxide and on the conditions of formation, nevertheless it is generally possible to identify the different species on copper surface by analyzing the characteristics of reduction.

Works in near neutral media are somewhat scarce. In this work an analysis of the cathodic cycle is used.

EXPERIMENTAL

The working electrode was made of high purity copper from Good Fellow Metals with an exposed area of 0.5 cm^2 . After mounting with epoxy resin the electrode and prior to every experiment the electrode was polished with emery paper up to 1000 grit, rinsed with water, cleaned with ethanol and finally dried with cold air.

Solutions were prepared from twice-distilled water and analytical grade chemicals. A conventional three electrode Greene cell was used throughout the work. Two platinum electrodes located symmetrically to the working electrode were used as counter electrodes. A saturated calomel electrode was used as a reference and placed in a separate compartment and connected to the cell via an external bridge with a Luggin capillary.

Conventional PAR equipment was used throughout.

RESULTS

Voltammograms for Cu in a 0.1 M NaClO₄ solution at room temperature and at different scan rates (*v*) were run. Potential limits were defined between -1.5 V(SCE) and +0.21V(SCE) to include breakdown. Before running the voltammograms a pre-polarization of 3 minutes at the cathodic limit was imposed with the objective of reducing surface oxides.

Two well defined anodic peaks related to the formation of Cu₂O and CuO/ Cu(OH)₂ at -0.300 and -0.030 V(SCE) respectively, were observed followed by a breakdown current with the reverse curve exhibiting the hysteresis typical of nucleation and growth of pits.

A number of cathodic peaks were observed with two of them, at -0.300 and -0.675 V(SCE), showing larger currents and corresponding to the reduction of CuO/Cu(OH)₂ to Cu₂O and Cu₂O to Cu⁰ respectively. Smaller peaks and shoulders were also observed at potentials of -0.825, -0.750, -0.150 V(SCE). Linear log-log relationship between the peak current density and the scan rate for all the anodic peaks in the voltammograms were drawn. For the anodic peaks the slope is ~0.7, indicating that the reactions in the corresponding potential domain are controlled by mixed kinetics, diffusional and surface processes.

The anodic oxidation of copper in sodium perchlorate solutions of pH 6.5 appears to be similar to oxidation of copper in mild alkaline solutions when pitting potential is not exceeded. Electroformation involves a base layer of Cu₂O formed via a solid-state process, it is suggested that transference of ionic species in the solid phase is rate controlling [14]. Regarding the participation of Cu²⁺, the reaction could happen in two stages: oxidation of Cu(I) to Cu(II) accompanied by oxidation of Cu(0) to Cu(II); at low sweep rates, the soluble product has time to leave the electrode by diffusion, at faster rates a layer of Cu(II) oxide is developed and the current is limited by solid phase formation.

In order to establish the relationship between the processes during the potential excursion in the anodic cycle and the various cathodic peaks a sweep reversal study was conducted. This results were discussed somewhere else[24].

Anodic to cathodic charge ratios for excursion potential in the sweep reversal experiments were also estimated. Values do not reached unity suggesting that the part of the soluble species are never recovered at the used scan rate. After Cu(II) oxide formation the ratio Q_a/Q_c stabilizes at ~0.5.

Figure 1 present a series of cyclic voltammograms run up to different potentials within the breakdown region in order to study in more detail the appearance of related peaks in the cathodic cycle when pitting corrosion is established. This is done with the objective of reducing the possibility of changing the characteristics of the oxide layers already studied since the oxide formed when using a potential step is thicker and rougher when compared with that formed by sweeping.

The first potential excursion up to +0.13 V(SCE) did not show hysteresis in the reverse cycle and exhibited only two cathodic peaks corresponding to peaks VI and VII in previous voltammograms. Cycling further up to +0.18V(SCE) hysteresis is not evident but an extra cathodic peak (VIII) is shown. It is to be noticed that peak VI and VII have suffered a displacement towards more cathodic potentials and peak current densities have increased more evidently for peak VI. At +0.20 V(SCE) hysteresis starts being evident and a shoulder to peak VII appears together with a small peak at 0.03 V. No alteration is noticed for peaks VI and VII with constant respective peak potentials and currents. Results suggest that peaks IV and VII" are related to pitting. At +0.21 V(SCE) hysteresis loop is well defined peak IV and VII" increase their current and peak V appears. Peak VII remains constant and there is a slight decrease associated to peak VI. When different resident times at 0.210 V(SCE) are allowed, peaks IV, V and VII" increase indicating their relation with the pitting process and with the presence of soluble species. In fact peak IV and V might be taken as a composite peak that contains two reduction processes with similar potentials associated to soluble species. Peak IV is associated to the breakdown region after the potential excursion into more anodic potentials gives way to hysteresis on the reverse scan.

Transient analysis is in progress.

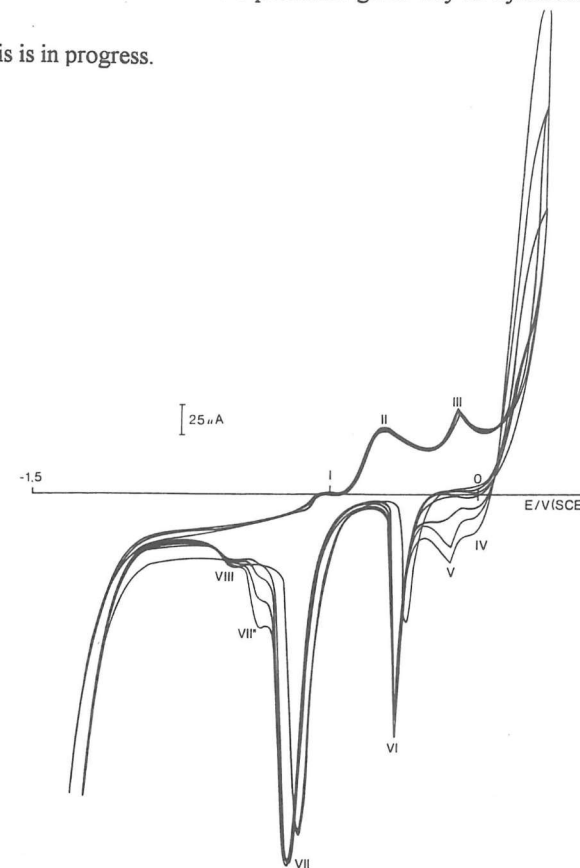


Fig. 1 -Cyclic voltammograms for the system Cu / 0.1M NaClO₄ run up to breakdown potential region at *v* = 25mV/s

CONCLUSIONS

- Cyclic voltammetry for the system revealed a complexity of peaks at low scan rates. The nature of the processes involves, specially those relates to the reduction cycle with oxidation states regarding Cu (I) and Cu (II) being separated and identified.
- Results showed that perchlorate ions do not interfere with the formation of the duplex oxide film on copper in the potential range before breakdown. In fact, results seem to be in agreement with the passivation model for Cu in mild alkaline solutions.
- Solubilization of the film occurs after Cu (II) formation. This is thought to be related to the formation of soluble Cu (I) complex associated to a cathodic peak formed at -0.874V(SCE).
- Soluble species of Cu (I) and Cu (II), related to breakdown, were detected in the cathodic cycle.

REFERENCES

- [1]- R. M. Souto, M. Pérez Sánchez, M. Barrera, S. González, R. C. Salvarezza and A. J. Arvia, *Electrochim. Acta*, **37**, 1437 (1992).
- [2]- M. M. Laz, R. M. Souto, S. González, R. C. Salvarezza and A. J. Arvia, *Electrochim. Acta*, **37**, 655 (1992).
- [3]- R. M. Souto, M. Pérez Sánchez, M. Barrera, and S. González, *Portugaliae Electrochim. Acta*, **9**, 43 (1991).
- [4]- J. Gomez Becerra, R. C. Salvarezza and A. J. Arvia, *Electrochim. Acta*, **33**, 613 (1988).
- [5]- U. Barsch and F. Beck, *Electrochim. Acta*, **35**, 759 (1990).
- [6]- S.Dong, Y.Xie, G.Cheng, *Electrochim. Acta*, **37**, 17 (1992).
- [7]- H. D. Speckmann, M. M. Lohrengel, J. W. Schultze and H. H. Strehblow, *Ber Bunsenges. Phys. Chem*, **89**, 392 (1985).
- [8]- M. T. San José, A. M. Espinosa, M. L. Tascón, M. D. Vázquez and P. Sánchez Batanero, *Electrochim. Acta*, **36**, 1209 (1991).
- [9]- E. M. Sutter, C. Fiaud and Lincot, *Electrochim. Acta*, **38**, 1471 (1993).
- [10]- M. Pérez Sánchez, M. Barrera, and S. González, R. M. Souto, *Electrochim. Acta*, **35**, 1337 (1990).
- [11]- H. H. Strehblow, H. D. Speckmann, *Werkstoffe und Korrosion*, **35**, 512 (1984).
- [12]- D. W. Shoesmith, S.Sunder, M. G. Wallace and F. W. Stanchell, *J. Electroanal. Chem.*, **143**, 153 (1983).
- [13]- I. T. E. Fonseca, A. Cristina S. Marin and A. C. Sá, *Electrochim. Acta*, **37**, 2541 (1992).
- [14]- D.W. Shoesmith, T.E. Rummery, D.Owen and W.Lee, *J. Electrochem. Soc.*, **123**, 790 (1976).
- [15]- J. Ambrose, R. G. Barradas and D. W. Shoesmith, *J. Electroanal. Chem.*, **47**, 47 (1973).
- [16]- M. R. Gennero e Chialvo, S. L. Marchiano, A. J. Arvia, *J. of Applied Electrochemistry*, **14**, 165 (1984).
- [17]- R. L. Deutscher, R. Woods, *J. of Applied Electrochemistry*, **16**, 413 (1986).
- [18]- Chong-Hong Pyun, Su-Moon Park, *J. Electrochem. Soc.*, **133**, 10, 2024 (1986).
- [19]- H. Shizhong, Z. Qibin, *9th European Congress on Corrosion*, Utrecht (1989).
- [20]- V. Ashword, D. Fairhurst, *J. Electrochem. Soc.*, **124**, 4, 507 (1977).
- [21]- B. Miller, *J. Electrochem. Soc.*, **116**, 12, 1677 (1977).
- [22]- I.T.E. Fonseca, A. C. Marin, *Corrosão e Protecção de Materiais*, **10**, 21 (1991).
- [23]- IN. A. Hampson, J. B. Lee and K. I. Macdonald, *J. Electroanal. Chem.*, **32**, 165 (1971)
- [24]- M.H.Simplicio, C.M.Rangel, Meeting of SPM, Aveiro, 1995

PORTUGALIAE ELECTROCHIMICA ACTA

Vol. 13, 1995

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