Figure 7 - Factors that affect the attainment of the critical pH inside the incipient pits

The reversible potential of tungsten is far greater than aluminium, which makes at least the thermodynamics of the alloy less favourable to dissolution. Assuming uniform dissolution of the alloy, its corrosion rate is dependent on the corrosion rates of the constituents and on the mole fractions they are present in the alloy. Owing to faster dissolution of the more reactive component, i.e. Al, the alloy surface becomes enriched in W so that the mole fraction of this element increases in the alloy, slowing down its rate of dissolution. Moreover the exchange current density for the hydrogen evolution reaction can be five orders of magnitude larger on W than on Al [14] which leads to a much higher rate of hydrogen evolution in the case of the W implanted alloy. This fact makes more difficult the attainment of the critical pH inside the pits, then contributing for retarding the establishment of stable pits.

REFERENCES

[1] A. H. Al-Saffar, V. Ashworth, A. K. O. Bairamov, D. J. Chivers, W. A. Grant and R. P. M. Procter, Corros. Sci., 20 (1980), 127

[2] P. M. Natishan, E. McCafferty and G. K. Hubler, J. Electrochem. Soc., 133 (1986), 1061

[3] W. C. Moshier, G. D. Davis, J. S. Ahearn and H. F. Hough, J. Electrochem. Soc., 133 (1986), 1063

[4] W. C. Moshier, G. D. Davis, J. S. Ahearn and H. F. Hough, J. Electrochem. Soc., 134 (1987), 2677

[5] P. M. Natishan, E. McCafferty and G. K. Hubler, J. Electrochem. Soc., 135 (1988), 321

[6] G. D. Davis, W. C. Moshier, T. L. Fritz and G. O. Cote, J. Electrochem. Soc., 137 (1990), 422

[7] B. A. Shaw, T. L. Fritz, G. D. Davis and W. C. Moshier, J. Electrochem. Soc., 137 (1990), 1317

[8] B. A. Shaw, G. D. Davis, T. L. Fritz, B. J. Rees and W. C. Moshier, J. Electrochem. Soc., 138 (1991), 3288

[9] R. C. Da Silva, M. F. Da Silva, A. A. Melo, J. C. Soares, E. Leitão and M. Barbosa, Nuclear Instruments and Methods in Physics Research, B50 (1990), 423

[10] J. C. S. Fernandes and M. G. S. Ferreira, Surface and Coatings Tech., 56 (1992), 75

[11] G.D. Davis, B.A. Shaw, B.J. Rees and M. Ferry, J. Electrochem. Soc., 140 (1993), 951

[12] M. F. Da Silva, M. R. Da Silva, E. Alves, A. Melo, J. C. Soares, J. Winand and R. Vianden, in Surface Engineering, eds. R. Kossowsky and S. C. Singhal, NATO ASI Series E85, Martinus Nijhoff (1984), p.74

[13] G.S. Frankel, R.C. Newman, C.V. Jahnes and M.A. Russak, J. Electrochem. Soc., 140 (1993), 2192

[14] J.M. West, "Electrodeposition and Corrosion Processes", Van Nostrand Reinhold Company, London (1970)

APPLICATION OF CYCLIC VOLTAMMETRIC TECHNIQUE ON DYE CONCENTRATION CONTROL IN AQUEOUS SOLUTIONS

M. de Fátima Esteves[1]*, M.T.Pessoa de Amorim[1], C. Comel[2]

[1]Departamento de Engenharia Têxtil, Escola de Engenharia, Universidade do Minho, P-4800 Guimarães

[2]Laboratoire de Chimie et Environnement, U.F.R. Sciences, Université d'Angers, F-49045 Angers Cedex

Abstract

This communication follows a previous work concerning indirect electrochemical reduction of dyes [1] and its application on dyeing control with sulphur dyes.

The study concerns the cathodic peak intensity variation with sulphur dye C.I. Leuco Sulphur Black 1 (Black Diresul RDT liq.) concentration, in the presence of a mediator, iron/triethanolamine (Fe^{III}/TEA), in alkaline media.

Key Words: Mediator redox couple, reversible electron-transfer, cathodic peak intensity, dye concentration

1.Introduction

Earlier cyclic voltammetric studies with glass carbon electrodes [1] showed a linear correlation between cathodic peak intensity and dye concentration. Experimental

conditions, namely, pH value and mediator electron-transfer potential [2] are on the limit of glass carbon application as working electrode material [3,4]. The observed electrode behaviour changes made the reduction peak detection more difficult [5].

In consequence of these facts, other materials were studied in order to be used as working electrodes. The results showed that copper allows a higher electron-transfer reversibility, as well as their reproducibility [5].

2.Experimental

Apparatus

A three-electrode cell was used: copper working electrode (Ø 4 mm, Radiometer) platinum counter electrode (Ingold), saturated calomel reference electrode, SCE (Ingold). This cell was connected to a HI-TEK PPR 1 wave generator and a HI-TEK DT 2101 potentiostat, as previous scheme [1,5]. A data acquisition program (Picolog) was incorporated in a connected computer.

Materials and Solutions

The mediator system was used in an earlier tested composition [5]. The cyclic voltammetric experiments were obtained at 25±0,1°C, with a [-800, -1200 mV] potential sweep and a 20 mVs-1 scanning rate.

3.Results and Discussion

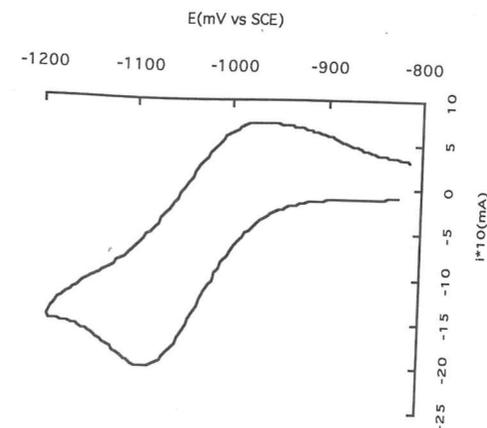Figure 1 represents the cyclic voltammogram for the mediator system Fe^{III}/TEA.

Fig. 1. Cyclic voltammogram for the mediator system
5 gL-1$Fe_2(SO_4)_3$.x H_2O ; 4 gL-1TEA ; 8 gL-1NaOH

In figure 2, mediator system voltammograms in the presence of dye are presented.
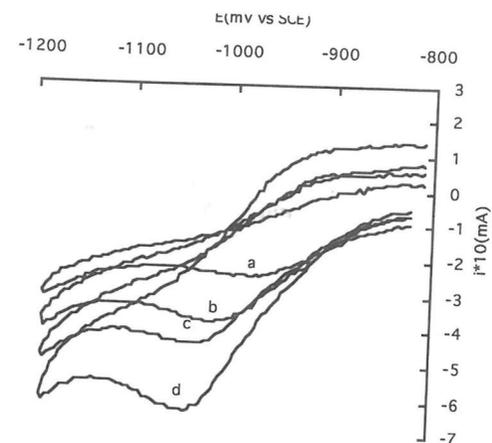
Fig. 2. Cyclic voltammograms for the mediator system in the presence of dye
$0.8^a, 1.6^b, 2.4^c, 3.2^d$ gL-1

Figure 1 analysis shows that, in these experimental conditions, Fe^{3+}-TEA/Fe^{2+}-TEA electron-transfer occurs reversibly, at a potential near to -1092 mV vs ESC [2].

In the presence of dye, figure 2, the anodic peak desappearence is detected, which agrees with a non electrodic mediator oxidation, due to the reduction of the dye into the solution[2]. An increase in cathodic peak intensity is also observed. This variation can be explained by an increase in mediator system action with dye concentration [2].

Figure 3 represents the relation between cathodic peak intensity and dye concentration, in the considered experimental conditions.
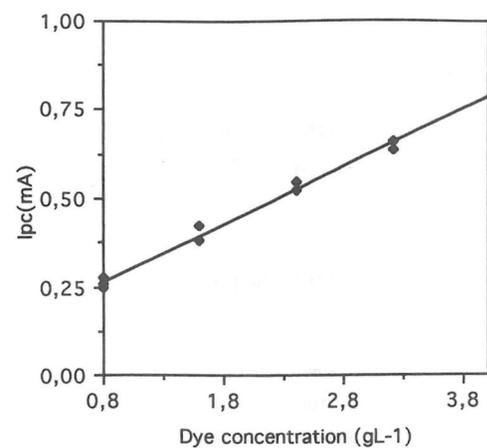

Fig. 3. Cathodic peak intensity and dye concentration relation

With least-squares method a correlation was established between cathodic peak intensity and dye concentration, with a coefficient of 0,990.

4.Conclusions

Considering all the presented experimental results we can conclude that, in the case of the studied sulphur dye, C.I. Leuco Sulphur Black 1 (Black Diresul RDT liq.) is possible to establish, in aqueous solution, a linear correlation between cathodic peak intensity and its concentration.

This relation seems to be independent of electrode material [2], being this one appropriate to pH and potential conditions.

These experimental results were obtained for aqueous solutions of the dye. The application of this technique to dyeing baths control will require a study with more complex solutions, of composition similar to those founded in dyeing processes to check the interference of the other chemicals products.

5.References

1-F.Esteves, M.T.Amorim, C.Comel, *4ª Conferência Nacional Sobre a Qualidade do Ambiente*, Lisboa (1994)

2-T.Bechtold, E.Burtscher, D.Gmeiner, O.Bobleter, *J. Electroanal. Chem.*, 306 (1991) 171.

3-EG&G Princeton Applied Research - Technical informations - Micro-Cell Accessories (1995) E4

4-D.T.Sawyer, A.Sobkowiak, J.L.Roberts, jr., *Electrochemistry for Chemists*, Jonh Wiley and Sons (1995) 208

5-M.Fátima Esteves, M.T.Amorim, *Portugaliæ Electroquímica Acta*, 14 (1996) 261-265