

REFERENCES

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INFLUENCE OF OXYGEN DIFFUSION ON THE MECHANISM
OF CORROSION PROCESSES UNDER THIN ELECTROLYTE FILMS

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In previous work (1), by using impedance measurements and zero resistance ammetry on Fe/Fe(ACM) multilaminar cells identical to those built by Kucera (2) and Mansfeld (3), a bilogarithmic correlation was found between the charge transfer resistance as estimated from the impedance spectra and the current density flowing between the two sets of electrodes of the cell. That law was valid for drying times over seven hours after a 1 mm thick sulphate electrolyte layer was placed on the surface of the cell, this simulating SO₂ polluted atmospheres (4).

However for low drying times (<7 hours) the above mentioned relationship was not followed, in spite of an increase in current density with time for periods over 3 hours. In Fig.1 results of the current density versus drying time are shown for concentrations corresponding to 50 µg SO₂/m³ of air. For other concentrations of SO₂ the same trends were found.

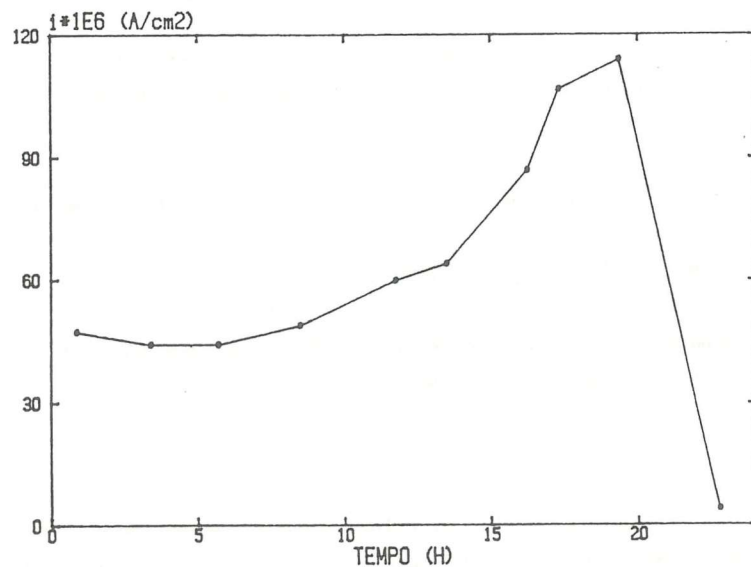


Fig.1 - Current density flowing between the two sets of electrodes of the multilaminar cell vs drying time in an atmosphere with RH = 85%.

The initial decrease of current with time ($t < 2$ hours) was interpreted on the basis of formation of a film on the metal surface.

The deviation the bilogarithmic law for the period of 3 to 7 hours was previously ascribed by the present authors (1) to a diffusion controlled process.

In the present work the variation of the cathodic limiting current for different thicknesses of electrolyte, i.e., corresponding to different drying times was studied.

In Fig.2 the cathodic polanzation plots are presented. They were obtained by using three electrodes multilaminar cells, a

modification of the previous mentioned cell, where a third electrode constituted by a steel plate was placed in parallel with the other two sets of steel plates (electrodes). Although this third electrode can not be considered a good reference it has been used by other authors (4,5) in identical situations where a conventional reference electrode is difficult to be employed.

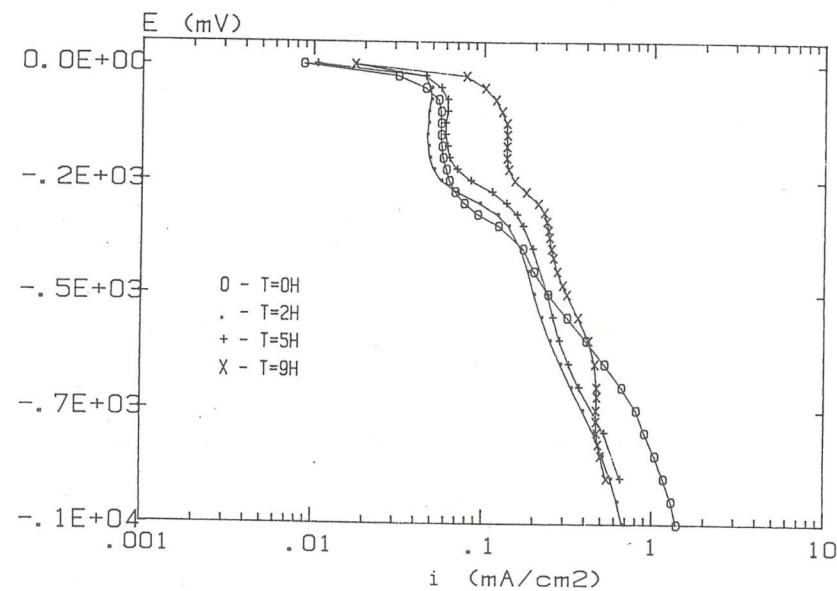


Fig.2 - Cathodic polarization plots obtained with the modified ACM, for drying times of 2,5 and 9 hours.

The results show that the limiting diffusion current slow down initially for times lower than two hours, then increasing for periods of time between 5 and 9 hours.

The increase of the diffusion limiting current i_L , with the electrolyte thickness, δ , is in agreement with the relationship

$$i_L = n F D \frac{C_{O_2}}{\delta}$$

where n is the number of electrons exchanged, D the diffusion coefficient of O_2 , and C_{O_2} the concentration of O_2 in the electrolyte. Identical results were established within certain limits by Rozenfeld (6) and Mansfeld (5), although they have found $i_L \delta = \text{Const}$, since the concentration of electrolyte was kept approximately constant during the experiments. In the present experimental conditions, the electrolyte changes to a more concentrated one with the drying time, the solubility of oxygen diminishes, thus a non constant value is to be expected for that product. This fact is observed and the results indicate during the period under study a control of the corrosion process by diffusion of the oxygen through the electrolyte layer.

References

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ELECTROCHEMICAL PREPARATION OF A COPPER TOOL-ELECTRODE UTILIZED IN ELECTRIC-DISCHARGE MACHINING

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1.INTRODUCTION

The Electric-discharge Machining (EDM) is an important industrial process.In the EDM process the preform or part to be machined is placed into a cell,as anode,opposite to a cathode or tool-electrode,which has the "negative" form of the model which we wish to reproduce.When the current supplied by a D.C. generator flows through the circuit,the preform is dissolved selectively into the bath,with a speed which is proportional to the current density in each superficial zone.This current density is stabilized uniformly while the part to be machined is jointed together facing the tool-electrode.

The electrochemical preparation of the copper tool-electrode utilized in electric-discharge machining(EDM),which will be used as cathode,consists of several paths: (a)making of a negative pattern of the model that we want to reproduce in the EDM process; (b) electrodepositing a thick copper coating,which properly stripped,will be utilized as tool-electrode(cathode) in the EDM process.

To make the copper tool-electrode the following operations must be carried through: (1)positive pattern surface preparation; (2) negative pattern preparation;(3) negative pattern activation; and (4) copper electrodeposition on activated negative pattern.

In the present work a method for preparation of a copper tool-electrode to be utilized as cathode in EDM process by means of the described paths is examined.

2.EXPERIMENTAL

2.1.Positive pattern preparation

The process was initiated by the cleaning of the positive pattern by means of a proper degreasing solution followed by a