CHARACTERIZATION OF PASSIVE FILMS ON STAINLESS STEEL BY PHOTOELECTROCHEMICAL AND IMPEDANCE TECHNIQUES^{*}

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ABSTRACT

Studies of passive film on AISI 304 stainless steel in alkaline medium (pH = 9.2) with and without Cl⁻ addition were carried out by using photoelectrochemical and impedance techniques. For the band gap energy of the oxide film values of 2.65 - 2.75 eV were estimated and for the flat potentials values between -430 and -530mV (SCE) were calculated. The variation of the capacitance of the film with the potential of its formation was also studied.

Key words: Passive films, Photoelectrochemistry, Impedance, Stainless Steel.

INTRODUCTION

The phenomenon of localized corrosion is intimately connected with the breakdown of the passive state. In this perspective, the knowledge of this state, through the characterization of the passive films, becomes essential to the understanding of the mechanisms leading to that type of corrosion.

In the past few years, several authors (1-6) have been envisaging passive films as semiconductors and characterizing them as so.

In this work, passive films are grown on stainless steel at several externally imposed potentials and their study is made by means of photoelectrochemistry and electrochemical impedance.

Portugaliæ Electrochimica Acta, 5 (1987) 59-69

^{*} Presented at the 3rd Meeting of the Materials Portuguese Society, (Materiais 87), Braga, April 1987.

EXPERIMENTAL

The study is made using commercial austenitic stainless steel (AISI 304), machined to produce a 4mm diameter cylinder. One of its bases is soldered to a copper wire and the set is inserted in an involving "Teflon" support, leaving exposed only the other base of the cylinder, which is then abraded with SiC paper up to 600 grit.

A three electrode cell is used, which contains a satured calomel reference electrode (SCE) and a platinum wire counter electrode. The experiments are performed at room temperature, in a nitrogen dearated solution with the following composition (pH 9.2).

Na2B407.10 H20	0.075M	
H ₃ BO ₃	0.05M	
NaC1	0-0.5 g/1	

The electrode is cathodically polarized to -lVolt^{*} during 10 minutes, after which the film is potentiostatically formed at the selected potential. The electrochemical measurements are initiated after 2 hours of film growth.

Photoelectrochemistry

The light source is a 150W xenon lamp. A monochromator (Jobin Yvon H25) and a light chopper (EG&G Brookdeal, 9479) are used (frequency 400 Hz), and the photocurrent is measured by means of a EG&G 5206 lock-in amplifier (Fig.1).

As the light source produces an amount of photons that is frequency dependent, the photocurrent has to be normalized with respect to the lamp emission, which is measured by means of a detector (Bentham DH-Si) and a current amplifier (Bentham 210E).

* All potentials are referred to the SCE.

The electrochemical cell has a quartz window to allow the radiation through.



Fig.1 - Set-up used for the photoelectrochemical and impedance measurements.

Electrochemical Impedance

The measurements are performed by applying to the cell sinusoidal potentials with 10 mV amplitude and 100 KHz - 1 mHz frequencies. At the high frequencies, the measurements are made using a lock-in amplifier (PAR 5206), while the algorithm of Fourier transform is used at the low frequencies. In this method, a harmonic series of potential sinusoids is simultaneously applied to the electrode, the result being then separately computed for each harmonic.

The control and analysis are made by an Apple microcomputer and adequate PAR software.

RESULTS AND INTERPRETATION

The passivity range is determined by a potentiodynamic sweep made at a rate of 1 Volt/hour (Fig.2).

The results show that the alloy is passivated between approximately -0.6V and +0.9V. At potentials around +0.5V the current slightly

— 63 —

increases originating a shoulder in the EvsI plot. This shoulder might be due to a structural and/or chemical transformation of the oxide, possibly due to the lack of stability of the chromium oxides at such anodic potentials. Based on the plot in Fig.2, the potentials of -0.2V, 0V, +0.3V, +0.575V and +0.8V were selected for the film growth.



Fig.2 - Polarization plot for AISI 304 in the buffer solution without C1 (pH = 9.2).

Photoelectrochemistry

Preliminar experiments were performed, aimed at determining the adequate working conditions.

Thus, several chopper frequencies were tried, and 400 Hz was chosen, because it provided good photocurrent intensities and stable phase angles (between current and illumination).

The photocurrent (I_{ph}) was also followed during the film growth, the results showing that I_{ph} increases as the film thickens, reaching an approximately steady value after about 30 minutes.

The band gap can be obtained from the photocurrent measurements, through the equation:

$$(h v \eta_q)^{2/n} = B (E_g - h v)$$

where h is the Planck constant, ν the frequency of the incident radiation, Ng the quantum yield, B a constant, and Eg the band gap. Because in this case the transition is indirect (3), thus requiring a phonon participation, n = 4. Eg can therefore be obtained by plotting $(h\nu\eta_{\rm fl})^{1/2}$ vs h ν . These plots, whose shape does not change with the working conditions, shows a maximum at about 340 nm, the photocurrent decreasing for larger wavelengths (Fig.3). The photocurrent intensity shows a dependence on the potential and the chloride concentration, although no consistent correlation has been detected so far. As already mentioned, the photocurrent depends upon the thickness of the oxide film, and this may be the explanation for those facts. Fig.3 also shows that both in the presence and in the absence of Cl⁻, the higher photocurrents come at +0.575V, which is the potential for which the passive current is higher (see Fig.2).



Fig.3 - Photocurrent plots for films formed at different potentials and NaCl concentrations (expressed in g/l).

- 62 -

The band gap values, which were determined from the extrapolation of the linear part of the curve to zero ordinate values, show a slight variation with the film growth potential (Fig.4), E_g becoming smaller as the potential becomes more anodic. This type of behaviour, although more pronounced, was obtained by other authors for ferritic





stainless steels (3), and reveals an influence of the applied potential on the composition of the passive film. This influence is greater than that of the chloride ion, at least for the low concentrations used (Fig.5).



Fig.5 - Band gap vs C1⁻ concentration (AISI 304, pH 9.2)

For the same type of experiments, made with high-purity iron in chloride free solutions (1), E_g was estimated as 2.67 eV, irrespective of the potential of film formation. This value is close to the one now obtained for 304 steel (2.66 eV at +0.8V without chloride). This behaviour is in accordance with Sato et al (9), who found experimental evidence for the formation of Fe-rich films at the high anodic potentials and Cr-rich films at less anodic potentials.

Electrochemical Impedance Measurements

The impedance plots obtained are typical of a difusion-controlled process (Fig.6), as should be expected for a passive state.

The plot of the capacitance determined for a 1 KHz frequency, as a function of the oxide growth potential (Fig.7), shows a decrease in the capacitance as the potential becomes more anodic, followed by a rise at about +0.8V. These results agree with those obtained by other authors (1,7,8). According to the literature (7), this rise of capacitance at the high anodic potentials could be ascribed to the adsorption of anions at the electrode surface, which in the present case would be borate anions.



Fig.6 - Impedance plot for a film formed at +0.575V in a Cl⁻ free solution (100 KHz - 0.55 Hz)



- 66 -

Fig.7 - Capacitance of the film (at 1KHz) for AISI 304 in a chloride free solution.

Another type of studies made by impedance measurements is based on the Mott-Schottky equation which, for a n-type semiconductor (3), can be written:

$$\frac{1}{c^2} = \frac{z}{\epsilon_0 \epsilon e N_D} (v - v_{fb} - \frac{kT}{e})$$

where

C = semiconductor capacitance

- ε_0 = vacuum permitivity (8.854 x 10⁻¹⁴ F.cm⁻¹)
- ε = dielectric constant
- e = electron charge

N_p= density of charge carriers

V = electrochemical potential

- V_{fb}=flatband potential
- k = Boltzmann constant
- T = absolute temperature

Thus, after the potentiostatic film growth, a potential sweep is made and impedances are measured at a constant frequency. From each of these measurements a capacity value is determined, assmuming $Z'' = 1/\omega C$, which is valid at the high frequencies (5).

The ${\rm C}^{-2}$ vs V plot (Fig.8) gives an estimate of the flatband potential, from the extrapolation of the linear part of the plot.



Fig.8 - Mott-Schottky plot for AISI 304, passivated at 0.3 V.

Although these experiments are still in an initial phase, the results so far obtained show a tendency for $V_{\rm fb}$ to increase with the chloride concentration and also with the anodic potential (Tables 1 and 2).

Table 1 - V_{fb} for AISI 304 (E = 0 Volt)

NaCl (g/1)	V _{fb} (V/ESC)
0	- 0.51
0.5	- 0.48
10.0	- 0.44

E (V/ESC)	V _{fb} (V/ESC)
0	- 0.48
+0.3	- 0.44
+0.575	- 0.43

These values of $V_{\rm fb}$ are more negative than those referred in the literature (1) for pure iron at the same pH: -380 to -400 mV.

CONCLUSIONS

The results show the interest of photoelectrochemistry and electrochemical impedance to the study and characterization of oxide films.

The values obtained for the band gap are in the range 2.65 - 2.75 eV, and decrease as the potential of film growth becomes more anodic. The E_g values also indicate the formation of Fe-rich films at the more anodic potentials, at which the chromium oxides become thermodinamically unstable.

The flatband potentials range from -530 mV to -430 mV (SCE), increasing with the chloride concentration and the film growth potential.

The confirmation and further interpretation of these results is expected during the progression of the study.

ACKNOWLEDGEMENTS

The authors thank the financial support granted by INIC-JNICT (Portugal) and CNRS (France).

REFERENCES

- |1| Faty, S.; These de Doctorat d'État, Université Pierre et Marie Curie (Paris), 1986.
- [2] Azumi, K.; Ohtsuka, T. e Sato, N.; J.Electrochem.Soc., <u>133</u>,1326 (1986).
- |3| Paola, A., Quarto, F., Sunseri, C.; Corr.Sci., <u>26</u>, 935 (1986).
- |4| Stimming, U., Schultze, J.W.; Electrochem.Acta, 24, 859 (1979).
- [5] Madov, M.J., Mckubre, C.H.; J.Electrochem.Soc., 30, 1056 (1983).
- |6| Wilhelm, S., Hackermann, N.; J.Electrochem.Soc., 128, 1668 (1981).
- [7] Okamoto, G.; Corr.Sci., 13, 471 (1973).
- [8] Ferreira, M.G.S., Dawson, J.L.; J.Electrochem.Soc., <u>132</u>, 760 (1985).
- [9] Sato, N., Okamoto, "Electrochemical Passivation of Metals", Comprehensive Treatise of Electrochemistry, vol.4, Plenum Press, N.York, 1981.

(Received 22 April 1987)