Electrochemical Properties of Passive Films on Stainless Steel

M. A. Catarino, A. M. P. Simões, M. G. S. Ferreira

D. E. Q. - Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisboa codex, Portugal

Passive films play a fundamental role in the protection of metals and alloys against corrosion. However, these films are generally prone to localized breakdown in the form of pitting corrosion. The characterization of passivity is therefore decisive for the understanding of the behaviour versus that form of attack.

In this work, the behaviour of AISI 304 stainless steel concerning passivity and pitting is studied as a function of chloride concentration and of temperature, by potentiodynamic polarization and electrochemical impedance spectroscopy, - EIS - in a borate / boric acid buffer solution (pH~9).

Potentials for transpassivity determined by potentiodynamic polarization and complemented by visual inspection have shown that the potential for pitting initiation is sensitive both to the conditions of temperature and chloride concentration. The results have shown that for low clhoride concentrations and low temperatures pits did not occur, critical conditions for the nucleation of pits having been determined. Under conditions for which pitting did not occur, potentials of transpassivation (between 0.85 V and 0.95 V, Fig.1) are due to the oxidation of the solution; these oxidation potentials were independent of the Cl^- concentration, but became less anodic as the temperature increased. The potentials for pitting nucleation (always below 0.75 V in Fig.1) becomes less anodic both with increasing Cl^- concentration and temperature.

For the temperature of 40° C, a logaritmic correlation was observed between the pitting potentials and the Cl^- concentration, in agreement with results obtained by other authors [1].

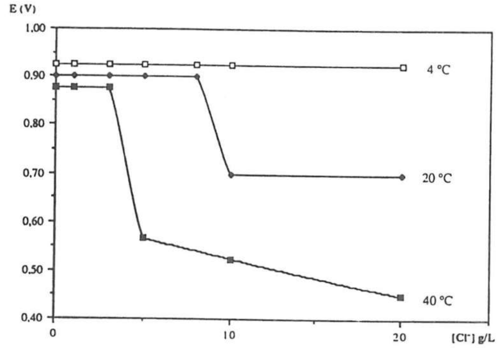

Fig. 1 - Potentials for transpassivation as a function of cloride concentration for three temperatures in a borate/boric acid buffer solution (pH ~ 9)

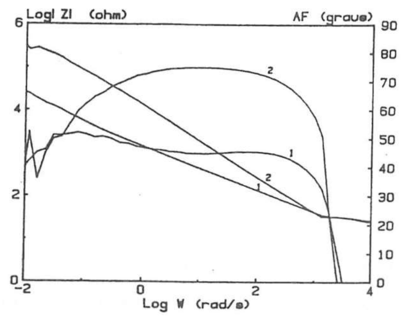

Fig. 2 - Bode plots for AISI 304 stainless steel in NaCl 10 g/L in a borate/boric acid buffer solution (pH ~ 9), T = 20° C: (1) with pits ; (2) passive

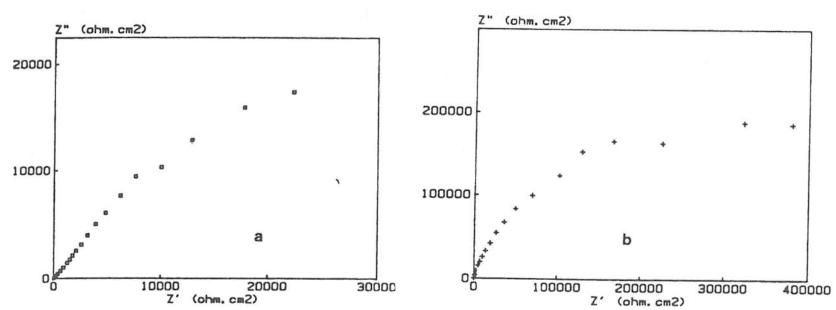

Fig. 3 - Nyquist plots for the situation in fig. 2
(a) with pits; (b) passive

EIS measurements made on samples at the open circuit potential after anodic polarization has clearly shown a different behaviour for pitted and for passive samples. Thus, the spectra of the passive samples reveal a capacitive behaviour, with a phase angle above 70º and a slope of about - 0.9 in the |Z| plot, the measured capacitance being close to 10 μF/cm2. The existence of pits on the surface is revealed by the presence of a second time constant at lower frequencies, which can be associated with the mass transfer process inside the pits. At high frequencies (~ 100 rad/s) there is a significant decrease in the impedance due to the fact that the measured capacitance is the sum of the passive and the pitted surface:

$$C_{measured} = (1-F)\,C_p + F\,C_{pit}$$

in which F is the fraction of attacked surface, C_p the capacitance of the passive surface and C_{pit} that of the pitted surface, according to the model by Mansfeld et al. [2].

After long exposure times at the open circuit potential the pits tend to repassivate , while the impedance spectra recover the shape observed in a surface free of pits. The development of the second time constant is always clearly observed in the Bode plots (Fig.2), in contrast with the low resolution in the Nyquist plots (Fig. 3).

[1] J-H. WANG, C. C. SU, and Z.SZKLARSKA-SMIALOWSKA, Corrosion Sci. **44**, 732 (1988)
[2] F.MANSFELD, S.LIN, S.KIM e H.SHIH, Materials Science Forum **44** e **45**, 83 (1989)