ELECTROCHEMICAL BEHAVIOUR OF AISI 304 STAINLESS STEEL IN BORATE/Cl^- SOLUTION.

Alda M.P. Simões and Mário G.S. Ferreira
Dept. de Engenharia Química, CECUL, Instituto Superior Técnico,
1096 Lisboa Codex, Portugal.

The surface processes occuring on AISI 304 stainless steel immersed in borate/boric acid solution (pH 9.2) were studied by linear polarization and a.c. impedance, in the presence and in the absence of Cl^- ion.

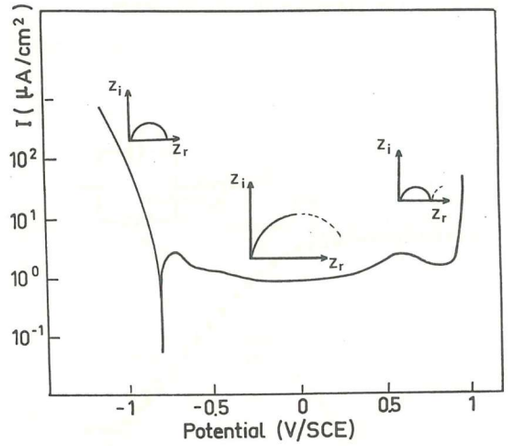


Fig. 1 - Linear plot for AISI 304 stainless steel in borate/boric acid solution and typical Nyquist plots for the different regions.

Fig.1 shows schematically the d.c. polarization plot, as well as the shape of the Nyquist plots obtained in the cathodic, passive and transpassive regions.

The cathodic and the transpassive impedance results are typical of charge transfer controlled processes, whereas the passive region is characterized by large diameter semi-circles with wide scattering at the low frequencies.

A) Cathodic Potentials

Typical Bode plots obtained in the cathodic region (-1.1V), as well as the equivalent circuit, are shown in Fig.2. The addition of 0.5g/l of NaCl does not significantly change the capacitance, but raises the value of the parallel resistance, meaning that the cathodic reaction

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

proceeds more slowly in the presence of the chloride.

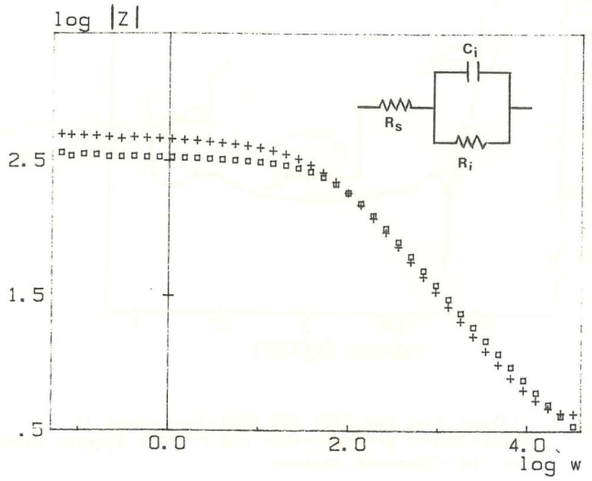


Fig.2 - Bode plots obtained at -1.1V, SCE
+ 0.5g NaCl/l
□ no NaCl

B) Transpassive Potentials

Transpassivity starts at about +0.9V (SCE), which is in the range of potentials for oxygen evolution.

The Nyquist plots show two semi-circles plus diffusion at the low frequencies (fig.4).

The small semi-circle at the higher frequencies in Fig.3 was proven to be due to the salt bridge used in the setup. The second semi-circle is sensitive to both the chloride addition and the anodic potential. Its diameter becomes smaller as the potential becomes more anodic, which is a symptom of the acceleration of the anodic reaction. The presence of Cl^- in a small concentration (0.5g/l) provokes an enlargement in the semi-circle, which can be explained by some degree of inhibition of the anodic reaction by the chloride ion.

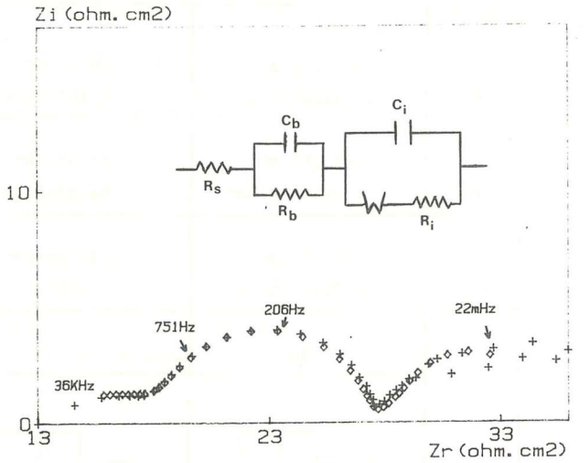


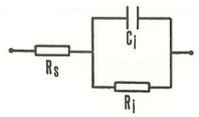
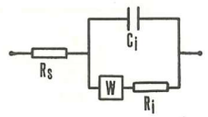
Fig.3 - Nyquist plot at +1.150V, without NaCl
+ experimental
◇ simulation

C) Passivation Potentials

The numerical simulations made for the passive region at 0V, 0.3V and 0.8V revealed the influence of a difusional process, only in the presence of Cl^-.

The values in Table I show that, in the presence of the NaCl, the measured capacitance rises about 30-40 $\mu F/cm^2$, the measured resistance decreases 1.25×10^4-2.6×10^4 $\Omega.cm^2$ and the depression angle increases from 16° to 21°.

TABLE I

V (SCE)		no Cl^-	0.5g NaCl/l
0V	C_i R_i	60 $\mu F/cm^2$ 3.25×10^4 $\Omega.cm^2$	90 $\mu F/cm^2$ 2×10^4 $\Omega.cm^2$
+0.3V	C_i R_i	62 $\mu F/cm^2$ 7.6×10^4 $\Omega.cm^2$	110 $\mu F/cm^2$ 5×10^4 $\Omega.cm^2$
+0.8V	C_i R_i	64 $\mu F/cm^2$ 4.3×10^4 $\Omega.cm^2$	90 $\mu f/cm^2$ 2.1×10^4 $\Omega.cm^2$
	β	16°	21°
			

D) Discussion

The results obtained for the cathodic and transpassive regions are compatible with inhibition of the surface reactions by the chloride ion, possibly due to specific adsorption (1).

In the passive region, adsorption of Cl^- on the surface normally increases the measured capacitance, due to the introduction of another capacitance in parallel in the equivalent circuit (2). The increase in the depression angle that occurs in the presence of chloride can also be explained by anion adsorption, leading to an increase in the heterogeneity of the film.

The results are not decisive in what concerns the process responsible for the diffusion impedance, but the following two are suggested:

- diffusion of Cl^- from the bulk of the solution to the oxide surface, and
- diffusion of metal-chloride complexes into the solution.

The main conclusion drawn from the data is that even very small Cl^- concentrations have a sharp effect on the surface reactions, by means of adsorption.

REFERENCES

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