CURRENT OSCILLATIONS IN AUSTENITIC STAINLESS STEEL INDUCED BY THE PRESENCE OF CHLORIDE IONS*

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Abstract—The conditions for current oscillations in austenitic stainless steel (AISI Type 303) in $1M H_2SO_4$ containing Cl⁻ ions are given. The periodic oscillations are produced in a close potential range determined at the active-passive transition region. It requires a non-homogeneous distribution of inclusions and carbides at the metal surface and a concentration range of Cl⁻ ion where active and passive areas coexist on the metal surface. The constraints at the surface determining these two regions are related to the Cl⁻ ion competitive adsorption and the local accumulation of corrosion products. Electrochemical data and SEM observations are correlated.

INTRODUCTION

UNDER certain conditions the potential region associated with the active-passive transition of metals exhibits an instability which is manifested through periodic oscillations of potential under galvanostatic conditions or of current under potentio-static conditions.^{1,2} These oscillatory effects have been particularly considered in relation to the anodic corrosion and passivation of pure polycrystalline metals in aqueous electrolytes.⁸⁻⁸ The same effects have been also reported in the pitting corrosion of different alloys, such as iron-chromium alloys in Na₂SO₄ + NaCl solutions,⁹ although in this case the phenomenology of the oscillatory effects has been considered without any further analysis of the influence of the different promoting variables.

The steady current oscillations observed in different stainless steels are closely correlated to the resistance of the materials to pitting corrosion. The current oscillations reflect the trend of the corroding system to vary between the two situations kinetically stable, namely, either that corresponding to passivity or that of anodic electrodissolution. The oscillatory phenomenon is strongly conditioned by variables linked to the corroding medium, to the electrical characteristics of the overall system and to the intrinsic properties of the metal. The latter appears through the influence of surface inhomogeneities on the type and kinetics of metal attack. The corrosion resistance of some impure metals and alloys may be appreciably changed through a controlled thermal treatment.¹⁰ The structure of the alloy is important in defining the protective characteristics of passive films. This is, for instance, true for austenitic structures of ternary alloys which are related to prior passive film protection.¹¹

This report attempts to study the conditions for the oscillation of current in different austentic stainless-steels immersed in $1M H_2SO_4$ under controlled external potentials, and the influence of Cl⁻ ion additions on the characteristics of the oscillatory phenomena. The electrical response of the system is correlated to the SEM configuration of the corroding metal surface.

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EXPERIMENTAL METHOD

Runs were made in a conventional three-compartment pyrex glass cell.⁶ The working electrode was a metal rod axially mounted in PTFE to serve as an active rotating disc of 0.385cm diameter. The composition of the different alloys is given in Table 1. The working electrode surface was polished to a mirror finish with successive grades of emery paper. The potential of the working electrode was measured against an SCE. The counterlectrode was a 25 cm³ Pt sheet. The electrolyte consisted of either 1M H₂SO₄ or 1M H₂SO₄ + x p.p.m. HCl ($500 \le x \le 50,000$). The electrolytic solutions were prepared from AR chemicals and triply distilled water. Runs were made under N₂ gas saturation at 25°C.

The potentiostatic stationary E/I curves of the different systems were recorded in the -0.50-1.0 V range to determine the potential range within which damped and undamped current oscillations are produced. They were obtained by stepwise changing the potential and making current readings 5 min afterwards. Then the current change was less than 1%/h.

The samples were examined by SEM using a Philips Model 500 EM and by electron microprobe analysis (CAMECA MS 46).

TABLE 1. CHARACTERISTICS AND PRETREATMENT OF THE DIFFERENT STAINLESS-STEEL ALLOYS

	Composition (%)						Thermal		
Standard	С	Mn	S	Cr	Ni	Мо	treatment	$E_{\rm cor}(V, SCE) E_{\rm pit}(V, SCE)$	
AISI 303	0.12	0.9	0.01	18	10	0.5		- 0.42	+ 0.80
AISI 304	0.05	1.3	0.03	18.5	9.5		10001100°C 5-20 min quenched in wat	- 0.39 er	+ 0.70
AISI 316L	0.03	1.7	0.03	17.5	13.5	2.7	1000-1100°C 5-20 min quenched in wat	er	

 $E_{\rm cor}$ = corrosion potential.

 $E_{\rm pit} = {\rm pitting potential}.$

EXPERIMENTAL RESULTS

The AISI Type 303 stainless steel, without any thermal treatment, exhibits a nonhomogeneous distribution of carbide components as reported in the literature.¹² Under these conditions the largest current oscillation effect is obtained when the potential is fixed at a definite potential (E_{os}) . The same material after thermal treatment shows a partial dissolution of carbides in the austenitic phase and simultaneously the magnitude of the oscillating current effect decreases to a great extent. The AISI Type 304 and 316 stainless steels thermally treated for 5 min at 1000-1100°C and immediately quenched in water show no potential range associated with the current oscillation even in electrolyte solutions containing 50,000 p.p.m. Cl⁻ ion. These results show a clear correlation between the surface inhomogeneities due to the minor components of the alloy and the oscillating current effect. From the pseudo-potentiostatic E/I curves (Fig. 1), the corrosion potential and the potential range of the damped and undamped oscillating current were determined. The E/I plane exhibits the usual active (I), passive (III) and transpassive (IV) regions. The active-passive transition region (II) is also indicated because it is closely related to the establishment of the oscillating current. At Cl⁻ ion concentrations > 3000 p.p.m. the rest potential becomes increasingly more negative as the Cl- ion concentration increases. Region I covers nearly a 0.2 V range and it is characterized by an initial Tafel line relationship



FIG. 1. Semilogarithmic plot of the potentiostatic E/I curves, at 25°C, (\odot) H₂SO₂ 1M, (\times) H₂SO₄ 1M + 3,000 ppm HCl. AISI Type 303 stainless steel without any thermal treatment.

whose slope decreases as the Cl⁻ ion concentration increases. Likewise, the maximal electrodissolution current also increases with the Cl⁻ ion concentration.

The active-passive transition potential and the transpassive region appears practically independent of the electrolyte composition. The pitting potential as determined in the conventional way decreases as the Cl^- ion concentration increases, which is in agreement with data reported by other authors.^{13,14}

The following description of the oscillating current is based on the behaviour of the AISI Type 303 stainless-steel without any thermal treatment (Fig. 2). The undamped current oscillations are associated with the critical potential value (E_{os}) which depends on the Cl⁻ ion concentration in 1M H₂SO₄ (when the Cl⁻ ion concentration exceeds 250 p.p.m.). At any Cl⁻ ion concentration associated with the establishment of the oscillating current the range of E_{os} is relatively small, covering approx. 0.010 V. Its value is always located at the initiation of the negative resistance portion of the E/I diagram and it becomes more positive as the Cl⁻ ion concentration increases. The average value of E_{os} increases with log C_{Cl^-} (Fig. 3), and the corresponding plot presents two linear portions, one at low concentration (< 6000 p.p.m.) with the slope approaching the 2.3 (RT/2F) ratio and another one at large concentrations (> 6000 p.p.m.) with a slope equal to the 2.3(RT/F) ratio. When E_{os} is shifted towards the negative potential values damped current oscillations are recorded (Fig. 4). The greater the damping, the larger the E_{os} shift exceeds the \pm 0.010 V range.

The undamped current oscillations are relatively simple, the maximum and



FIG. 2. Current/time displays at different HCl concentrations in 1M H₂SO₄ solution at 25°C. (a) 500 ppm HCl, $E_{os} = -0.115$ V; (b) 4000 ppm HCl, $E_{os} = -0.085$ V; (c) 8000 ppm HCl, $E_{os} = -0.0825$ V; (d) 15,000 ppm HCl, $E_{os} = -0.055$ V.

minimum current values and oscillating frequency depend on both the electrolyte composition and the hydrodynamic conditions prevailing in the system. Linear relationships result between either the maximum current (I_{max}) and the charge Q_T taking part in each oscillating current cycle, with the logarithm of the Cl⁻ ion concentration (Figs. 5 and 6). The slope x of the I_{max} vs log C_{Cl^-} plot is $0.25 \le x \le 0.33$. The oscillating current frequency (f) vs $C_{Cl^{-1/4}}$ also approaches a linear relationship (Fig. 7). The minimum current read of each undamped oscillation is practically independent of the Cl⁻ ion concentration. The frequency of the undamped oscillating current increases with the rotation speed of the working electrode (w), but no simple relationship is found (Fig. 8). Thus, at low Cl⁻ ion concentration the f vs w^{1/2} plot exhibits a break. There are two reasonable linear portions, the lower one approaching a straight line which goes through the origin of coordinates, and the upper one which gives a finite f at w = 0. The value of f at w = 0 decreases as the Cl⁻ ion concentration increases.

Microscopic observations

The as-received samples show the presence of Si, S, Mn and Al inclusions in a



FIG. 3. The dependence of $E_{\rm as}$ on log [HCl] concentration in 1M H₂SO₄ solution, 25°C.



FIG. 4. The damping effect on the current oscillations at different E_{os} values in $1 \text{ M H}_2\text{SO}_4 + 8000 \text{ ppm HCl}, 25^{\circ}\text{C}.$

longitudinal observation^{15,16} by electron probe. These results coincided with those given in the literature.¹⁵ Both the longitudinal and transverse metallographic observations by optical microscopy show a clear common localization of carbides and inclusions.

The SEM observations (Fig. 9) show a drastic localized metal corrosion in Region I giving an island-type surface image probably related to the non-uniform distribution of surface inclusions in preferential sites.^{17,18} A large density of secondary crystal is



FIG. 5. The dependence of I_{max} on log[HCl] concentration in 1M H₂SO₄ solution, 25°C.

also distinguished. Region II is characterized by the formation of large and deep pits. Apparently the corrosion products produce a constraint on the surface, separating active from passive areas at the metal surface through the formation of cavern-type structures. This peculiar distribution of the surface area is linked to the oscillating current effect. In Region III the metal is completely covered by a film of corrosion products. It comprises a low density of pits of small circular section surrounded by a relatively large amount of secondary crystals.

DISCUSSION

The results confirmed that pits in commercial austenitic stainless steels are initiated at mixed sulphide inclusions¹⁵ since sulphide ions are thermodynamically unstable in those materials yielding, in the $1 M H_2 SO_4$, micro areas of acid solution which assist pitting formation.^{17,18} The oscillation of the current requires certain well



FIG. 6. The dependence of the charge density per cycle per second on log[HCl] concentration in $1M H_2SO_4$ solution, 25°C.



FIG. 7. The dependence of the frequency of the periodic current oscillation on the chloride ion concentration in $1M H_2SO_4$ solution, $25^{\circ}C$.



FIG. 8. The dependence of the current oscillation frequency on $w^{1/2}$ in 1M H₂SO₄ solution, (\odot) 500 ppm HCl; (\times) 1500 ppm HCl; (\bullet) 8000 ppm HCl; 25°C.

defined conditions, namely, (i) a definite applied potential, (ii) a concentration of Clion exceeding a threshold value and (iii) a certain non-homogeneity of inclusions and carbides at the metal surface. The response is, then, sensitive to the hydrodynamic conditions, solution composition and characteristics of the electrical circuitry. These facts indicate that various processes are simultaneously involved in defining the conditions for the occurrence of the current oscillations.

In principle, periodic oscillations of any variable in chemical and electrochemical systems can be described in a relatively simple way by the Lotka-Volterra model corresponding to a generalized two body oscillatory mechanism,^{19,20} where the two competing variables in the present case can be ascribed to the covered metal (passive area, A_p) and to the uncovered metal area (active area, A_c). These areas are determined by physical constraints resulting either from a partial coverage produced by Cl⁻ ion adsorption or by the proper corrosion products. In this way, the corresponding differential equations can be written as

$$\frac{\mathrm{d}A_{\mathrm{c}}}{\mathrm{d}t} = F_1\left(A_{\mathrm{c}}, A_{\mathrm{p}}\right) \tag{1}$$

and

$$\frac{\mathrm{d}A_{\mathrm{p}}}{\mathrm{d}t} = F_2 \left(A_{\mathrm{c}}, A_{\mathrm{p}} \right) \quad . \tag{2}$$

The current fluctuations under controlled potential conditions are proportional to the fluctuations of the active and passive areas, respectively. Both the Cl⁻ ion and the corrosion products play a definite competing role in establishing the A_c/A_p ratio. Thus, the Cl⁻ ion threshold should be related to the minimum Cl⁻ ion concentration required for the anion nucleation at a metal active centre to initiate the metal electrodissolution. On the other hand, at a very large concentration of Cl⁻ ion, generalized attack of the metal occurs. Then, values of the A_c/A_p ratio which are compatible with the simultaneous validity of equations (1) and (2) should be achieved between the two above mentioned limiting situations. When the average A_c/A_p value is maintained, undamped current oscillations result. Otherwise, the oscillatory effect is damped when A_c/A_p changes with time so that either dA_p/dt or dA_c/dt approaches zero. On the basis of this general model different types of oscillations, either damped or undamped, or non-linear, can be computed, as reported in the literature.²¹

The distribution of the A_p and the A_c microscopic sites localized at the electrode surface as it is shown through the SEM observations correlate with the oscillatory response of the electrochemical system. The same conclusion is arrived at from the rotating disc electrode experiments. If the transport of Cl⁻ ion is rate-controlling in the oscillatory effect at a constant w, a linear relationship between I_{max} and the Cl⁻ ion concentration would be expected. The fact that this is not observed (Fig. 10), except as a limiting situation when $C_{Cl^-} \rightarrow \infty$, namely, in the absence of current oscillations, the latter must be ascribed to a change of the A_c/A_p ratio as the Cl⁻ ion concentration changes. The complex dependence of the current oscillation frequency on w (Fig. 8) also points out the participation of partial electrode blockage, as this plot can be correlated with the electrochemical behaviour of a partially blocked



FIG. 9. Scanning electron micrographs showing the attack of the AISI Type 303 electrode in 1M H_2SO_4 + 3000 ppm HCl, 25°C in Region I (I A and I B), Region II (II A and II B) and Region III (III A and III B) of the potentiostatic stationary E/I curve. (A) corresponds to x8333 and (B) corresponds to x16,666.



FIG. 10. The dependence of I_{max} at $w^{1/2} = 5$ on the square root of the Cl⁻ ion concentration in 1M H₂SO₄ solution, 25°C.

rotating disc electrode.²² The overall process generating the conditions required at E_{os} for the periodic oscillation of the current in the alloy/1M H₂SO₄ + x M HCl interphase can be put forward through the following physical picture. The initial stage involves the adsorption competition between water, Cl⁻ and HSO₄⁻ ions

$$S(H_2O) + HSO_4 = S(HSO_4) + H_2O,$$
 (3)

$$S (HSO_4^-) + Cl^- = S (Cl^-) + HSO_4^-$$
 (4)

where the parentheses denote adsorbed species, S refers to an active site on the alloy such as those either in boundaries between austenitic (γ -phase) matrix and carbide particles¹¹ or involving sulphide inclusions¹⁸ where pits are preferentially nucleated. The nucleation of Cl⁻ ions at S initiates pitting and defines the particular A_c/A_p ratio resulting at each Cl⁻ ion concentration. During current oscillation, when the current increases, A_c increases, and the number and size of pits tend to increase, but this produces a local accumulation of corrosion products which systematically inhibits the corrosion process. The accumulation of corrosion products acts as a negative feedback for the forward reaction.²³ Consequently, the current decreases since there is a tendency for the pits to repassivate. In reaction (3) the excess of HSO₄⁻ ion in solution probably produces an inhibiting action while in reaction (4) the excess of Cl^- ion in solution promotes the active dissolution of the metal through pitting.

When pitting corrosion occurs under potentiostatic conditions any tendency to increase in the current should be automatically compensated through the repassivation of freshly produced pits. Thus, the oscillation of the current at E_{os} tends to keep the average A_c/A_p area constant with time. The current oscillates between two limiting situations, one in which there is for a short time a tendency for pit nucleation and another in which pit repassivation predominates. The former situation implies the trend of the A_c/A_p ratio to increase, while the latter corresponds to the decrease of the A_c/A_p ratio. Under the potential-controlled conditions these changes of the A_c/A_p ratio back and forth between the limiting values are repeated during the current oscillating cycles. This description of the periodic current phenomena is *mutatis mutandis* equivalent to that theoretically described by Schwenk for the potential oscillations when pitting corrosion occurs under certain well-defined galvano-static conditions.²⁴

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REFERENCES

- 1. J. WOJTOWICZ Modern Aspects of Electrochemistry (edited by J. O'M. BOCKRIS and B. E. CONWAY), Vol. 8, p. 47, Butterworth, London (1973).
- 2. K. VETTER, Electrochemical Kinetics, Academic Press, New York (1967).
- 3. K. F. BONHOEFFER, Z. Elektrochem. 51, 24 (1948).
- 4. U. F. FRANCK, Z. Naturforsch., 4, 378 (1949).
- 5. U. F. FRANCK and K. WEIL, Z. Elektrochem. 56, 814 (1952).
- 6. J. J. PODESTÁ, R. C. V. PIATTI and A. J. ARVÍA, J. electrochem. Soc. 126, 1363 (1979).
- 7. J. J. PODESTÁ, R. C. V. PIATTI and A. J. ARVÍA, Electrochim. Acta 24, 633 (1979).
- 8. R. C. V. PIATTI, J. J. PODESTÁ and A. J. ARVÍA, Electrochim. Acta 25, 827 (1980).
- 9. Z. SZKLARSKA-SMIALOWSKA and M. JANIK-CZACHOR, Br. Corros. J. 4, 138 (1969).
- 10. T. P. HOAR and K. W. J. BOWEN, Trans. Am. Soc. Metals 45, 443 (1953).
- 11. E. LUNARSKA, Z. SZKLARSKA-SMIALOWSKA and M. JANIK-CZACHOR. Corrosion 31, 231 (1975).
- 12. R. STEFEC and F. FRANZ, Corros. Sci. 18, 161 (1978).
- 13. T. P. HOAR and W. R. JACOB, Nature Lond., 216, 1299 (1967).
- 14. N. STOLICA, Corros. Sci. 9, 455 (1969).
- 15. M. SMIALOWSKI, Z. SZKLARSKA-SMIALOWSKA, M. RYCHCIK and A. SZUMMER, Corros. Sci. 9, 123 (1969).
- 16. V. SCOTTO, G. VENTURA and E. TRAVERSO, Corros. Sci. 19, 237 (1979).
- 17. G. S. ELKUND, J. electrochem. Soc. 121, 467 (1974).
- 18. G. WRANGLÉN, Corros. Sci. 14, 331 (1974).
- 19. A. LOTKA, Elements of Mathematical Biology, Dover, New York (1956).
- 20. V. VOLTERRA, Leçons sur la Théorie Mathématique de la Lutte pour la Vie, Gauthiers-Villars, Paris (1931).
- 21. J. HIGGINS, Ind. Eng. Chem. 59, 19 (1967).
- 22. F. SCHELLER, R. LANDSBERG and H. WOLF, Electrochim. Acta 15, 525 (1970).
- 23. U. F. FRANCK, Ber. Bunsenges. Phys. Chem. 84, 334 (1980).
- 24. W. SCHWENK, Corros. Sci. 3, 107 (1963).