

STOCHASTIC AND DETERMINISTIC BEHAVIOURS OF 316 STAINLESS STEEL PITTING CORROSION IN PHOSPHATE-BORATE BUFFER CONTAINING SODIUM CHLORIDE

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(Received 27 August 1986)

Abstract—The pitting corrosion of 316 stainless steel (SS) in phosphate-borate buffer (pH 8.00) containing 0.5 M NaCl at 25°C is studied through current transients run under a constant potential step, potentiodynamic runs and scanning electron microscopy. According to the potential and time windows different laws for pitting kinetics are observed. For small number of pits, the kinetics of pit growth is governed by a stochastic law whereas for a large number of pits a deterministic law which corresponds to an instantaneous nucleation and growth is obeyed. At the initial stages two different rate constants for pit nucleation are obtained. This fact correlates with two well distinguishable types of pits observed through SEM observations. Results are discussed through a model involving the penetration of chloride ions through the passive film and the existence of at least two types of sites at the metal surface which in turn become centers of pit nucleation. Pit stability is directly related to the Cr(III) content in the passive layer which can be shifted by changing the applied potential with respect to that of the $\text{Cr}_2\text{O}_3/\text{CrO}_4^{2-}$ redox couple.

INTRODUCTION

The initiation of localized corrosion has been considered as a rare event both in space and time and consequently it can be treated as a statistical phenomenon[1-4]. Current bursts associated with pit activation (birth) and pit repassivation (death) are observed during potentiodynamic and potentiostatic experiments[5, 6]. Birth processes can be analyzed in terms of a nucleation rate, whereas death processes are accounted for by the probability of pit dying. Potential dependent nucleation rates derived from induction times for pit initiation as a statistical variable are given in the literature[1, 2]. On the other hand, death processes are related to the ability of the passive layer for self repairing. The latter process for stainless steel depends on both water[7, 8] and chromium content in the passive film which in turn change with the applied potential and temperature[9]. Recently a potential dependent nucleation rate for stable pits, a potential independent rate for unstable pit formation and a potential independent probability for pit dying could be distinguished from experiments run within a relatively narrow potential window[4], although no correlation between those parameters with the number of pits and pit morphology from microscopic examination was established. In this respect one could expect a great influence of the applied potential on the number of centres for pit growth so that the transition from stochastic or deterministic models for the kinetics of

pitting processes could change according to the selected potential window.

This work deals with the localized corrosion of 316 SS in a strong buffered chloride ions-containing medium, studied by using potentiodynamic and potentiostatic techniques complemented with scanning electron microscopy observations. Special attention is paid to the influence of the applied potential on the early stages of the nucleation and growth of stable pits with the purpose of establishing the condition for application of either a stochastic or a deterministic model to interpret pitting kinetics.

EXPERIMENTAL

Working electrodes were made of 316 SS rods axially embedded in Araldite holders to obtain circular exposed areas of 0.2 cm² geometric area. Occasionally, iron electrodes (Johnson Matthey, 0.5 mm dia. rod) prepared as described in[9] were used. Firstly, the metal surface was mechanically polished with fine grained emery paper followed with alumina paste (1 μm dia.) on polishing cloth to obtain a mirror surface. Each polished specimen was rinsed with twice distilled water and dried in air at room temperature. A new pretreated specimen was used for each run.

Measurements were made at 25°C with a conventional Pyrex glass cell containing the electrolyte solution (0.2 l). The potential of the working electrode was measured against a saturated calomel electrode (*sce*) provided with a Luggin-Haber capillary tip. All potentials in the text are referred to the *sce*. The electrolyte prepared from A.R. chemicals and bidistilled water consisted of 0.10 M KH_2PO_4 + 0.05 M $\text{Na}_2\text{B}_4\text{O}_7$ (pH 8.00) containing 0.5 M NaCl. Previously to each

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run the solution was purged with purified nitrogen during 3 h. Polarization curves [apparent current density (j) vs potential (E)] were run by applying to the specimen a singular triangular potential sweep (STPS) between the cathodic ($E_{s,c}$) and the anodic ($E_{s,a}$) switching potential at different scan rate (v). Potentiostatic current transients were recorded after applying to the specimen a potential program which included successively a cathodization at $E_c = -1.10$ V for 90 s to electroreduce the metal surface, an anodization at $E_a = -0.50$ V for 90 s to form a prepassive layer, and finally, a potential step to E_s . For each E_s , 40–80 measurements were made.

Induction times (t_i) were obtained from the current transients at constant potential. Due to the ambiguity to define t_i by setting an arbitrary threshold current value to be exceeded, only t_i values for stable pit growth were considered. These values were taken as the last time at which the current shows a low value similar to that recorded for the completely passive specimen. This means that for any time, t , greater than t_i the specimen is not able to repassivate. Complementary SEM micrographs were taken by using a Philips 500 electron scanning microscope.

RESULTS

Voltammetric results

Voltammograms resulting for 316 SS specimens in phosphate–borate buffer run at 0.02 V s^{-1} between $E_{s,c} = -1.20$ V and $E_{s,a} = 1.00$ V (Fig. 1) show three anodic current peaks at -0.60 V (peak A_I), at -0.30 V (peak A_{II}) and at 0.70 V (peak A_{III}) (Fig. 1). The returning scan presents two cathodic current peaks one located at 0.1 V (peak C_{III}) and another one at -0.50 V (peak C_{II}). Peak A_I can be assigned to the electroformation of a $\text{Fe}(\text{OH})_2$ layer on the pre-existing Cr_2O_3 layer [10]. The hydrous $\text{Fe}(\text{OH})_2$ film is electro-oxidized to hydrous FeOOH at potentials corresponding to current peak A_{II} yielding a complex film of inner Cr_2O_3 and outer FeOOH [10, 11]. Peak A_{III} was associated with the electro-oxidation of $\text{Cr}(\text{III})$ to $\text{Cr}(\text{VI})$ into the passive film and to the formation of soluble CrO_4^{2-} [10]. The electroreduction of $\text{Cr}(\text{VI})$ in the film to $\text{Cr}(\text{III})$ was related to peak C_{III} while the broad peak C_{II} was assigned to the electroreduction of the hydrous

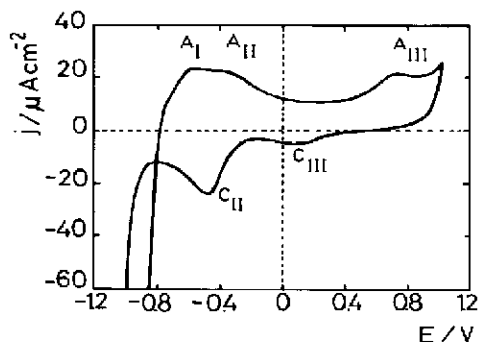


Fig. 1. j/E profile in phosphate–borate buffer, $\text{pH} = 8.00$; $v = 0.02 \text{ V s}^{-1}$, $E_{s,c} = -1.10$ V; $E_{s,a} = 1.0$ V.

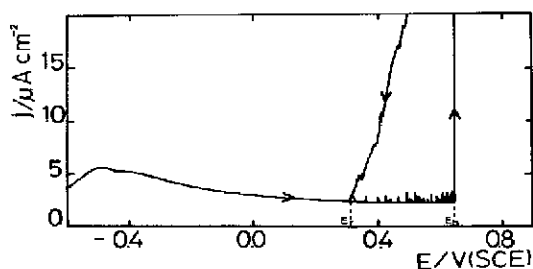


Fig. 2. j/E profile in phosphate–borate buffer + 0.5 M NaCl , $\text{pH} = 8.00$; $v = 0.0002 \text{ V s}^{-1}$, from $E_{s,c} = -1.10$ V to E_b and then returning to the repassivation potential E_r .

FeOOH film [11, 12]. The j/E profiles recorded in the phosphate borate buffer containing 0.5 M NaCl show similar current peaks although when the potential exceeds a certain critical value (E_b) a remarkable increase in current due to the initiation of pitting corrosion can be observed (Fig. 2). Current instabilities related to breakdown and repair events at the passive film are detected in the potential range preceding E_b . The returning scan exhibits a considerable hysteresis loop which extends from E_b to a potential E_r located at ca 0.30 V. At E_r the passive film has been fully restored. Similar runs made with pure iron specimens exhibit the initiation of pitting at lower potential and the current instabilities prior to E_b are practically absent.

Potentiostatic current transients

The current transients were run at constant potential values ranging from -0.30 V to 0.70 V. Each current transient was preceded by the following electrochemical pretreatment. The specimen was firstly held at -1.10 V for 90 s to achieve a reproducible electroreduced surface and later stepped to -0.5 V to form the prepassive layer. According to the value of E_s , different current transients can be obtained (Fig. 3). Thus, for $E_s < 0.30$ V, the current transient decreases continuously resembling the characteristics of already known passive metal surfaces (Fig. 3a). In this case the current transient is mainly determined by the growth of the passive film and the simultaneous electrodisolution of the metal through it [13]. Otherwise, for E_s set in the 0.30 – 0.50 V range different current transients can be obtained for experiments performed under nominally identical conditions. For a rational analysis, these transients can be divided into two groups, one of them showing a behaviour similar to that described for those resulting at $E_s < 0.30$ V and another one exhibiting an initially decreasing current which reaches a minimum value and afterwards a remarkable increasing one. The current minimum determines an induction time (t_i) for stable pit initiation and the increase in current is associated with stable pit growth. However, in many cases stable pitting is not achieved and in this case a considerable number of fluctuations in the current is seen. Some runs exhibit a rather abrupt decrease in current to attain a value similar to that observed in passive specimens (Fig. 3b). Current fluctuations are also recorded during both the induction period and the rising part of the current transients

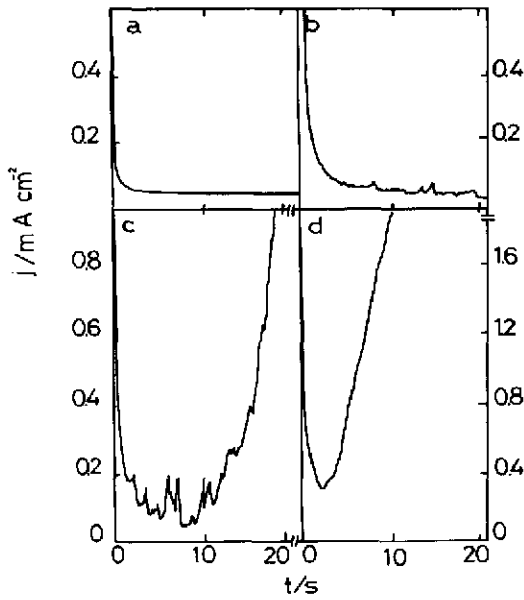


Fig. 3. Current transients at constant potential (E_s) in phosphate-borate buffer +0.5 M NaCl, pH = 8.00. After cathodizing 90 s at $E_c = -1.10$ V, another 90 s at $E_a = -0.50$ V, and finally stepped to E_s . (a) $E_s < 0.30$ V, (b) and (c) $0.30 \leq E_s \leq 0.50$ V, (d) $E_s > 0.50$ V.

associated with pit growth (Fig. 3c). The number of specimens presenting stable pitting increases according to E_s . For $E_s > 0.5$ V, the corresponding current transients become progressively better defined, more reproducible and practically noiseless (Fig. 3d). The probability, $P_{n \geq 1}$, to form at least one stable pit[14] can be evaluated from the current transients resulting for different E_s (Fig. 4). The value of $P_{n \geq 1}$ increases according to E_s and for $E_s > 0.5$ V, $P_{n \geq 1} \rightarrow 1$. Therefore, as E_s increases, the survival time of specimens is drastically reduced (Fig. 5, a and b). Finally for the current transients, the rising part of the current

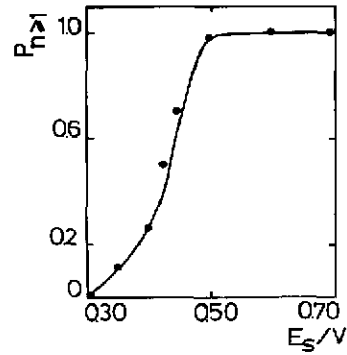


Fig. 4. $P_{n \geq 1}$ vs E_s plots.

resulting for $E_s > 0.50$ V obeys a linear j vs t^2 relationship (Fig. 6).

SEM observations

SEM micrographs of surfaces resulting from anodizing in the $0.30 < E_s < 0.50$ V range ($t_s = 210$ s) show for many specimens a single large pit on the surface (Fig. 7a), where others present a small number of pits with a broad distribution in size. The number of pits increases according to E_s and for $E_s > 0.60$ V a great number of pits with radii as large as $50 \mu\text{m}$ can be observed (Fig. 7b). Furthermore, the SEM micrographs also shown that a large number of pits of smaller size are also present together with large pits (Fig. 7, b and c). These results suggest that the two different types of pits either involve a long time for initiation or the corresponding growth rates are substantially different. Likewise for $E_s > 0.6$ V, the number of large pits becomes independent of the anodizing time. The mean number $\langle n \rangle$ and standard deviation, σ , for large pits resulting at different E_s and $t_s = 210$ s are assembled in Table 1. It can be noticed that $\sigma/\langle n \rangle$ ratio decreases as E_s increases. Preliminary results show that the increase either in E_a or in the anodization time at constant E_s reduces strongly the $\langle n \rangle$ values.

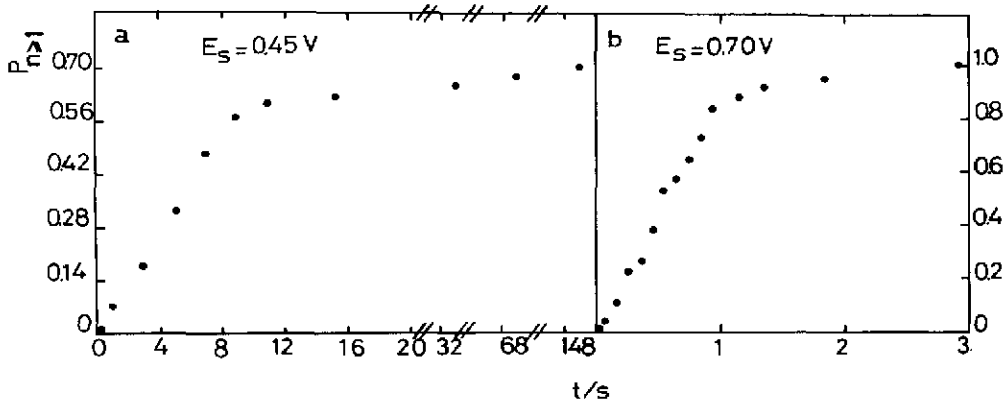


Fig. 5. $P_{n \geq 1}$ vs t plots for different E_s values. (a) $E_s = 0.45$ V, (b) $E_s = 0.70$ V.

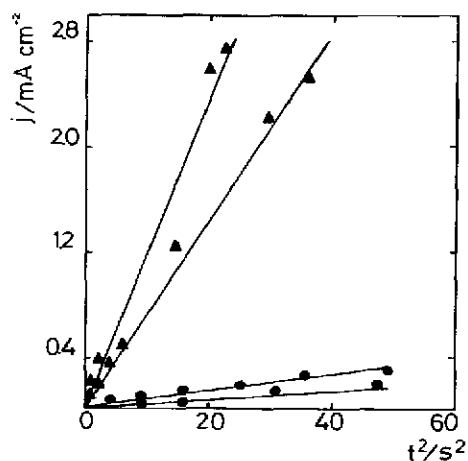


Fig. 6. j vs t^2 plots for different E_s values. (●) $E_s = 0.60$ V, (▲) $E_s = 0.70$ V.

DISCUSSION

The stochastic range for pitting of 316 SS

The pitting corrosion of 316 SS in neutral buffered media containing chloride ions is a complex process involving passive film breakdown, pit propagation and pit repassivation. Further understanding of the initial stage of the mechanism of pitting can be attempted through the analysis of a large number of potentiostatic current transients. In principle, both the shape of the current transients and the voltammetric loop resulting in the pitting corrosion domain for 316 SS resembles those for localized corrosion of other metals and alloys in aqueous environment containing chloride[13]. Nevertheless, 316 SS in these aggressive media as compared to other metals exhibits a rather unusual behaviour because most of the samples are in fact not corroding but become passive and stable. This electrochemical behaviour is accompanied by the relative scattering in pitting parameters and strong current oscillations observed for 316 SS. It is also established that as E_s increases current fluctuations either disappear or become sufficiently small as compared to the mean transient current value that they are no longer distinguishable. As a first approach, the phenomenology of current fluctuations for 316 SS in chloride-containing solutions can be described through recently stochastic models advanced for pitting corrosion of SS[4]. Accordingly each current burst can be associated with the birth and transient growth of a pit which can be followed by the abrupt stop of the process due to the death of the growing pit leading to repassivation. The birth and growth of a pit can be analyzed in terms of the rate of conversion of a surface site into a pit nucleation centre, whereas the death can be accounted for the probability of pit dying. Otherwise, when the current burst exceeds a given value, the system attains irreversibility the stable pitting domain. At this stage, the system has not self repassivation ability and as the activation process

cannot be counterbalanced the first current burst becomes effective to produce stable pitting.

The rate of conversion of a surface site into a nucleation centre for stable pit growth, λ , can be estimated from the time dependence of the probability of formation of at least one nucleus for stable pit growth ($P_{n \geq 1}$) at a constant potential by means of the Poisson distribution law. The expression for ($P_{n \geq 1}$) corresponding to a stationary value of λ is given by[14]:

$$P_{n \geq 1} = 1.0 - \exp(-\lambda t). \quad (1)$$

According to equation (1), λ can be estimated by plotting $\ln(1.0 - P_{n \geq 1})$ vs t (Fig. 8) where the first term is the logarithm of the probability of maintaining the specimen out of stable pitting. In agreement with previous observations reported in the literature[1, 3] for the pitting corrosion of stainless steel in chloride solutions, these plots for different E_s values exhibit two reasonable linear portions with their corresponding slopes λ_1 and λ_2 , respectively. The values of λ_1 and λ_2 fit reasonable straight lines by plotting either $\ln \lambda_i$ vs E_s (Fig. 9) or $\ln \lambda_i$ vs $(E_s - E_b)^{-1}$, where $E_b = 0.30$ V corresponds to the value of E where $P_{n \geq 1} = 0$ (Fig. 4). The dependence of λ_i on potential could be interpreted, in principle, on the basis of either atomistic or classical simple nucleation models, through the evaluation of the number of atoms or molecules (g^*) involved in the formation of a critical nucleus. The corresponding g^* values from λ_i leads to physically unrealistic figures, namely either to negative values for the atomistic model or to values smaller than one for classical models. Hence, the experimental results are inconsistent with simple nucleation models and the explanation of λ_i values must be sought through another mechanistic approach for the early stage for pitting of 316 SS in chloride-containing solutions.

A reasonable interpretation for λ_i values can be based upon the passive film/anion interaction and the corresponding structure of the passivating layer. In this respect it should be noticed that there is a firm evidence for the penetration of chloride ions into the passive film of iron and SS as recently concluded by ESCA[15] and SIMS[16] data. This fact suggests that λ_i values could be related to the time required for the aggressive anion to penetrate the entire passive film thickness to reach the metal surface instead of considering it as the time required to form a nucleus for stable pit growth. The new assumption is also consistent with linear $\ln \lambda_i$ vs E_s relationships[17] but the high values of slopes can be related to the kinetics of the processes occurring at the passivating layer. The immediate conclusion from this interpretation is that the initial stage for stable pit formation should be controlled by the rate of penetration of the aggressive anion through the passive film and correspondingly the characteristics of the passive film should play a substantial role in determining the λ_i values.

It was suggested that both the rate of pit nucleation and current fluctuations recorded for a 240 grade polished 316 SS in dilute sodium chloride are related to the production of persistent gradients of acidity at the scale of surface roughness of the metal[4]. However, this statement appears as a partial explanation of a more complex process as in the present case oscillations are also found in strong buffered solutions. The

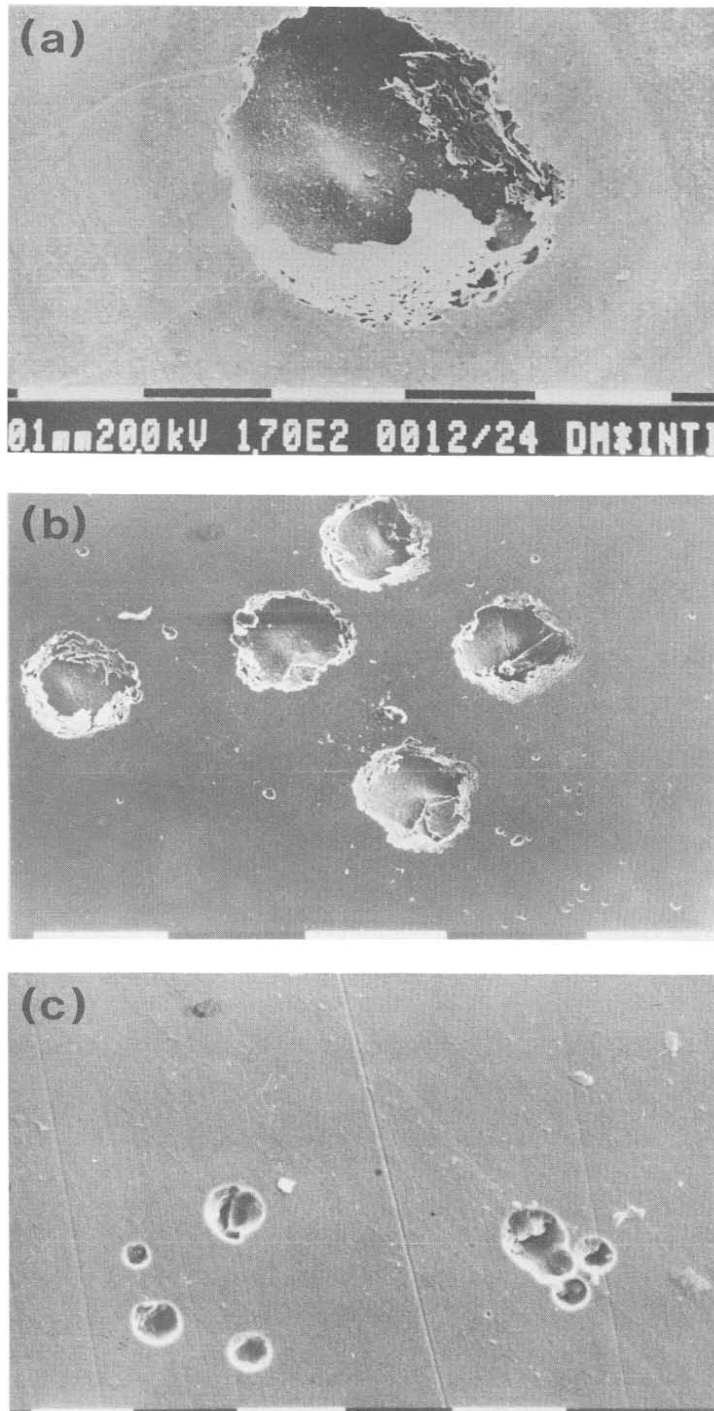
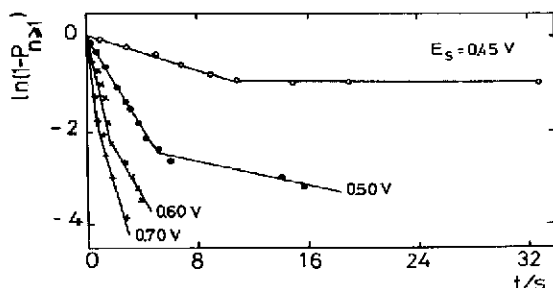
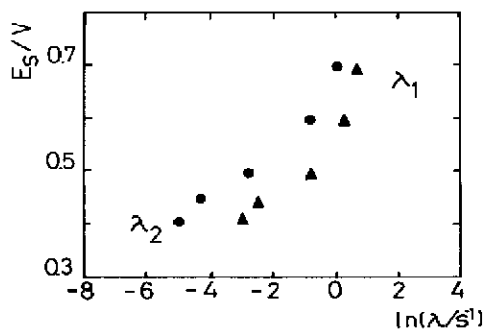


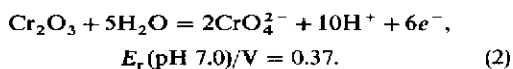
Fig. 7. SEM microphotographs obtained after anodizing a 316 SS specimens during 210 s at different E_s . (a) $E_s = 0.35$ V, scale = 0.1 mm, (b) $E_s = 0.60$ V, scale = 0.1 mm, (c) detail of (b), scale = 10 μm.

Table 1. Number of pits resulting at different E_s values and $t_s = 210$ s

E_s (V)	$\langle n \rangle$	σ	$\sigma/\langle n \rangle$
0.45	2	2	1
0.50	14	11	0.79
0.60	25	19	0.76
0.70	100	67	0.67

Fig. 8. $\ln(1 - P_{n \geq 1})$ vs t plots for different E_s values.Fig. 9. E_s vs $\ln \lambda_1$ plots.

repassivation ability of stainless steel depends on the content of both Cr(III) and water in the passive film [8, 9], and the corresponding breakdown potential and current oscillations are closely related to the chromium content in the passive film which in turn is determined by the electrode potential and temperature [9]. Likewise, the role of chromium in the self-repair ability of 316 SS was clearly demonstrated by using an iron electrode in chromate solutions containing chloride ions. These facts point out that the initiation and growth of pits at a constant potential should depend on the probability of pit dying, μ which is directly related to the chromium content in the passive layer [9]. The latter depends on potential through the following equilibrium at the electrochemical interface:



Accordingly, as E_s becomes more positive the Cr(III) content in the passive film decreases and the ability of the film to self-repair diminishes. Hence, for 316 SS as

the Cr(III) content in the passive film decreases, μ should also decrease and the pit activation process continues without hindrance. Consequently, operating conditions can be accomplished where the first burst becomes effective for stable pitting corrosion.

The deterministic range for pitting of 316 SS

As E_s increases stable pitting nucleation events become gradually more frequent, that is λ increases resulting in a large number of growing pits at the metal surface. Hence, at this stage each growing centre becomes less significant in relation to the total number of centres. Both progressive decrease in μ and the increase in λ lead to current transients with a gradual disappearance of oscillations. Consequently, beyond the transition range for $E_s > 0.50$ V, the kinetics of pitting can be described through a deterministic model, and in this case it is possible to derive some interesting information about the nucleation process involved in the pitting corrosion of 316 SS.

Let us start by assuming that pit growth involves a conical growth as it is approached by SEM micrographs and that the process undergoes under charge transfer control. Then, the apparent current density (j_s) is given by the expression [18]:

$$j_s = zFk'_{3c} \left[1.0 - \exp\left(-\frac{\pi M^2 k_{3c}^2 N_0 (t - t_i)^2}{\rho^2}\right) \right]$$

$$= P_1 [1.0 - \exp(-P_2 (t - t_i)^2)] \quad (3)$$

for instantaneous nucleation and,

$$j_s = zFk'_{3c} \left[1.0 - \exp\left(-\frac{\pi M^2 k_{3c}^2 N_0 \lambda (t - t_i)^3}{3\rho^2}\right) \right]$$

$$= P_1 [1.0 - \exp(-P_2' (t - t_i)^3)] \quad (4)$$

for progressive nucleation where

$$P_1 = zFk'_{3c} \quad (5)$$

$$P_2 = \pi M^2 k_{3c}^2 N_0 / \rho^2 \quad (6)$$

and

$$P_2' = \pi M^2 k_{3c}^2 N_0 \lambda / 3\rho^2. \quad (7)$$

k'_{3c} and k_{3c} are the rate constants perpendicular and parallel to the metal surface, respectively; M is the molecular weight; ρ is the density and N_0 is the number of sites available for the nucleation process.

Equations (3) and (4) for $(t - t_i) \rightarrow 0$ after series expansions of the exponential terms lead to the following simplified equations:

$$j_s = P_1 P_2 (t - t_i)^2 \quad (8)$$

and

$$j_s = P_1 P_2' (t - t_i)^3. \quad (9)$$

For $E_s > 0.5$ V the experimental results obey linear j vs t^2 plots (Fig. 6). In principle, this result is consistent with an instantaneous nucleation of pits at the 316 SS passivated surface, and it agrees with λ values previously estimated. Accordingly, the number of sites converting into pits (N) is related to t through the equation [18]:

$$N = N_0 [1.0 - \exp(-\lambda t)]. \quad (10)$$

For $t = 1$ s and λ_1 values resulting for $E_s = 0.60$ V and $E_s = 0.70$ V, respectively, equation (10) results:

$$N \approx N_0.$$

The number of growing centres for an instantaneous nucleation which leads to a deterministic behaviour through reproducible practically fluctuation free current transients is about 80[19]. This figure is approached for $E_s > 0.5$ V by considering only large size pits. The existence of different λ values correlates to different types of pits in the SEM micrographs and can be accounted for by considering that inclusions contribute together with the aggressive anion penetration through passive layer to the pitting corrosion of 316 SS. It is known that sulphide inclusions are preferred sites for the nucleation of corrosion pits on SS[20, 21]. In this case, the surface concentration of sulphide inclusions was estimated between 3000 and 5000 cm^{-2} and the corresponding average radius results close to 1.5 μm . From the standpoint of the metal structure, the inclusions participating in the pitting process can be distinguished into two different types, namely, those lying part in the passive layer and part in the metal (type I centres), which causes an appreciable modification of the structure and characteristics of the passive layer, and those inclusions located just under the passive layer skin (type II centres), which have a minor influence on the passive layer. At early stages of pitting one should expect that only centres of type I become relevant, and therefore it is reasonable that λ_1 values be associated with the attack of the metal at centres of type I. These centres can be completely converted into pits in a short period of time leading to large pits (Fig. 7b). Otherwise, values of λ_2 presumably refer to pitting process at centres of type II, yielding small pits (Fig. 7c) as the kinetics of the process is determined by the lower λ_2 value. Specimens with type I centres can also offer type II centres for pitting, this possibility should depend on the proper structure of the passive layer.

In conclusion the pitting corrosion mechanism of 316 SS in neutral buffered solutions containing chloride ions can be described in terms of stochastic and deterministic formalisms depending on the time and potential windows of the experimental approach. In any case the reaction model implies that pit nucleation occurs at centres on the metal surface whose reacting characteristics depend on both the charac-

teristics of the passive layer at the points of attack and the presence of inclusions at the metal surface.

Acknowledgements—This work was financially supported by the Consejo Nacional de Investigaciones Científicas y Técnicas and the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires.

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