



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Corrosion Science 48 (2006) 1004–1018

**CORROSION
SCIENCE**

www.elsevier.com/locate/corsci

Evolution of current transients and morphology of metastable and stable pitting on stainless steel near the critical pitting temperature

M.H. Moayed^a, R.C. Newman^{b,*}

^a *Department of Materials Engineering, Faculty of Engineering, Ferdowsi University, Mashad, P.O. Box 91775-1111, Iran*

^b *Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, Toronto, Ont., Canada M5S 3E5*

Received 11 February 2005; accepted 11 March 2005

Available online 23 May 2005

Abstract

Type 904L austenitic stainless steel with a critical pitting temperature (CPT) of 56 °C was polarized at 750 mV (Ag/AgCl) in 1 M NaCl at 45, 49 and 54 °C. Current transients due to metastable pitting were recorded at these three temperatures, and a smaller number of stable pit current transients were recorded at 62 °C. The metastable pit current, I , followed a power law relationship $I \sim t^n$ during initial growth prior to repassivation. The exponent n increased with temperature, from 0.5 to 1.5. To grow at the lower temperatures, the pits need to be more occluded (lower value of n ; lower pit current density). The repassivated metastable pits showed two morphologies: small occluded cavities associated with the small transients, and open ones with polished surfaces for large transients recorded close to the CPT. A new type of deterministic repassivation was identified for the latter type of pit. The stable pit currents rose in proportion to $t^{3/2}$, just like the faster-growing metastable pits, but only for a few seconds; then there was a drop in current and a further noisy increase occurred with a lower exponent. These pits undercut the metal surface, producing a lacy metal cover. The results are broadly consistent with a model that attributes the CPT to the onset of passivation in the saturated pit

* Corresponding author. Tel.: +1 416 946 0604; fax: +1 416 978 8605.
E-mail address: newman@chem-eng.utoronto.ca (R.C. Newman).

solution. A new feature requiring explanation is that, very close to the CPT, pits can precipitate a salt film but fail to undercut the surface. It is hypothesized that since a higher anodic current density is required at the undercutting site than at the pit base, there will be a range of temperatures where the former but not the latter would exceed the critical current density for passivation and is thus disallowed.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Pitting corrosion; Stainless steel

1. Introduction

Metastable pit growth is a well-documented early stage in pitting corrosion of stainless steel in chloride solution. Metastable pitting can be observed as negative excursions in potential for open-circuit conditions or anodic galvanostatic polarization, or as anodic current excursions under potentiostatic control. Each event reflects the initiation, growth and repassivation of a micropit. Metastable pit transients can be recorded at potentials below the pitting potential but above the critical pitting temperature (CPT) [1], or over a wide range of potentials below the CPT [2].

The CPT is a deterministic type of transition, highly reproducible for modern low-sulfur steels, in which stable pitting abruptly vanishes at all potentials below a particular temperature [3]. The CPT depends slightly on surface finish [4] but hardly at all on potential or chloride concentration within a certain range. The present work is a development of the study reported in [2], in which various new observations were reported, including a peak in metastable pitting activity at intermediate potentials. It was proposed that an anodic salt film (FeCl_2) was playing a dual role in pit stability: as an intermediary in passivation below the CPT, and as a stabilizing factor for pit growth above the CPT. Similar behaviour has been known for iron in sulfuric acid for nearly a century, and repassivation of artificial pit electrodes under anodic chloride salt films can be observed when they are polarized at high potential to precipitate the salt film, then cooled down whilst maintaining the applied potential [5]. The critical temperature obtained in such experiments is higher than the CPT, because the passivation under the salt film obeys a critical current density type of criterion: deep cavities have lower diffusion-limited current densities, and thus repassivate with more difficulty (i.e. require a lower temperature to repassivate).

Nearly all the investigations on metastable pit current transients on stainless steels have been carried out by applying an anodic potential lower than the pitting potential at a temperature above the CPT.¹ Two main kinds of information may

¹ It should be mentioned that modern low-sulphur 316L steel has a CPT very close to 25 °C, and should not be studied at an uncontrolled room temperature, as virtually any result is possible within a range of a few degrees. Authors who have obtained pitting of 316L steel at 'room temperature' are either living in a warm climate or using non-optimal material. Fortunately, most academic investigations, including some of our own, are performed on inferior 316[L] material, for which room temperature is well above the CPT.

be obtained from such investigations: stochastic data such as a relationship between the nucleation frequencies of metastable and stable pits [6], and kinetic data deduced from individual current transients [1]. Frankel et al. [7], working with wire electrodes of 304SS that had rather high apparent pitting potentials, showed that the metastable pit current increased approximately as t^2 over most of the potential range, and often showed a sharper increase (due to opening of a hole in the pit cover) just before the final decay due to repassivation. The transients showed lifetimes between 5 and 15 s, and their magnitude varied from 4 nA to as much as 20 μ A. Williams et al. [8], working with plate material, showed that metastable pit transient shapes varied from $I \sim t^{1/2}$, through a linear law, to some that showed $I \sim t^2$ for a short time. The relative lack of the ' t^2 ' transients in their work may be attributed to the restricted range of potentials available, since stable pitting (due to large sulphide inclusions) intervened at a much lower potential than in the work of Frankel. Balkwill et al. [9] stated that if the current is limited by the resistance of the solution outside the pit, or the resistance to current flow of a cap of corrosion products over the pit, then the relationship $I \sim t^{1/2}$ is expected. At higher potentials they found a shift in the distribution of the shapes of transients, from transients that were mostly resistance limited ($I \sim t^{1/2}$) to transients that indicated another kind of control (e.g. $I \sim t$). Any such interpretation must invoke a change in pit geometry with time and potential, especially for the ' t^2 ' transients which imply constant current density—an impossibility for a growing hemisphere, since there is always a significant IR potential drop that must grow with pit depth. Therefore the determination of the state of the pit surface (bare or salt-filmed) is not a trivial matter if all we have are the metastable pitting transients at various potentials. Pistorius and Burstein [1] believed that all their pits, stable or metastable, contained anodic salt films and grew under anodic diffusion control from the moment of their nucleation. Varying pit growth laws were interpreted in terms of different time-varying boundary conditions for diffusion. Unless the instantaneous potential dependence of the current from a single, growing pit can be measured (Pistorius did this, but for transients recorded at very high potentials where the presence of a salt film is not surprising), it is unlikely that the issue of the state of the pit surface can be resolved conclusively. However, there are situations in which pit growth is definitely under ohmic/activation control, such as the pitting of stainless steel in chloride/thiosulfate solutions [10], where individual pits are easy to initiate, show very stable growth, and are easy to subject to potential excursions.

In a study of the growth-rate distribution of metastable pits using several stainless steels, Ezuber and Newman [11] confirmed that transients with $I \sim t^{1/2}$ occur in relatively occluded cavities and $I \sim t$ in more open cavities. Increasing the potential gave a relatively higher proportion of $I \sim t$ transients, as shown by Balkwill. Addition of an inhibitor or alloying with nitrogen eliminated the faster-growing pits whilst leaving the slow (more occluded) ones relatively unaffected. Alloying with Mo shifted the growth-rate distribution to lower rates, at a given potential, without changing the shape of the distribution, suggesting that Mo was inhibiting active dissolution with no salt film present, though other interpretations based on the presence of a salt film are possible.

It turns out that the effect of temperature is a promising way to attempt a resolution of the issue related to the necessity of a salt film; by using a high-alloy material and working close to the CPT, insights may be gained that cannot be achieved with ordinary 300-series steels (unless perhaps by working in cooled solutions).

2. Experimental procedures

2.1. Specimen preparation

Specimens from 904LSS plate (6 mm thickness, composition given in Table 1) were cut with a surface area of 4 cm² for CPT measurements and 0.1 cm² for recording of metastable and stable pit current transients. Each specimen was welded to Nichrome wire for electrical connection. The Nichrome wire was covered with a heat shrinkable plastic tube to provide insulation from the environment. Specimens were mounted in resin, and allowed to set overnight in air. All specimens were mechanically wet polished to a 3 μm diamond-paste finish, then degreased with ethanol prior to drying with air. In order to prevent crevice corrosion, the gap between the resin and the specimen was masked with lacquer and dried with warm air.

2.2. Electrochemical procedures

The electrochemical cell was a 250 ml beaker open to air. In general, 150–200 ml of test solution were used for each test. A commercial Ag/AgCl/sat. KCl electrode was used as a reference electrode for all experiments. The auxiliary electrode was a bright platinum sheet, area 2 cm². The cell was suspended in a water bath to control the solution temperature.

A potentiostat (ACM instruments, UK) was used to control the electrode potential. The current between working and auxiliary electrodes was measured across a resistor inserted into the circuit, or by a digital electrometer in series with the cell for more sensitive measurements. The analogue output of the electrometer or voltage corresponding to the current output of the potentiostat was read by an A/D card and the data were processed in a PC.

For SEM examination, most of the samples were gently rinsed and dried, but some with stable pits were subjected to ultrasonic treatment in deionized water to remove the lacy pit cover.

Table 1
Composition of the alloy used in this work

Grade	Alloying elements, wt.% (balance Fe) ^a			
	Cr	Ni	Mo	Mn
904L	20.06	25.04	4.32	1.41

^a Actual composition supplied by Avesta Sheffield.

2.3. Determination of the CPT

The potentiostatic CPT determination involves polarization of the working electrode just below the transpassivity potential (a suitable value is 700 or 750 mV vs. Ag/AgCl), and gradually increasing the solution temperature. After 5 min immersion at 5 °C, an anodic potential of 750 mV (vs. Ag/AgCl) was applied and the electrolyte temperature was increased at a rate of 0.4 °C/min. In other work [12] the CPT has been evaluated as the temperature at which the current density exceeds 100 $\mu\text{A}/\text{cm}^2$. Recording of metastable pit transients as large as 160 μA led us to define the CPT slightly differently as the temperature at which the current starts to increase rapidly with no repassivation after 1 min. Few problems with crevice corrosion were experienced in this procedure compared with potentiodynamic studies of 300-series steels.

2.4. Measurement of pitting transients

Metastable and stable pitting transients were recorded at 750 mV (Ag/AgCl) in 1 M NaCl at several temperatures. The main aim of these experiments was to record individual transients. To achieve this, small working electrodes of $\sim 0.1 \text{ cm}^2$ were used to reduce the overlap of events. The specimen (working electrode) was left at its rest potential for 5 min and then polarized with a scan rate of 10 mV/s to 750 mV (vs. Ag/AgCl). The current transients were recorded from 5 s after reaching 750 mV. The current transients of metastable pits were recorded at 45, 49 and 54 °C, which are about 11, 7 and 2 °C below the alloy CPT. In order to record stable pit current transients, a temperature of 62 °C was selected (6 °C above the CPT).

3. Results and discussion

3.1. Critical pitting temperature

An example of the determination of CPT by the potentiostatic method for 904L stainless steel is illustrated in Fig. 1, in which the final parts of three current–temperature relations are shown. The CPT is the temperature where unconditionally stable pits start to grow. Prior to stable pitting, some metastable pit transients with different sizes were observed at temperatures as low as 32 °C. Four experiments were carried out and the average value of the CPT was considered as the final value. It is evident that the range of the results is about 1 °C and the alloy has a CPT of ~ 56 °C for this particular surface finish; coarser finishes have slightly lower CPT values [4].

3.2. Metastable pitting current transients

Fig. 2 illustrates typical anodic current decays recorded at 750 mV and temperatures of 45, 49 and 54 °C. The lifetime of metastable pits could be as long as 30 s, but typically they had shorter lifetimes. The average size of transients increased with

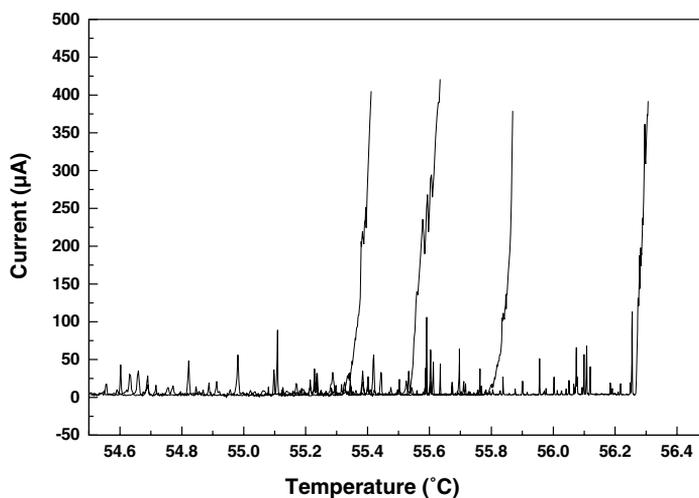


Fig. 1. Final part of four current–temperature curves obtained from potentiostatic CPT measurements on 904L SS at 750 mV (Ag/AgCl) in 1 M NaCl.

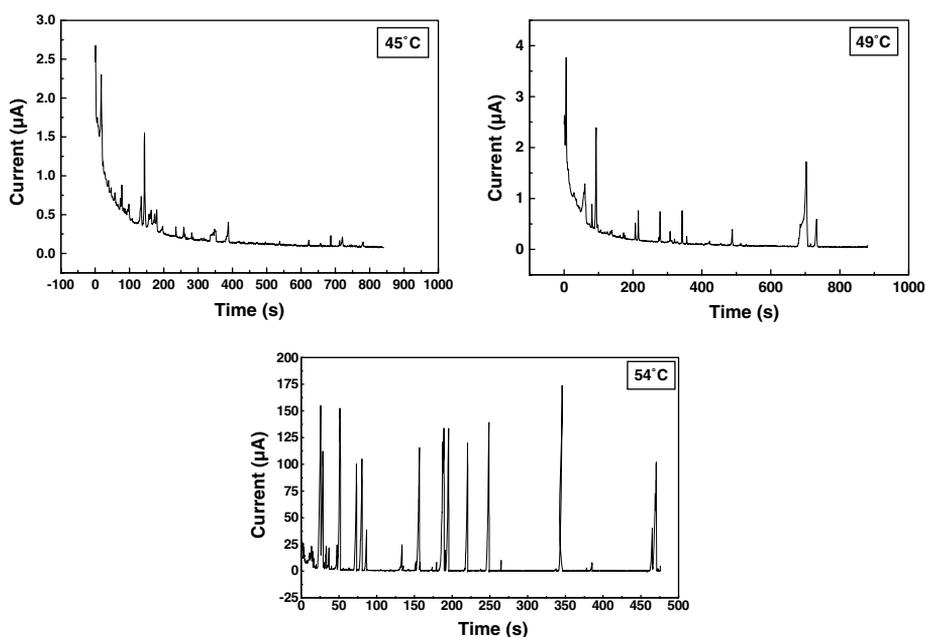


Fig. 2. Current transients from metastable pit growth in 904L stainless steel held at 750 mV (Ag/AgCl) in 1 M NaCl at three temperatures below the CPT: 45, 49 and 54 °C (potential scanned to the set value at 10 mV/s).

increasing temperature below the CPT. A new kind of very large repetitive transient can be seen at the temperature closest to the CPT (54 °C). Repassivation of these

very large events appears to be governed by some relatively deterministic process, and is quite different in character from that observed in the usual kind of metastable pitting study, i.e. where $E < E_{\text{pit}}$, $T > \text{CPT}$.

The transients had different shapes depending on the test temperature. At temperatures close to the CPT repassivation was rapid compared with the rise time, whilst at lower temperature the transients tended to display both relatively and absolutely longer times for repassivation (Fig. 3). Such a result is consistent with the idea that only highly occluded sites can sustain pitting at low temperatures; such a site will have a long effective diffusion path and thus there is slow dilution of the pit solution leading to slow, progressive repassivation. At higher temperatures the pits are nearly open, and in fact they appear to be completely open, though not hemispherical, in the case of the huge transients recorded at 54 °C.

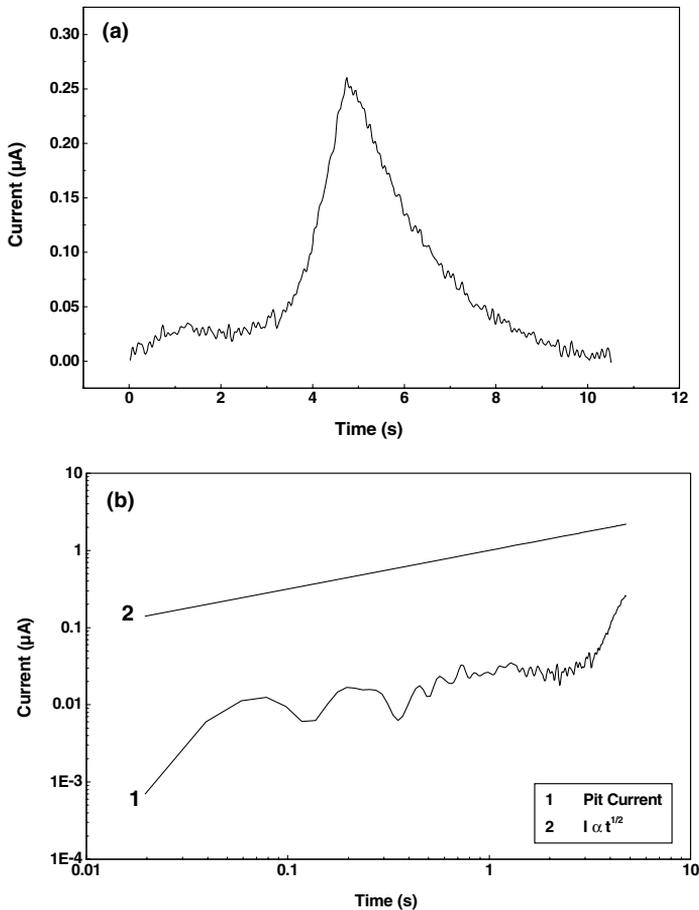


Fig. 3. (a) Metastable pit current transient of 904L SS at 750 mV (Ag/AgCl) in 1 M NaCl solution at 45 °C, (b) double logarithmic plot showing “ $t^{1/2}$ ” behaviour.

During the pit growth stage, different current–time relationships were observed; Figs. 3–5 explore this behaviour, and Fig. 6 shows the type of pit geometry required to account for the variability in pit growth law. In general, the pit current, I , was observed to follow (approximately and with deviations) a power law relationship $I \sim t^n$. The value of n was found to vary with temperature, being very close to 1.5 for the majority of transients with a magnitude of more than $50 \mu\text{A}$ (Fig. 5).

If it is assumed that all the pits have a capped-hemispherical geometry in their early stage of growth (Fig. 6), then prior to salt precipitation the solution resistance for current flow from the pit (or, equivalently, the effective diffusion length) is controlled by the radius of the exit hole (a^0). The value of n depends on this resistance

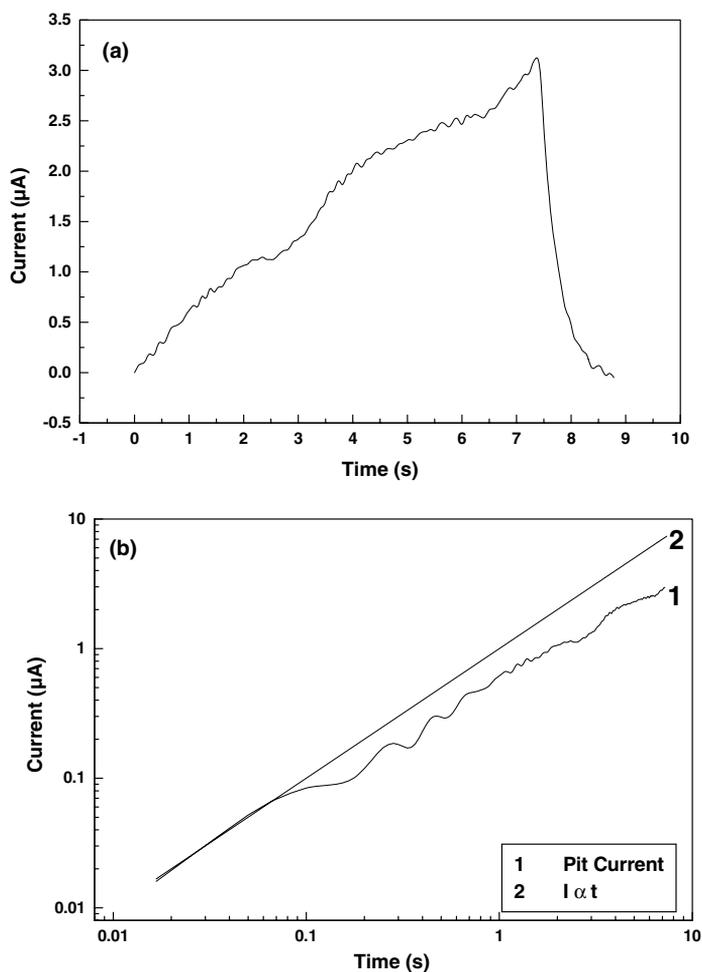


Fig. 4. (a) Metastable pit current transient of 904L SS at 750 V in 1 M NaCl solution at 49 °C, (b) double logarithmic plot showing roughly linear current increase.

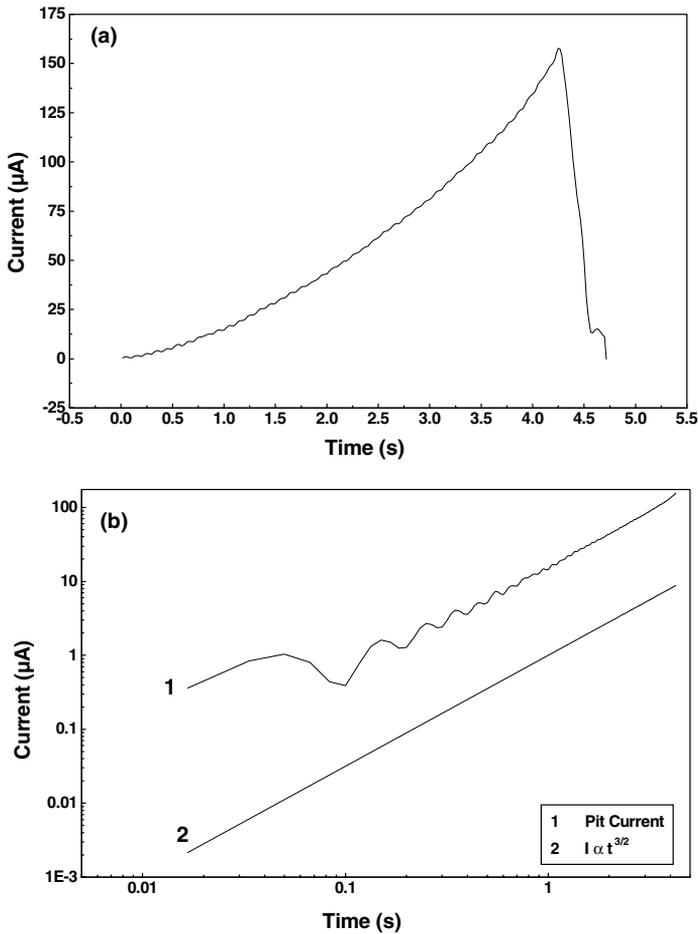


Fig. 5. (a) Metastable pit current transient of 904L SS at 750 mV in 1 M NaCl at 54 °C, (b) double logarithmic plot showing “ $t^{3/2}$ ” behaviour.

and how it changes with time [1]. Smaller hole diameter in the cap over the pit corresponds to slow pit growth at low temperatures and leads to a parabolic increase in the pit current and pit depth. Rapid enlargement of the hole lowers the solution resistance steeply, and the current shows a behaviour $I \sim t^n$ with n greater than 0.5. Pits that grow slowly show a low value of n in the current–time relation; such transients predominate at 45 °C.

As the temperature increases towards the CPT, the cap hole radius (a^0) increases relative to the pit radius (a), and the pit becomes more open in geometry with time; the current–time behaviour thus follows a higher n value ($n \geq 1$). As pointed out by Pistorius and Burstein [1] such an observation does not distinguish between ohmic and diffusion control in the pit, since the effective diffusion length and the specific solution resistance scale similarly with changes in pit geometry. Eventually (on the

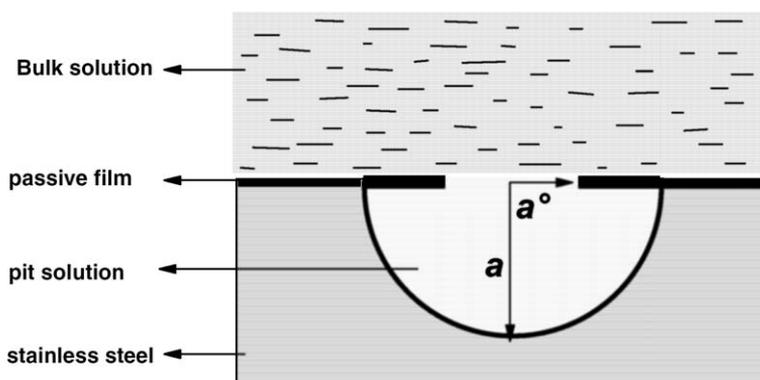


Fig. 6. A schematic of a capped-hemisphere pit geometry. a^0 and a are cap hole and pit radii. The pit mouth may be occluded by the passive film, by a deposited corrosion product, or by a lacy metal cover resulting from undercutting of the metal.

active-dissolution hypothesis), salt precipitation occurs at the bottom of the pit, and now the behaviour depends critically on temperature.

3.3. Stable pitting current transients

Fig. 7 illustrates a typical stable pit current transient obtained after applying 750 mV in 1 M NaCl solution at 62 °C. The current shows a steady increase, followed by a sudden drop to 160 μ A after 4 s, then the current rises again slowly and noisily. This type of current–time behaviour was observed in all stable pit transients (see inset for another example), and represents a more convincing version of the noisy two-stage behaviour observed in 304SS by Frankel et al. [7]. Current transients from stable pits showed an initial shape similar to that of metastable pits recorded at 54 °C. Comparison of the stable pit transient with a metastable pit transient revealed that in both cases the current rises approximately in proportion to $t^{3/2}$, but only for a few seconds. The feature is well demonstrated in Fig. 8 where double logarithmic current–time plots for metastable and stable pit transients are displayed. This graph includes a metastable pit current transient recorded at 54 °C (2 °C below the CPT) and the initial part of a stable pit current transient recorded at 62 °C.

3.4. Pit morphology

Fig. 9 shows the kind of occluded metastable pit formed at low temperature; this kind of pit was associated with a current exponent of less than 1.

Fig. 10 shows the new kind of large metastable pit observed at 54 °C. The notable features are the complete absence of undercutting and the largely polished interior surface indicating at least local salt-film precipitation. This kind of pit was associated with the $t^{3/2}$ type of current transient.

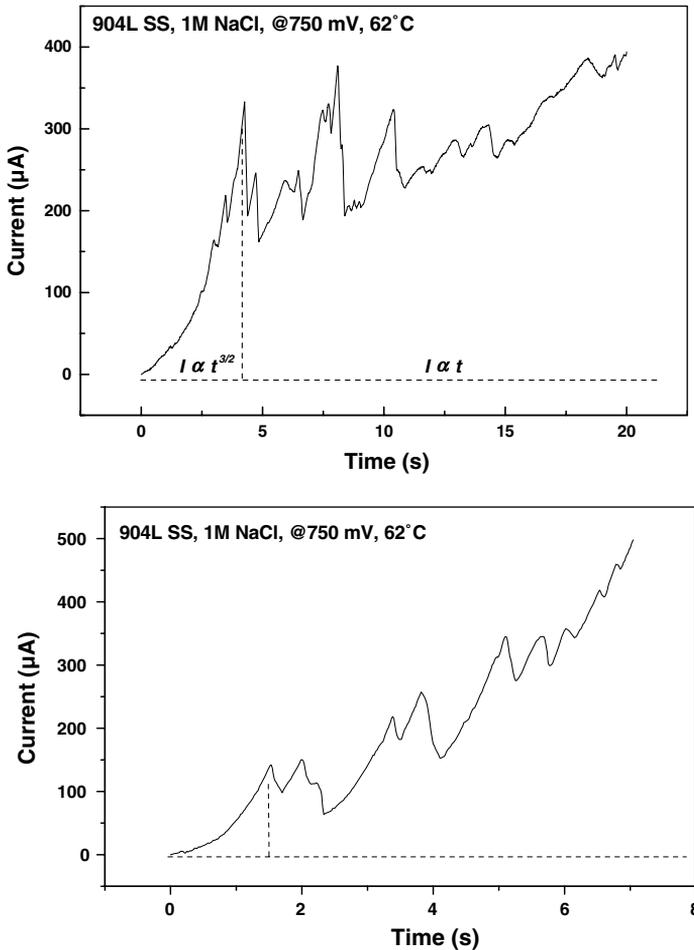


Fig. 7. Early stages of the growth of two stable pits in 904L SS at 750 mV (Ag/AgCl) in 1 M NaCl at 62 °C. The current initially increases as $t^{3/2}$, but rises more slowly and noisily in proportion to $t^{1/2}$ or t^1 after the dotted line. The drop in current and transition in kinetics might be ascribed to salt precipitation, but is more likely the onset of undercutting of the metal surface.

Fig. 11 shows the normal morphology of a stable pit. This is also revealed to be mostly polished when the cover is removed by ultrasonic treatment. Undercutting and lacy cover formation clearly initiates in such pits when they are smaller than the open, non-undercut pits formed at 54 °C and illustrated in Fig. 10.

3.5. Further discussion of pit morphology and the CPT

We proposed earlier [2] that for temperatures below the CPT salt precipitation does not stabilize the pit but promotes passivation, similar to that of iron in

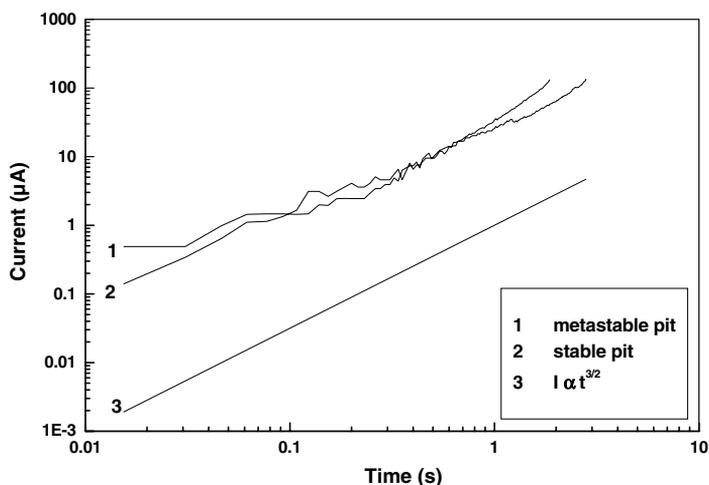


Fig. 8. Double logarithmic current–time plot for a metastable pit and the early stage of growth of a stable pit transient from 904L SS at 750 mV (Ag/AgCl) in 1 M NaCl at 54 and 62 °C. The line corresponding to $I \propto t^{3/2}$ is also illustrated.



Fig. 9. SEM photomicrograph of a metastable pit in a 904L SS sample after a potentiostatic test at 750 mV (Ag/AgCl) in 1 M NaCl at 49 °C.

sulphuric acid. The present results reveal a further subtlety—that polished pit morphologies do occur just below the CPT (Fig. 9), but this does not unconditionally stabilize the pit. An explanation may be sought in the way that the undercut pit morphology develops in stainless steels [13,14]. No pit is completely covered by the anodic salt film. All stable pits contain areas of diffusion-controlled dissolution (at the bottom), passive metal (the lacy cover), and active, film-free dissolution (at the junction of these, where undercutting of the passive surface occurs). In particular, active dissolution at a very high rate is required to initiate each undercutting event that

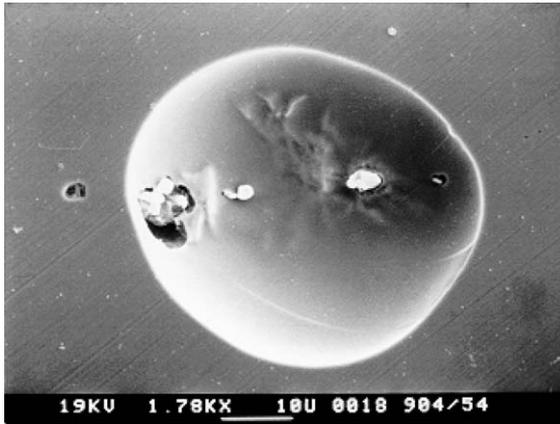


Fig. 10. SEM photomicrograph of a metastable pit on 904LSS after a potentiostatic test at 750 mV (Ag/AgCl) in 1 M NaCl at 54 °C (just below the CPT).

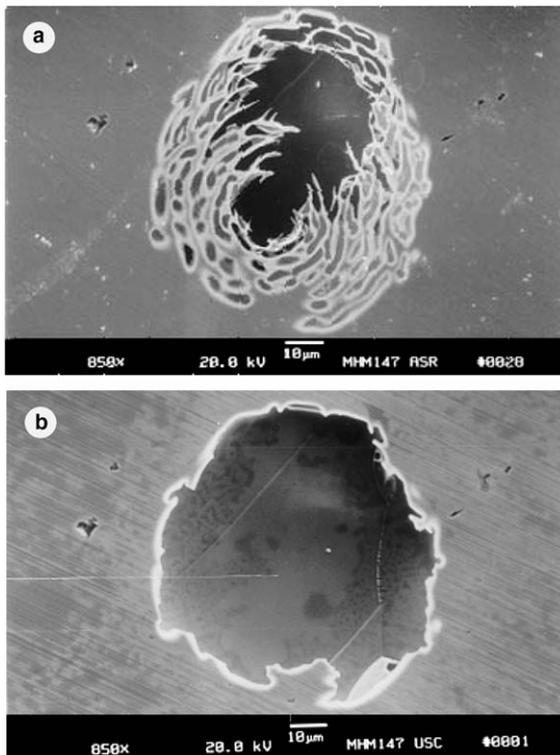


Fig. 11. SEM photomicrographs of a stable pit on 904LSS after potentiostatic test at 750 mV (Ag/AgCl) in 1 M NaCl at 62 °C: (a) SEM image after the test, (b) SEM image after ultrasonic cleaning.

produces a new ring of holes in the pit cover. Temperature and potential affect the kinetics of this undercutting process (which is essential for pit stability) more than they affect the rate of the diffusion-controlled dissolution process across the salt film. Thus at temperatures below but very close to the CPT, huge pit transients occur but these pits undergo deterministic repassivation due to continual widening of the pit mouth relative to the depth—they are unable to undercut the surface at the necessary rate. This must be because the high-rate dissolution at the undercutting site becomes impossible below a certain temperature because it would exceed the critical current density for passivation. This represents a slight modification of our earlier model for the CPT [2].

What about the anodic salt film? Initial inspection of the stable pit transients shown in Figs. 7 and 8 suggested a simple interpretation, similar to that given by Frankel et al. [7] on the basis of their smaller, noisier transients: the initial rise in current is occurring in the active (salt-free) state, and the first drop in current represents the precipitation of the salt film, after which further growth is parabolic or nearly so, controlled by diffusion. But the drop in current also coincides with the onset of undercutting of the metal surface, which is triggered by passivation near the mouth of the pit [13,14]. So the base of the pit could be growing under ohmic or diffusion control—it does not matter. The important aspect is the small region of metal near the mouth of the pit where, as the pit mouth widens, the chemistry becomes too dilute to maintain active dissolution and the metal passivates. Closer to the pit base, the metal continues to dissolve. If the metal can maintain active dissolution without the salt film, even over a narrow range of dissolved chemistries (e.g. from 90% to 100% saturation in ferrous chloride salt, not considering the possibility of supersaturation), then it is possible for the local ohmically limited current density to exceed the diffusion limited current density at the pit base. This leads to undercutting of the metal surface, formation of the lacy metal cover, and stabilization of the pit. But if there is no active dissolution rate accessible that is higher than the diffusion-controlled rate, then the pit widens continually and must eventually repassivate.

So the answer suggested by this work is that both Pistorius/Burstein and Williams/Balkwill were right. The base of a pit usually carries a salt film, even in many metastable pits, but the key events that determine the transition to stability occur near the pit mouth, in a region where the salt film is not present because of the natural concentration gradient that exists within the pit.

4. Conclusions

1. Increasing the temperature from 10° to 2° below the CPT increases the typical value of pit growth exponent by favouring the stability of more open cavities. This mirrors the behaviour as a function of potential above the CPT.
2. Very near the CPT, a new type of very large metastable pit with a markedly deterministic repassivation behaviour has been identified. Such pits are unable to undercut the surface and achieve stability because the extreme anodic current densities required at the undercutting site are unavailable.

3. Very convincing two-stage pit growth transients are observed in this kind of high-alloy steel just above the CPT. On the one hand, this might confirm the conclusion drawn by Frankel et al. from experiments on low-alloy materials at room temperature: that pit stabilization is associated with the precipitation of an anodic salt film. But it is also possible to generate an abrupt drop in current and change in current–time relation by invoking passivation near the pit mouth followed by undercutting of the metal surface (lacy metal cover formation).
4. The view that the anodic salt film per se is responsible for pit stabilization is only partly correct. The key event in pit stabilization is the onset of surface undercutting, and this requires high-rate active dissolution without a salt film, even though the metal at the pit base may carry such a film.

Acknowledgments

The first author wishes to thank the Iran Ferdowsi University of Mashhad for their financial support. We also thank Avesta Polarit for supplying the 904L stainless steel.

References

- [1] P.C. Pistorius, G.T. Burstein, *Phil. Trans. R. Soc. Lond.* 341 (1992) 531–559.
- [2] N.J. Laycock, M.H. Moayed, R.C. Newman, *J. Electrochem. Soc.* 145 (1998) 2622–2628.
- [3] R. Qvarfort, *Corros. Sci.* 29 (1989) 987–993.
- [4] M.H. Moayed, N.J. Laycock, R.C. Newman, *Corros. Sci.* 45 (2003) 1203–1216.
- [5] R.C. Newman, K.H. Liew, *Corrosion* 43 (1987) 58–60.
- [6] D.E. Williams, C. Westcott, M. Fleischmann, *J. Electrochem. Soc.* 132 (1985) 1796–1804.
- [7] G.S. Frankel, L. Stockert, F. Hunkeler, H. Boehni, *Corrosion* 43 (1987) 429–436.
- [8] D.E. Williams, J. Stewart, P.H. Balkwill, Nucleation, growth and stability of micropits in stainless steel, in: G.S. Frankel, R.C. Newman (Eds.), *Critical Factors in Localized Corrosion*, The Electrochemical Society, Pennington, NJ, USA, 1992, proceedings volume PV 92-9.
- [9] P.H. Balkwill, C. Westcott, D.E. Williams, *Mater. Sci. Forum* 44–45 (1989) 299–313.
- [10] E.M. Franz, R.C. Newman, Growth and repassivation of single corrosion pits in stainless steel, *Corrosion* 40 (1984) 325–330.
- [11] H. Ezuber, R.C. Newman, Growth-rate distribution of metastable pits, in Ref. [8], pp. 120–133.
- [12] P.E. Arnvig, A.D. Bisgard, Determining the potential independent critical pitting temperature (CPT) by potentiostatic method using the Avesta cell, Avesta-Sheffield publication in (ACOM), vol. 3, 1996, pp. 2–12.
- [13] P. Ernst, R.C. Newman, *Corros. Sci.* 44 (2002) 927–941.
- [14] P. Ernst, R.C. Newman, *Corros. Sci.* 44 (2002) 943–954.