Metastable Pitting and the Critical Pitting Temperature

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ABSTRACT

For any particular stainless steel, a critical pitting temperature (CPT) can be measured, below which stable pits do not occur at any potential up to the onset of transpassivity. The more highly alloyed the steel, particularly with molybdenum, the higher the CPT. The CPT for 304L austenitic stainless steel with a 240 grit surface finish has been determined as 48 to 49°C, and metastable pitting events have been analyzed in detail at lower temperatures. Below the CPT, metastable pitting activity peaks at around 300 mV (SCP), but occurs at all potentials up to the transpassive range. The morphology of these pits has been examined using SEM and a model is proposed in which precipitation of an anodic salt film within pits is the critical factor; above the CPT, a salt film is essential for stable pit growth, while below the CPT, the salt is an intermediary in oxide passivation, like that of iron in sulfuric acid. This is an outcome of a complex dynamical system and does not require the properties of the salt itself to change suddenly with temperature.

Introduction

The pitting potential of stainless steels shows a discontinuous variation with temperature. The critical pitting temperature (CPT) for a given alloy and surface finish is defined as the temperature below which no stable pitting can occur, and is indicated by a step increase of the breakdown potential with increasing temperature, from a value in the transpassive range to a moderate value representing a true pitting potential. The concept of a CPT was introduced by Bragg and Dyer as a means of screening austenitic stainless steels of differing molybdenum content. Quarrington demonstrated independence of the CPT on chloride concentration in the range 1 to 5 M NaCl, and also found it to be independent of pH in the range 1 to 7. Quarrington's results also indicate that the CPT represents a very sharp transition and, in the absence of unwavering crevice corrosion, it can be defined within an absolute accuracy of ±1°C. Obviously the CPT results from some deterministic process; it does, however, depend on the geometry of possible pit initiation sites; recently we have found that the CPT varies appreciably with surface finish.

It was found that molybdenum content was the most important factor in determining the CPT of a given alloy but the effect of other elements can also be included to produce an empirical pitting resistance equivalent (PRE). Different authors have quoted different equations for the PRE (e.g., Eq. 1), but the CPT in all cases increases linearly with increasing PRE.

PRE = Cr (wt. %) + 3.3 Mo (wt. %) + 30 N (wt. %) [1]

The CPT is a transition related to early growth of stable pits. Propagation of stable pits, or initiation of metastable pits, may occur at lower temperatures. In order to understand the CPT, we must recognize that the driving force for metal dissolution is enormous at high anodic potentials such as 750 mV (SCP) where CPT tests are commonly carried out. It is unlikely that alloying could enable the steel enough to prevent the establishment of a concentrated pit chemistry by rapid metal dissolution at this potential. The mechanism of the CPT transition must therefore involve passivation, not embrittlement, and this is the hypothesis on which we have based our recent work in this area.

In order to gain a microscopic understanding of the CPT, one first hopes to find a similar transition that occurs on larger electrodes and in a deterministic manner. Newman and Liew used artificial pit electrodes of stainless steels and high nickel alloys to measure repassivation temperatures for localized corrosion. They found that propagation of deep pits held at high anodic potentials was possible at temperatures well below the CPT, but, on cooling, these pits repassivated abruptly under their anodically generated salt films at a lower critical temperature Tc. It was suggested that smaller pits would have repassivated nearer the CPT. Later, Salinas-Bravo and Newman used electrochemical noise from duplex stainless steel to show that metastable pitting could occur at temperatures below the CPT, but stable pitting was only detected at the conventional CPT value. This suggested that the CPT was related to the transition from metastable to stable pit growth, and they suggested the following explanation: Assume all stable pits must develop and maintain an anodic salt film. Assume further that there is a critical current density for passivation in the saturated salt environment of the pit nucleus, iSat, which increases with temperature, T. There is also a limiting current density, iLim, given by the saturation concentration of metal ions, Cm, and Pick's first law, which increases more gradually with T than iSat. The CPT corresponds to the temperature at which iSat = iLim, since below this temperature the alloy cannot generate the anodic current density required to maintain the necessary pit chemistry. The present paper combines some ideas from the work of Liew and Salinas-Bravo by grouting the salt film a causative role in passivation as suggested by Liew, but considering also the balance between dissolution and mass transport in a small cavity.

Experimental

All electrochemical experiments used a potentiostat made by ACM Research together with a sweep generator made by Thompson Instruments. Data were recorded digitally by a computer fitted with a Keithley Instruments data acquisition card used as an analog to digital converter, in conjunction with Keithley Emphasis LX software. A saturated calomel electrode (SCE) or silver/silver chloride (Ag/AgCl) electrode was used as the reference electrode, and a 10 mm length of 1 mm diameter platinum wire as the counter electrode. All test solutions were made from analytical grade chemicals and deionized water.

The work was performed on 304L stainless steel plate (20 Cr, 25 Ni, 4.3 Mo, 0.5 Ca, 1.4 Mn, < 0.03 Si), machined into 4.0 mm diameter rod specimens. The steel was supplied by...
Avesta Sheffield AB, Sweden. It should be noted that this particular heat of steel does not have the best possible corrosion resistance for this grade, and that tests performed in this manner are less resistant than plate (because they expose orientations other than the rolling plane). The CPT was measured with two different methods, using simple immersion of the rod specimen with a waterline to eliminate crevice effects. In both methods, a surface area of 5 cm² was exposed and samples were used for many tests, but were re-abraded with 240 grit SiC paper and rinsed with deionized water prior to each test.

Method A.—Anodic polarization curves were obtained in nitrogen-purged 0.61 M, 0.1 M, and 1 M NaCl at controlled temperatures from 3°C up to 85°C (within ±2°C). A sweep rate of 0.5 mV s⁻¹ was used and the breakdown potential, E_b, was defined as a sustained anodic current density of 10 μA cm⁻².

Method B.—Potentiostatic tests were carried out at 750 mV (Ag/AgCl) with the temperature ramped upward at ~0.5 min⁻¹, until pitting breakdown occurred (as defined above).

Potentiostatic data on metastable pitting of 904L were obtained as a function of potential in 1 M NaCl open to the air at room temperature. To obtain low noise data and well-separated events, a 1200 grit finish was used on 1 mm diam rod electrodes positioned so that the test surface area was only 0.1 cm². The sample surface was freshly abraded before each test, and the simple potential was stepped to the test potential; the current was recorded for the next 350 s at 9 Hz. For all tests, the first 50 s of data following the potential step were ignored since the total current was usually too high for the resolution of individual pitting events. The remaining 300 s were analyzed by plotting in 50 s intervals and counting all distinguishable pitting events by eye (the minimum transient height was 20 nA). From the results of these tests, a test potential of 300 mV (SCE) was chosen for a further sequence of potentiostatic tests on freshly abraded surfaces at controlled temperatures (±1°C) from 2 to 27°C.

In addition, many tests were carried out using flat samples with various surface finishes at 750 mV (Ag/AgCl) in deaerated 1 M NaCl at various controlled temperatures. A large number of metastable pitting events were characterized by assuming the pits were hemispherical and calculating the pit radius and pit current density as a function of time using Parada's second law. Some of these samples were then transferred to an STM for examination of individual pits. These data will be reported in detail elsewhere but are outlined here in order to show evidence relevant to pit morphology and the role of salt films.

Results and Discussion

The CPT.—904L is a modern austenitic stainless steel and is highly resistant to localized corrosion. Polarization curves measured for this alloy in 1 M NaCl at various temperatures indicated a CPT between 45 and 50°C, and potentiostatic tests placed it more accurately at 48-49°C, which is in good agreement with literature results for this alloy.13 Also, in agreement with other reports,14 the CPT was found to be independent of [Cl⁻] in the bulk solution (Fig. 1). Immediately above the CPT, measured pitting potentials showed the well-known increase with decreasing log([Cl⁻]) although the gradient of this variation was greater than the 90 mV measured for low alloy stainless steels.120 E_b Incurred only a slight decrease with increasing temperature above the CPT.

Metastable pitting as a function of potential.—Metastable pitting was clearly evident at temperatures below the CPT, and the magnitude of these metastable events was often several micrometers (Fig. 2). Pit initiation is frequent and metastable growth regularly occurs, but the transition to stable pitting is impossible at temperatures below the CPT. A further observation which can be made from these data is that metastable pitting activity appears to reach a peak at 200-250 mV and then decrease at higher applied potentials. This might be an uninteresting effect due to exhaustion of active sites. However, the existence of a genuine peak in pitting activity was confirmed by the potentiostatic experiments shown in Fig. 3, which shows the number of observable metastable pits (>20 nA above background) as a function of potential for separate experiments carried out at a number of different potentials at one temperature.

It has been proposed14 that for low alloy stainless steels at room temperature, the transition from metastable...
bility to stability requires the precipitation of a salt film within the pit, and the ability to maintain this salt film upon closure of the layer (passive film recomm. This theory suggests two possible mechanisms by which metastable pits could repassivate: either the salt film is never precipitated, or the pit covers ruptures and the salt layer cannot be maintained. This explains the observed behavior of stainless steels above the CPT that is more likely to be formed and maintained as the potential increases, thus leading to the existence of a pitting potential. However, for 804F below the CPT, the apparent frequency of metastable pitting decreases above 400 mV, which is inconsistent with increased stability due to salt film formation. In this case, either the pit initiation or nucleation process is affected by increasing applied potential, or the average peak current reached by metastable pits is decreasing below the detection level.

There is no reason to expect the pit initiation rate to decrease with increasing potential and, in fact, all initiation theories suggest the opposite. Therefore, it seems likely that the average peak current of metastable pits reached a maximum near 400 mV and then decreased until, at 800 mV, almost no pits reached the 20 nA detection limit. These two effects combined to produce the distribution seen in Fig. 3.

**Pit repassivation at high potentials below the CPT.**—A model for the CPT transition was proposed by Salinas-Bravo and Newman. This assumed that a salt film must be maintained in an open cavity to sustain stable pitting, as suggested by many authors (e.g. Ref. 14 and 15). In order to precipitate this salt film, an anodic current density greater than or equal to the anodic limiting current density, $i_{an}$, must first flow in the cavity where pitting initiates. A critical current density, $i_{cr}$ for passivation was proposed to exist even in the most aggressive pit environment, and was a weaker function of temperature than the anodic limiting current density, $i_{an}$. The CPT then simply corresponds to the condition $i = i_{cr}$. In this model, salt film precipitation is impossible below the CPT (since the necessary current density $i_{cr}$ is not available), and so stable pitting is prevented. In the metastable pitting range, only well-covered (i.e., low current density) metastable pits could exist. This could explain satisfactorily the form of Fig. 3, but a slight modification to this model, recognizing that the salt film can be an intermediate in passivation at low temperatures, may help to explain the sharpness of the CPT transition (defined to -1°C). The Salinas-Bravo/Newman model predicts a CPT value which depends somewhat on the geometry of the individual pits and how this affects $i_{cr}$. Consequently, a range of values would be expected, which seems at odds with experience, yet this model is not refuted, and the effect of surface finish and/or inclusion size on the CPT may provide an experimental test.

The modal current density of metastable pits has been shown to increase with potential, and it is therefore reasonable to suggest that the higher the potential, the sooner pits will precipitate a salt film. Above the CPT, early precipitation of salt is beneficial since it stabilizes a pit against loss of its cover. However, below the CPT, faster salt precipitation correlates with the apparent decrease in pit lifetimes and suggests that salt precipitation could be responsible for pit repassivation, as shown by Newman and Low. This is below the CPT the precipitation of a salt layer leads to passivation in a manner similar to the passivation of iron in sulfuric acid. If the ability to passivate requires the presence of a salt and is mostly a function of temperature, then the anodic current density in the pitting system (i.e., the cavity size), the dependence of the CPT on pit geometry is reduced compared with the Salinas-Bravo model, since below the CPT, salt precipitation over a large range of current densities causes passivation. We show later that such a model does not require the presence of the salt film to control the \\n
phenomena showing discontinuity, passivation can result from the interaction of processes that individually vary continuously with temperature.

**Salt films and their role as intermediaries in passivation.**—The properties of metastable salt films have been studied extensively with many of these authors reporting a competition between salt and oxide. First, we discuss the physical nature of the salt film including its porosity. According to Bunsen, the salt film is a porous low-field (low) condenser that thickens linearly with potential. Hunkeler et al. also considered the salt film to be porous. For chloride salt films on nickel, Danielsson found low field conduction and operated and calculated a porosity of approximately 0.1%. Probably there is a nonporous salt layer which may be covered by a porous salt in certain conditions, as argued by Beck. Grim et al. used an impedance to study the salt film formed on iron in an FeCl₃ electrolyte and modeled their results using a duplex film structure; the inner, compact film was thought to be amorphous with the outer, porous film being hydrated. They suggested that the duplex structure was, in fact, only an idealized description of a film whose properties varied continuously with deposition. Beck also used the duplex model to explain the difference for the same system and calculated the porosity of the outer layer to be between 0.2 and 0.8%.

Alkire et al. suggested that transient salt films could be precursors to oxide passivation and proposed a model which, for iron in sulfuric acid, showed good agreement with experiments. In fact, the formation of a de-passivating pitting passivation of iron in sulfuric acid has been studied by many authors with Bartlett and Stephens describing precipitations of a salt occurring together with oscilations in the current density near the active-passive transition. An early model for these oscillations was proposed by French and Pitts and later developed by Beck and others to include the role of a salt film. For passivation, the surface potential under the salt film must exceed the passivation potential, $E_{p}$, but for the low pH of concentrated sulfuric acid solutions, this potential could never be reached due to IR effects in the device. However, the pH under the salt layer is higher than that of the bulk solution, because hydrogen ions are preferentialy migrated outward under the prevailing electric field. If a steady-state is assumed, then neglecting hydrolysis of Fe⁷⁺, the flux of H⁺ across the salt layer would be zero and Eq. 3 can be derived, where $E$ is the potential difference across the salt film and $d$ is the pH increase at the metal/salt interface as a result of salt precipitation.

$$\Delta \phi = \Delta \mu / \delta \phi$$

Since the passivation potential and critical current density fall as the pH increases, the likelihood of oxide film formation increases when the salt precipitates and as the potential increases. Beck calculated a 1% porosity for the salt film, but a computer model was later developed by Russell and Newman and further adapted by Russel and Newman with the salt film now considered to be nonporous. In a galvanostatic study of induction times for FeCl₃ film formation on iron, Kuo and Landolt observed that a final nickel film different to the initial salt was possible or oxides, and for an Fe₅Na₃ alloy. Grim and Landolt found evidence of local oxide passivation beneath a salt film in chloride solutions.

For stainless steel artificial pits in chloride containing solutions, Newman and co-workers have reported current oscillations similar to those observed on iron in sulfuric acid. These oscillations were explained by the occurrence of local passivation events. Later it was shown that the frequency of the oscillations varied with the width of the pit there is a radial wave of passivation and recrystallization. Period doubling was also observed. For 302SS in NaCl solution, the oscillations were prevalent at high potentials and low temperatures; they vanished at 50°C. In chloride/nitrate solutions, the magnitude of current
oscillations increased with increasing potential until complete passivation occurred, consistent with the observation that natural pitting is prevented at high potentials by lower levels of nitrate. These results clearly show that small drops of sample solution can cause pit nucleation and propagation on stainless steel, particularly when the sample solution is relative to the salt film formed at high potentials. It is a small step from these observations, together with those of Newman and Liew, to the present suggestion that the CPE corresponds to a change in the role of the salt film.

Physical phenomena that the salt itself changes abruptly at the CPE. The dynamic system, as defined by the equations of Fraden and Fitzpatrick, shows feedback effects that can drive the electrode to complete activity or passivity, or to a state where it oscillates between the two. Microscopically, as the temperature is lowered from a value above the CPE, oxide nucleates beneath the salt film but is undermined by dissolution when the salt layer thins above it. This gives rise to the oscillations seen by Newman and Ajiwaj. At the CPE, the nucleation and/or growth rate of the oxide patches is such that they cannot be undermined before the local solution starts to dilute by loss of dissolved film, and passivation ensues. Factors that vary continuously with temperature, such as pH variation across the salt film, dissolution kinetics, oxide nucleation, etc., combine to give a discontinuous variation of pitting with temperature. The extent of greatly increasing the pit depth, as in Liew's experiments, is to slow down the rate of escape of ions from the pit, so that there is more time for the oxide to be undermined, and the original temperature decrease.

**Computer generation of metastable pitting regimes.** The object of this simple model is to show how the decreasing size of metastable pitting transients with increasing potential below the CPE may be produced by coupled and fairly conventional assumptions about the pitting mechanism, together with the assumption that salt precipitation terminates pitting below the CPE. The model is not meant to be strictly predictive, since we know that pit densities are very important in practice, and we do not know how to model them. Pit nucleation is assumed to occur in a pre-existing hemispherical cavity of radius r, with fresh metal exposed inside the cavity (for example, this might be due to some event at the vicinity of an inclusion). Pit growth will occur provided that a sufficiently concentrated pit solution can be maintained (about 3 M in dissolved cations, as shown by Hakkonen and Qaudt et al.). An equation involving previously to describe the kinetics of pit growth can be written generally and applied to salt-free pits, at any potential

\[ E_p = E_{corr} + 0.059 \log i_{corr} + m_r \]

where \( E_{corr} \) is the applied potential, \( i \) is the current density in the pit, \( E_{corr} \), \( m_r \), and \( m \) are the corrosion potential, corrosion current density, and anodic Tafel slope in the saturated pitting environment, \( E \) is the solution resistance, and \( F \) is the pit current. A saturation concentration \( c_{sat} \) of the metal chloride in the pit is assumed. Tafel's law is assumed to apply up to the point of precipitation of salt; this is not quite true, since the pH is changing and the reactions are pH dependent; however, we can at least be sure that classical concentration polarization does not exist for dissolution of stainless steel, since in the absence of a back reaction (metal plating), which is only true for high exchange current systems that dissolve fast near their equilibrium potentials (e.g., sulfuric acid). If the initial parameters produce an initial metal ion concentration \( c_m \), pit growth is allowed to proceed. At temperatures below the CPE, it is proposed that a pit will continue to grow until precipitation of a salt film causes repassivation. Since supersaturation is known to occur, repassivation is assumed to occur when the metal ion concentration reaches 6 M.

The effects of a pit cover are difficult to model and so pits are assumed to be open and hemispherical. Any other consistent (including coated) geometry would give qualitatively similar results. The bulk solution is assumed to be highly conducting. The model of metastable pit growth then involves the following steps:

1. For an initially open, hemispherical cavity of radius r, calculate the resistance for current flow out of the cavity, \( R \), using Eq. 4, where \( p \) is the solution resistivity

\[ R = \frac{p}{r} \]

2. Actually this is a simplification, since an open hemispherical cavity cannot be an equipotential surface and must degrade into a conical shape when it dissolves, hemispherical pits are only hemispherical because they have a cover with a hole or holes in it.

3. Calculate the current density in the pit for an applied potential, \( E_{corr} \), using the Wenston-Hancock technique to solve iteratively for a from Eq. 3.

4. Calculate the concentration of metal ions, c, at the pit bottom assuming all the current to be carried by diffusion so that Fick's first law modified for a hemispherical geometry can be used

\[ C = \frac{2i}{nFD} \]

where \( D \) is the effective diffusion coefficient (\( 10^{-9} \text{ cm}^2 \text{ s}^{-1} \)) and \( n = 2.2 \) for stainless steel. If \( M < C < 6 \text{ M} \), pit growth is allowed to continue. If not, the pit repassivates at this time.

4. Calculate the total current from the pit and the corresponding current density. Assume the latter is constant for a small time interval, \( \Delta t \), and use Faraday's second law to calculate the amount of pit growth in this time, and therefore a new pit radius. Return to step 2.

Some reasonable assumptions and simplifications are made about electromechanics in the pit environment, such as that a constant average solution resistivity of \( 10 \text{ Ohm cm} \) regardless of metal ion concentration. This is a good assumption when the bulk solution is highly conducting but would fail for dilute bulk solutions where there is an exponential potential distribution with depth in the pit. For 304 SS in a simulated pit environment, \( E_{corr} \) and i were measured as 250 to 300 mV, and around 1 mA cm\(^{-2} \), respectively. 904 L is more highly alloyed, so the anodic kinetics are inhibited relative to 304; in this case, \( E_{corr} \) and i were estimated as 300 mV (iSCM) and 0.1 mA cm\(^{-2} \), respectively. The anodic Tafel constant was assumed to be 180 mV. A range of initial cavity radii from 0.01 to 10 \( \mu \text{m} \) was assumed, corresponding to the variety of pit initiation sizes available, and on the scale of inclusion size (since inclusions provide the initiating cavities in practice). Starting with larger sizes may simulate (to some extent) the presence of a pit cover during early stages of growth, since the cover increases the effective diffusion length.

For each specified initial cavity size it was found that pit growth was only possible over a narrow range of potential (e.g., 200 to 250 mV, for \( r = 0.1 \mu \text{m} \)). At lower potentials, the initial cavity cannot support a metal ion concentration \( > 3 \text{ M} \), and at higher potentials a salt film is precipitated immediately causing repassivation. Figure 4 shows: an example of computer generated metastable transients in current and current density, to be compared with Fig. 5 which shows a real metastable potential transient from 904 L with a similar lifetime, but a smaller current than the model pit in Fig. 4. The current densities in Fig. 5 were calculated from the currents and Faraday's second law, assuming a hemispherical geometry and \( n = 2.2 \). This quantitative discrepancy is a result of the relatively high current density in the model pit which is due to the absence of a pit cover in the model. Real transients display a variety of relationships from \( i \sim r^{-3} \) to \( i \sim r^{-2} \), with these differences clearly being associated with the pit cover.

The initial radius used for the birth of pits in this model can be considered to correspond to an effective radius accounting for the complicated real-life effects of inclusion
size and reentrant surface roughness (presence of microcavities). As expected, at low applied potentials where the pit current density is low, only cavities with large initial radii can acquire the necessary local chemistry to support metastable pitting, but as the potential increases the smaller cavities become accessible to pitting. Plotting the peak currents reached by pits of any radius as a function of potential gives Fig. 6, which can be compared with the polarization curve measured below the CPT for 904L (Fig. 2). The computer generated results show qualitative agreement with Fig. 2 in that larger transient sizes occur at relatively low potentials (100 to 300 mV) and smaller ones are seen as the potential increases. In fact, the quantitative agreement is quite good in that the absolute value of the pitting initiation potential is well reproduced, and an order of magnitude decrease in the transient height occurs with only about a 50 mV increase in potential in both the experiment and the simulation.

Pit morphology.—The morphology of pit surfaces on stainless steel has often been studied, usually in attempts to ascertain the conditions within growing pits. At low potentials, Schwenk1 found square and hexagonal etch pits, but at more noble potentials, hemispherical pits with circular edges and either dull or polished interiors were found. Pickering and Frankenthal12 also found a mixture of crystallographic etch pits and hemispherical pits despite only using a high applied potential, while Ko and Alkire9 found that all pits initially grow as crystallographic hexagonal pits before growing into hemispherical cavities. Saty10 distinguished carefully between etch pit and polishing (or brightening state) pits formed due to salt-film dissolution at more noble potentials.

Sustained dissolution beneath salt is necessary to produce polished surfaces, and since salt film-mediated passivation would normally occur immediately after salt precipitation, pits passivated this way would appear etched, except in some cases where oscillatory salt passivation and reactivation could cause polishing before passivation. For 904L at temperatures well below the CPT (e.g., 40°C), all pits were still at least partly covered after testing, but in cases where this cover could be removed by ultrasonic cleaning, these pits were found to have etched interior surfaces and often had straight edges (Fig. 7a). Near the CPT (45°C), more open pits were found, leading to a hemispherical and partially polished interior, suggesting that, at least for part of their lifetime, these pits were growing with salt films present (Fig. 7b). Above the CPT, stable pits grew with polished interiors and lacy metal covers which are discussed later (Fig. 7c).

Morphology alone is not a perfect guide to the change in pit behavior at the CPT, since the most covered (low current density) events are immune to the CPT criteria up to the time that they become open. Thus highly covered (low current density) metastable events could be well polished, as their current densities and effective diffusion lengths could be in the range studied by the new1 but they would passivate immediately on losing their covers.

Pit covers.—It is well known that pits undermine the passive film such that remnants of the film, and even some of the metal itself, at least partially cover the pit cavity during early growth. Schwenk1 detected such pits after testing by examining the surface with a fine metal pin, while Rosenthal and Damask found that destroying the shielding layer during pit growth caused direct repassivation of the pit. Isaac and Kessel12 also found that puncturing the cover led to repassivation except in the case of some very large pits which were able to survive. Suki13 and Marinkovic14 watched pits develop using a stereoscopic microscope and saw that the covers were convex, possibly due to the remote pressure of the concentrated solution (or formation of hydrogen) within the pit. Pickering and Frankenthal12 had earlier found lacelike covers over pits and believed that the cover was perforated due to attack from underneath by the aggressive solution. It is a common idea that if a metastable pit survives the eventual collapse of its cover than it has become a stable pit. During metastable growth the cover is seen either as a protective barrier or a diffusion barrier which helps to keep the pit from repassivating. It would be ex-
expected then, that all pits below the CPT would be growing with a cover present.

In the model, the cover and its behavior during pit growth could not be simulated, but in practice many pits will repassivate by destruction of the cover. For a modern alloy such as 904L, inclusion radii are unlikely to be greater than 1 μm, but computer-generated pits could only exist at low potentials if larger initial radii were specified; for a 1 μm cavity, the lowest potential for pitting was

210 mV. Metastable pits found in practice at lower potentials can only survive because of the pit cover, which increases the effective diffusion length. This will often rupture before precipitation of a salt. Figure 3 can now be explained in full: at low potentials only the nearest killed sites support pitting (since lower current density is required in these sites to maintain the necessary chemistry) and these pits are repassivated even by a partial rupture of their cover. As the potential increases, pit can survive in more open cavities and complete loss of the cover is required to repassivate them, so that the number of observable pits increases. At high potentials extremely high pit current densities are accessible, so all pits have the potential to survive even in the uncovered state, but any pits surviving to this state will be repassivated by the precipitation of salt followed by oxide formation under the salt film. The largest transient heights will be observed at the lowest potentials where open pits propagate. The higher the potential, the sooner the salt film is precipitated, thus the sooner passive passivation occurs, and transient heights decrease as shown in Fig. 3 and 6.

Metastable pitting as a function of temperature—Even at 2°C, nearly 95°C below the CPT, metastable pitting was still detectable, and the number of metastable pits increased sharply as the temperature increased. However, despite the significant number of quite large metastable pits observed in all types of tests below the CPT, no stable pits were detected.

Galvani first showed that the product ir, of pit current density and depth was the critical quantity in determining pit stability, pits reaching critical value of ir (the pit stability product) would have a sufficiently concentrated local chemistry (concentration of dissolved cations, c - c°) to sustain further growth. In the case of stainless steel at room temperature, we know that the critical chemistry is about 3 M in dissolved cations. Assuming a hemispherical pit geometry and using Faraday's second law to calculate the pit radius (with n = 2, 2), current densities from numerous metastable pits at 250 mV and several temperatures below the CPT were analyzed to give charge, radius, and current density, giving numerous values of the product ir at the critical chemistry (DC°). Equation 6 was then used to calculate theoretical ir values for these chemistries in open transversal pits. The results of this exercise will be reported in another paper. Pits possessing a cover will be able to exist with ir values lower than those required in open pits, because the cover increases the effective value of r. For example, at 40°C the data indicate that all pits studied were growing with pit covers, while at 90°C the larger pits had ir values approaching that for the repassivation chemistry in open pits, while at 48°C the ir values for the larger pits were near the saturation chemistry for open pits. Above the CPT, e.g., at 82°C the stable pits showed lacy metal covers (as in Fig. 7c) and were polished inside. Any pits that did survive to be open were always dish-shaped, since the hemispherical shape is not stable under anodic diffusion control.

The presence of lacy metal covers on stable pits casts doubt on the stability of any truly open pit cavity. While the presence of lacy metal covers has followed the conventional wisdom (assuming that n mature pits are open), it has been known for decades that lacy metal covers are present over most mature pits in stainless steel. The mechanism of formation of this cover was presented qualitatively by Smith et al., and modeled numerically by Laycock et al. Essentially, the pit solution is more dilute near the mouth, allowing passivation of the pit perimeter followed by unravelling of the passive film. The spacing of the holes in the lacy cover depends on the ratio C°/C°. The importance of the lacy cover in determining the CPT is not shown, but very recently we have found that adding sulfate lowered the

Fig. 7. (a) SEM micrograph of a pit with an etched bole surface from 904L at 750 mV (SCE) and 40°C. (b) SEM micrograph of a partially polished pit from 904L at 250 mV (SCE) and 45.5°C. (c) SEM micrograph of a stable pit with a lacy cover at 52°C.
CPT of 904L by forming a stronger (less porous) layer cover, despite the inhibiting action of sulfate above the CPT.

Conclusions

The critical pitting temperature (CPT) for 904L stainless steel is 48-49°C and is independent of bulk solution chloride concentration from 0.01 to 1 M NaCl.

Metastable pitting temperature occurs at temperatures as low as 2°C and at anodic potentials right up to the onset of transpassive dissolution. The CPT transition concerns the ability of a metastable pit to become stable.

Below the CPT, there is a peak in observable metastable pitting activity for 904L SS at around 360 mV (SCE). It is proposed that, below the CPT, salt film precipitation mediates the oxide passivation of pits in a manner similar to the passivation of iron in sulfuric acid; earlier precipitation of salt at high potentials accounts for the reduction in size (and apparent frequency) of metastable pitting transients. Model calculations of metastable pitting transients show good qualitative agreement with experimental results, and better quantitative agreement is expected once the effects of the pit cover can be incorporated in the model.

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REFERENCES