2001 W.R. Whitney Award Lecture:
Understanding the Corrosion of Stainless Steel

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ABSTRACT

In order to predict corrosion damage on passive metals, it is essential to use statistical methods and semi-empirical models, but at the same time we must maintain active inquiry into the fundamental deterministic processes that occur during localized corrosion. If it were the case that atomistic events occurring within the intact passive film were responsible for, say, the beneficial effect of alloyed molybdenum, then we would have a gigantic job to do. Luckily, it appears that the quality of the passive film mainly affects the nucleation frequency of pits and has little or no bearing on the effects of environmental or metallurgical variables: T, Cl⁻, Br⁻, H₂S; Mo, N, σ .... We find that the anodic kinetics of the metal in the already-developed microenvironment of a pit can account for the effects of a large number of variables in pitting corrosion. Specifically, above the critical pitting temperature (CPT), the potential required to precipitate an anodic salt film in a cavity of relevant size is susceptible to straightforward modeling and experimentation and provides a robust predictor of the pitting potential. The CPT itself is associated with the inability of the metal to maintain active dissolution because passivation intervenes, even in the most aggressive possible microenvironment. Crevice corrosion is easier than pitting because the associated diffusion length is longer and the required anodic current densities are smaller.

Chloride-induced stress corrosion cracking (SCC) always initiates in actively growing corrosion sites and will occur whenever the rate of localized corrosion is lower than the rate of crack growth, the latter being governed mainly by the alloy composition and structure and by temperature. Critical temperatures for SCC arise naturally from this approach, which was first developed by Tsujikawa. In sour environments, H₂S activates anodic dissolution within pits

and cracks, but is easily depleted in deep cavities, accounting for various threshold effects.

KEY WORDS: crevice corrosion, critical pitting temperature, films, localized corrosion, passive metals, pitting, stainless steel, stress corrosion cracking

INTRODUCTION

Stainless steels are the most important passive materials. Passivity is due to a thin surface film whose composition and structure have been determined exhaustively for various passivating treatments. For most purposes, the passive film can be considered as 2 nm of microcrystalline chromium oxide (Cr_2O_3).

Early corrosion scientists assumed that the quality of the passive film was the critical factor in localized as well as uniform corrosion, but there are many clues that the passive film is not all that influential in localized corrosion. For example, there is a faster and greater enrichment of chromium in acid than in neutral solution,[1] yet the pitting potential remains fairly constant over this range of pH.[2] Pitting vanishes abruptly at a particular temperature (the critical pitting temperature or CPT),[3] yet no one has reported any abrupt change in the passive film properties with temperature (and to be relevant, such changes would have to occur at a different temperature for every alloy). Whenever we examine critically the effect of some variable on pitting (except perhaps chromium content), we find that the results are more easily understood in terms of *pit propagation and stability* than pit nucleation per se.[4] This is not to say that an improved passive film has no value; it is usually, though not always, better to have a few pits

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than many pits. One can also point to the fact that the cathodic reaction has to occur on top of the passive film. Without this reaction (oxygen reduction... chlorine reduction...), there would be no localized corrosion. In the future, we can hope to have inexpensive treatments that poison oxygen reduction on stainless steel, and this would provide a good focus for passive film studies.

Localized corrosion is known to initiate mainly or exclusively at nonmetallic inclusions. In the basic grades, these tend to contain manganese and sulfur and can be large or small, round or flat, depending on steel quality and processing. In higher-alloy steels, they tend to be small and equi-axed in appearance and are rarely of the "manganese sulfide" (MnS) type. Even the basic austenitic grades are very resistant to pitting when such second phases are minimized by sputter deposition[5] or by laser surface melting.[6] In hydrochloric acid (HCl) solution, there is a sharp threshold for pitting at 16% to 17% Cr, which is ascribed to a high-density percolation threshold for Fe in the alloy.[5] Below 17% Cr, dissolution along Fe-like clusters can penetrate deep into the material, creating an occluded environment without needing the gross discontinuity that would be imparted by a second-phase particle.

Such results emphasize the importance of *geometry* in the initiation of localized corrosion. Pitting cannot start until a crevice-like cavity has been created to allow accumulation of a special local environment. In this sense, all pitting is crevice corrosion. Meanwhile, all crevice or under-deposit corrosion appears to initiate by pitting, which would be "metastable" if it occurred on a free surface but is stabilized by the geometry of the crevice or surface deposit.[7-8] Microbially influenced corrosion will be discussed later.

PIT PROPAGATION AND STABILITY

Around 1970, aspects of the local chemistry of pitting in stainless steel were worked out, coinciding with a period of great creativity in corrosion science. Extremely low pH values were measured in pit environments containing high concentrations of dissolved metals: less than zero in some cases.[9-11] The details of this chemistry remain to be determined, especially the exact speciation among metal-ion complexes containing OH, Cl, or both. The simplest view of the low pH is that it results from a large ionic activity coefficient (due to the concentrated solution) superimposed on a simple hydrolysis reaction such as:

$$Cr^{3+} + H_2O = CrOH^{2+} + H^+ \quad (K = 10^{-3.8}) \qquad (1)$$
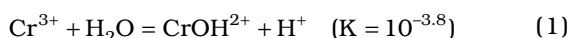
The pH of ca. 1.9 that would be predicted for a pit environment containing, say, 4 M ferrous chloride ($FeCl_2$) and 1 M chromic chloride ($CrCl_3$) drops to
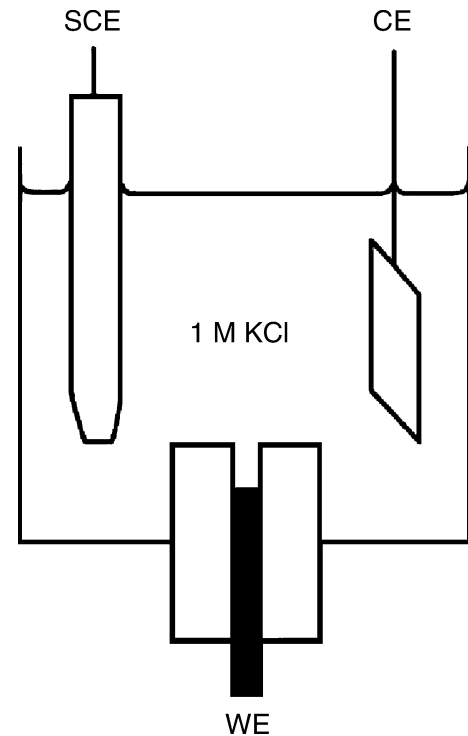

FIGURE 1. *Artificial pit (pencil electrode) assembly.*

<1.0 when the activity coefficients are taken into account. This was nicely illustrated by Mankowski and Szklarska-Smialowska, who added 0.1 M HCl to strong $FeCl_2$ solution and obtained very low pH values near those measured in pits.[11] Needless to say, it is simplistic to neglect the formation of chlorocomplexes; according to Tsuru, et al.,[12] iron is mainly present as $FeCl^+$ and chromium possibly as higher-order complexes (more work is needed on these chromium complexes). These will hydrolyze differently from the simple aquo-ions.

The groundwork for treatment of pitting as a rational anodic dissolution process was laid by Tester and Isaacs, who showed, using pencil electrodes (artificial pits [Figure 1]), that stainless steel would dissolve under anodic diffusion control across an iron-rich salt film.[13] Another finding from the "high-rate dissolution" literature, which turned out to have implications for pitting, was made by Grimm and Landolt, who showed that it was difficult to maintain this diffusion-controlled state when the chromium content was increased to 25%.[14] Oxide formation tended to intervene, or else the salt film was some kind of basic salt. This will have relevance to the CPT, to be discussed later.

Although a careful distinction was always made between "polishing" pits that contain anodic salt films and "etching" pits that do not,[15] it was evident in the 1980s that stainless steel requires a very concentrated pit solution, and that it might be hard to maintain stable corrosion much below the saturation
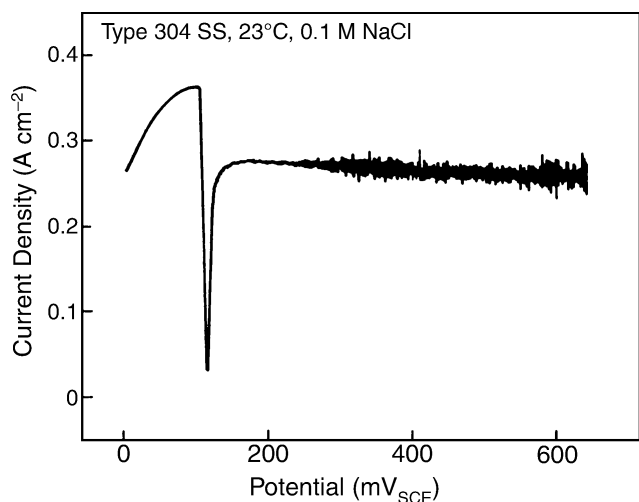
FIGURE 2. *Anodic behavior of an artificial pit in Type 304 SS (50 μm diameter, ~500 μm deep) that was pre-dissolved in the diffusion-controlled region, then subjected to a positive-going potential scan from a potential just below the transition to active (film-free) dissolution. Successive stages from left to right are active dissolution resulting in supersaturation with salt, excess salt precipitation giving a deep minimum in current, diffusion-controlled dissolution, and current fluctuations indicative of passivation attempts under the salt film. These fluctuations intensified when nitrate was added but disappeared when the temperature was increased to 55°C. (Figure taken from Reference 21.)*
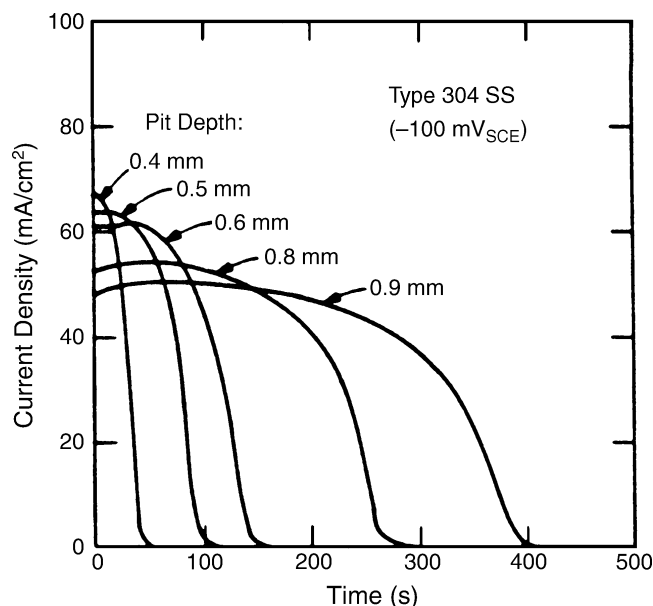

FIGURE 3. *Current transients obtained upon dropping the potential applied to artificial pits of Type 304 SS that were initially dissolving in the diffusion-controlled state. Initially, the metal maintains active dissolution but this is insufficient to maintain the correct local chemistry, and repassivation ensues. (Figure taken from Reference 19.)*
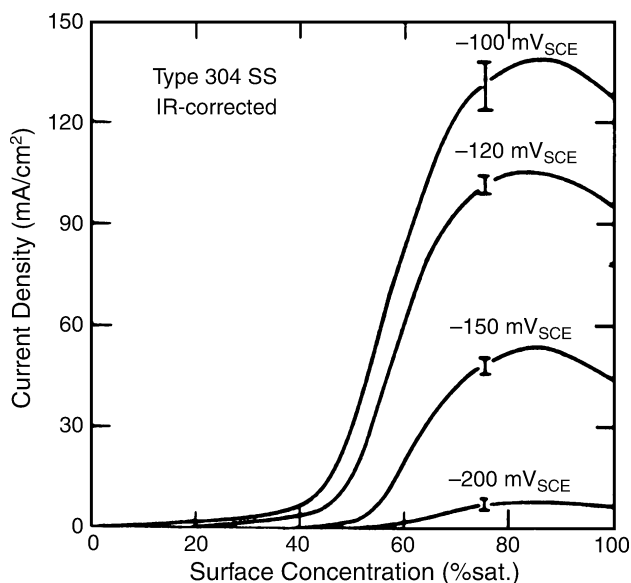

FIGURE 4. *Plots of dissolution rate vs concentration of dissolved products for experiments like those shown in Figure 3, here showing the effect of potential. By superimposing straight lines representing the diffusion kinetics, steady states of varying stability can be identified (Figure taken from Reference 19.)*

level in FeCl₂.[16-19] Nevertheless, in artificial pits, it was possible to maintain stable anodic dissolution below, above, and at the anodic limiting current (Figure 2).

By dropping the potential on an artificial pit that was dissolving at the limiting current, an unsteady-state response was obtained that reflected the dependence of anodic dissolution rate on the concentration of dissolved products in the pit (Figure 3). A Fourier series solution to Fick's second law can be used to model these transients, or the calculation can be done numerically with finite differences. These transients could be converted to current density vs concentration of dissolution products, giving results like those of Figure 4.

Typically, it was impossible to sustain pitting at <70% of saturation for Type 304 (UNS S30400)[(1)] stainless steel (SS) at room temperature. Armed with these results, it was possible to propose a multiple steady-state model for pit propagation (Figure 5).

By activating the anodic process with thiosulfate addition, the necessity for the anodic salt film vanished, and it was shown that the normal mode of pit propagation was active (film-free) dissolution at some fraction around 30% to 80% of saturation in metal salt, and with exceptional stability.[20]

An interesting observation of Newman and Ajjawi (Figure 2) was irregular oscillation of the diffusion-limited current from artificial pits of Type 304 SS at room temperature.[21] This was ascribed to nucleation of oxide under the anodic salt film and undermining

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[(1)] UNS numbers are listed in *Metals and Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers (SAE) and cosponsored by ASTM.

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or destruction of these oxide nuclei when the salt film started to thin above them. The oscillations vanished at 55°C. Recently, Laycock and Newman showed, using wires of different diameter but equal depth, that these oscillations involved radial oscillation in salt-film thickness and showed period-doubling and other interesting dynamic features.[22] This observation of Ajjawi was the first step in our current hypothesis as to the nature of the CPT, namely that it represents the temperature where irreversible passivation occurs upon precipitation of an anodic salt film in a small cavity. In other words, as already noted by Grimm and Landolt,[14] the salt film has a dual effect: it stabilizes dissolution by providing a reservoir of acid-generating salt, but it consumes acidity in the interface, thus tending to promote passivation.

CRITICAL POTENTIALS FOR SALT FILM FORMATION

Although some workers have proposed the existence of a quasi-thermodynamic potential for salt-film stability,[23] in small pits this potential must be determined by kinetics,[24] and in particular by the diffusion length associated with the pit cavity, which determines the current density required to maintain the salt film. A simple analysis was developed by Laycock and Newman[4] and works very well with the hypothesis that the pitting potential is equal to the "transition potential" for salt film formation (E_T) in a cavity of a particular size. The IR drop within the pit cavity at the limiting current, which at first sight would appear to be a complicated issue, is actually a constant for a given bulk solution (since doubling the pit depth doubles the resistance but halves the limiting current density). So, in order to compare two steels such as Type 304 and Type 316 (UNS S31600), the following relationship needs to be considered:

$$E_r = E_{corr} + b_a \log\left(\frac{i_L}{i_{corr}}\right) + \phi_s \qquad (2)$$

where E_{corr} and i_{corr} are the corrosion potential and corrosion current density, respectively, in the saturated pit solution; b_a is the anodic Tafel slope; i_L is the anodic limiting current density; and ϕ_s is the ohmic potential drop in the pit cavity (= constant).

It turns out that the IR drop outside the pit becomes significant for smaller pit depths and at lower solution conductivities, but for relatively concentrated solutions very clean linear plots of E_T vs log i_L can be generated using artificial pits. The very best results are obtained with very narrow pits such as those made from 10 μm wire (Figure 6). However, the more readily available 50 μm wires are adequate for determining the effects of various metallurgical and environmental variables. Some IR drop external to
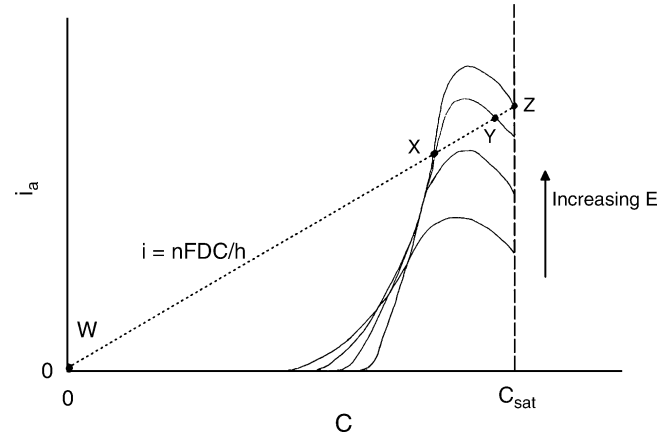

FIGURE 5. *Definition of steady states for a one-dimensional pit of a particular depth. State W is passive. State Z is diffusion-controlled dissolution and will persist at all potentials higher than the critical one shown. State Y is in a stable active (film-free) state. State X is unstable under potentiostatic conditions but stable under galvanostatic conditions.*
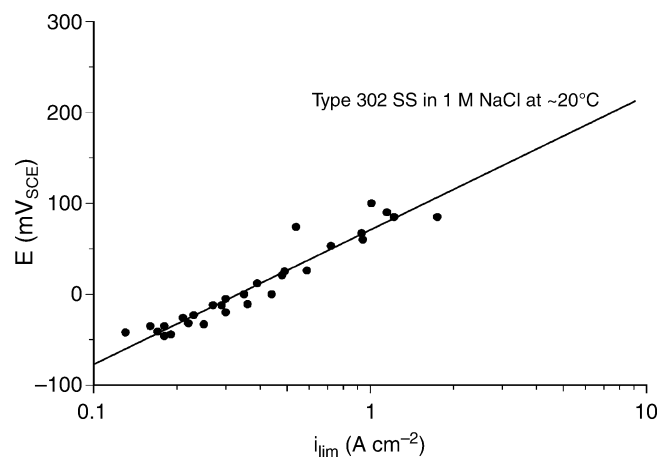

FIGURE 6. *Dependence of the transition potential for salt film formation on the pit depth, via the anodic limiting current density, i_{lim}, obtained using 10-μm-diameter Type 302 SS wires. With negligible IR drop external to the pit, a very good straight line is obtained with a slope of 120 mV. (Figure taken from Reference 4.)*

the pits is detectable with these wires but is not critical. Such measurements can be used to rationalize directly the effect of molybdenum on the pitting potential[4,25] and its lack of effect in bromide solutions where soluble molybdenum complexes are formed[25] (Figure 7). The fundamental understanding of bromide effects developed in this research was useful when it came to devising a room-temperature test for deleterious phase precipitation in duplex stainless steel (in unpublished research by M. Dominguez at UMIST)—the chromium- and molybdenum-depleted zones around particles such as sigma (σ) phase react quite differently in various chloride/bromide mixtures, and the solution can be optimized to emphasize either chromium or molybdenum depletion as
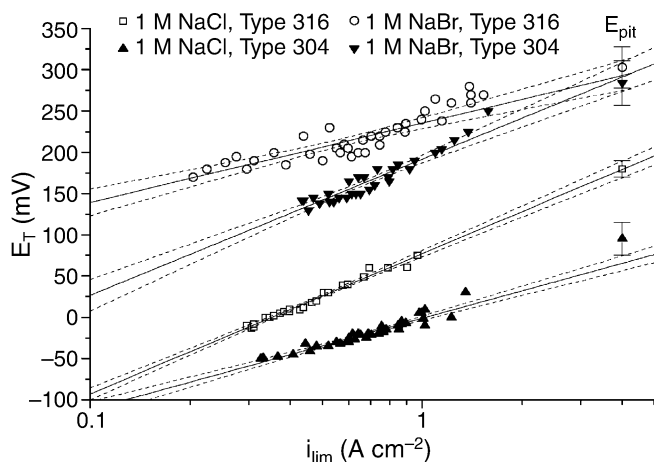
FIGURE 7. *Plots of E_T vs i_{lim} for artificial pits of Type 304 SS and Type 316 SS in chloride and bromide solutions, obtained using 50-μm-diameter wires; pitting potentials are indicated on the right-hand side. The effects of bromide compared with chloride (higher pitting potential but reduced effect of molybdenum) are very well rationalized by the artificial pit experiments. (Figure taken from Reference 25.)*
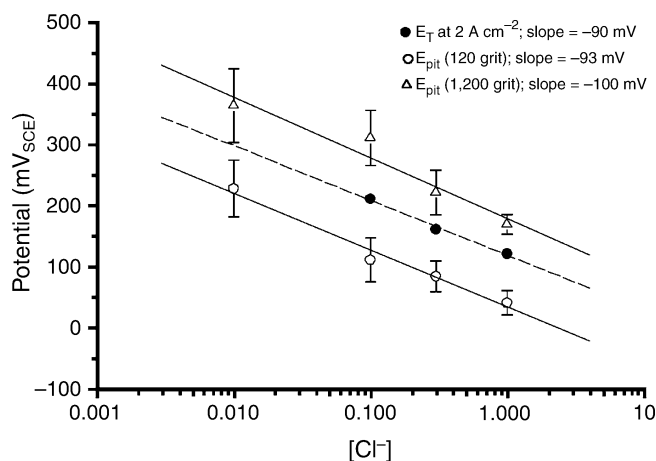

FIGURE 8. *Illustration of the ability of the artificial pit technique to rationalize the dependence of pitting potential on chloride concentration. (Figure taken from Reference 4.)*

required. For example, chi (χ) phase is very high in molybdenum but not as embrittling as σ phase, so if embrittlement is the problem of concern, it is good to use a bromide solution which de-emphasizes molybdenum effects.

What happens as we vary the bulk chloride concentration? By making similar measurements, we find that the IR drop ϕ_s varies with the chloride concentration (or more strictly the activity) as:

$$\phi_S = A - B \ \log \ [Cl^-] \qquad (3)$$

with B being ~90 mV. This mirrors exactly the well-known behavior of the pitting potential as a function of chloride concentration (Figure 8).

Why does the IR drop in the pit at the limiting current not vary in proportion to the solution resistivity? Obviously, this is associated with the enrichment of ions inside the pit—due to dissolution of metal and inward electromigration of chloride. It was known already in the 1970s that the correct result could be deduced from the steady-state distribution of a nonreacting ion such as Cl^-.[26] Since the net flux of such a species must be zero at steady state, its diffusion and migration fluxes must be equal and opposite; solution of the resulting partial differential equation gives us:

$$\log\left(\frac{C_{in}}{C_{out}}\right) = \left(\frac{2.3RT}{zF}\right)(\phi_{out} - \phi_{in}) \qquad (4)$$

where C_{out} is the bulk solution concentration and C_{in} is a constant (i.e., the saturation level of chloride for the case where an anodic salt film is formed in the pit); $(\phi_{out} - \phi_{in})$ is the IR drop. Note that, for chloride, z is negative.

According to the above equation, the slope B in Equation (3) should be 59 mV at 298 K; the actual value of 90 mV found for stainless steel may be associated with the formation of chloro-complexes of chromium[12] (since the correct slope of 60 mV is found for pure iron).

The artificial pit technique also rationalizes the weak temperature dependence of the pitting potential above the CPT, and shows that this is mainly due to a change in the activation overpotential required to generate a particular anodic current density (i.e., a change in the corrosion current density in the pit solution), rather than the ohmic drop in the pit (Figure 9).[27]

The beneficial effect of alloyed nitrogen in pitting corrosion has so far resisted interpretation via the artificial pit technique. There is a good reason for this: studies using strong HCl solutions show that the inhibiting effect of nitrogen on the anodic dissolution process in pit-like solutions is only manifested at very high current densities, > ca. 1 A/cm² (Figure 10).[28] Such current densities are hard to sustain in artificial pits. However, one can anticipate a successful result along the same lines as the molybdenum effect, since there was already evidence in the 1970s that nitrogen alloying primarily affected the stability of pits rather than their initiation.[29] Ezuber and Newman showed that nitrogen alloying of a 316-type material preferentially eliminated the faster-growing metastable pitting events while leaving the "slow" (<1 A/cm²) events largely unaffected.[30] This appears a convincing basis for explaining the effect of nitrogen as one of inhibiting anodic dissolution, rather than strengthening the passive film (although remarkable interfacial enrichment of nitrogen is observed during passivation[31-33]).

CRITICAL PITTING TEMPERATURE (CPT)

While the pitting potential is a distributed quantity, the CPT is much more reproducible, at least for modern materials lacking large inclusions. Qvarfort reported that he could reproduce the CPT to within 1°C or 2°C,[3] and Moayed has achieved an even tighter distribution of values.[34] However, the CPT does vary with the surface treatment, being higher for smoother surfaces.

Metastable pitting events are conspicuous below the CPT, and clearly the CPT is a growth or stability transition and has nothing to do with the properties of the intact passive film. According to Salinas-Bravo and Newman, the CPT could be understood in terms of passivation of the alloy occurring at a finite critical current density (i_{crit}), even in the most aggressive local environment that can be generated in the pit.[35] Further work at UMIST, some still to be published, refined this picture to some extent,[36] but the essential concept remains intact. We only have to propose that i_{crit} varies more steeply with temperature than the anodic limiting current density, i_L, which is trivially true for experiments carried out in strong HCl solution mimicking the pit environment (no precise data are available for real pit environments, and this is a future priority, though the experiments will be difficult to carry out at appropriately high current densities).

Since metastable pitting occurs below the CPT, and these pits grow in many cases at anodic current densities ca. 1 A/cm², the i_{crit} value relevant to the CPT transition is obviously higher than this—around 2 A/cm² to 8 A/cm². A modification of the Salinas model was made by Laycock, et al., who suggested that the CPT corresponds to anodic passivation occurring under a freshly precipitated $FeCl_2$ salt film.[36] According to this interpretation, the metastable pits that grow below the CPT are in a film-free state but cannot develop into stable pits (which require a salt film) because the salt film destabilizes them rather than stabilizing them (as it would do above the CPT). One would predict, therefore, that below the CPT the application of high anodic potentials would restrict the amount of pit growth by facilitating early salt precipitation, and this is indeed true, as shown in Figure 11 for Type 904L (UNS N08904) steel. Below the CPT, pitting is most evident at intermediate potentials.[36] This is like the effect of nitrate in conventional pitting,[2] where again the passivating effect of low levels of nitrate is only evident upon salt precipitation, and thus only at high anodic potentials.

The passivating effect of salt precipitation is familiar in nonchloride systems such as iron in sulfuric acid (H_2SO_4).[37-39] For chloride systems it was first observed by Newman and Liew, who cooled artificial pits while holding the potential at a positive value.[40] The critical temperatures generated by this
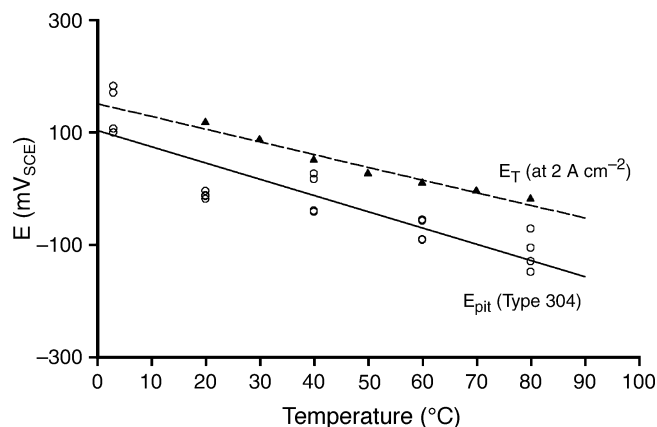
FIGURE 9. *Weak dependence of the pitting potential above the CPT, as rationalized by the transition potential for salt film formation. (Figure taken from Reference 27.)*
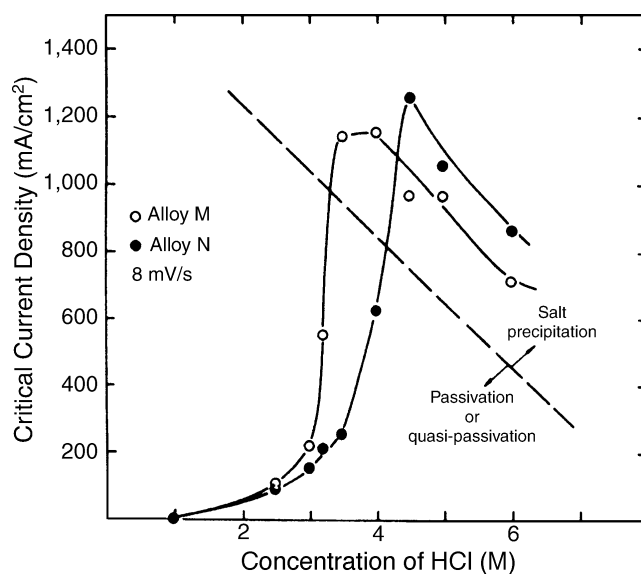
FIGURE 10. *Subtle effect of alloyed nitrogen (Alloy M = Type 316L; Alloy N = Type 316LN) on the anodic kinetics of stainless steel in strong HCl solutions simulating a pit environment. Around 3 M to 4 M HCl, the nitrogen-containing alloy showed highly reversible quasi-passivation indicative of surface enrichment of nitrogen. Note that the range of HCl concentrations where this effect is seen is higher for stirred solutions, extending >5 M according to unpublished work. (Figure taken from Reference 28.)*

procedure were lower, obviously, than the CPT of the alloys concerned, but they were similar to reported critical temperatures for crevice corrosion (CCT) (Figure 12). Anomalous effects of potential are earlier observed in this work, with enhanced passivation at very high potentials, similar to that shown in Figure 11.

The results of Newman and Ajjawi shown in Figure 2 are obviously relevant to this issue too.[21] A rough indication of the CPT can easily be obtained by simply measuring anodic polarization curves in 4 M
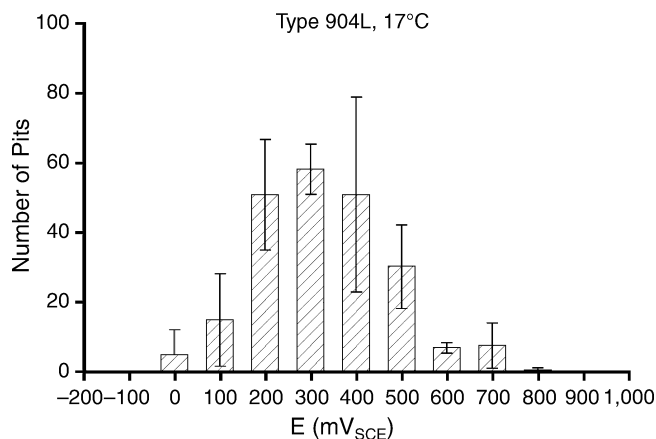
FIGURE 11. *Number of detectable metastable pitting transients obtained for Type 904L SS in a fixed period after separate potential steps performed on fresh surfaces from low potential to the potentials shown. This method avoids effects due to site exhaustion that might occur in a potential scan and proves that the apparent pit nucleation frequency goes through a peak with potential below the CPT, owing to passivation occurring under an anodic salt film at the higher potentials. (Figure taken from Reference 36.)*
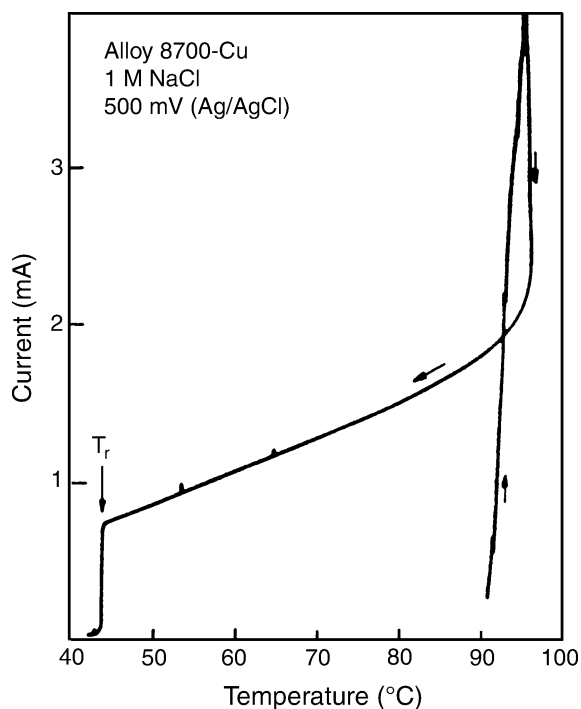

FIGURE 12. *Repassivation under an anodic salt film, observed upon cooling an artificial pit while holding the potential at 500 mV in the diffusion-controlled region. (Figure taken from Reference 40.)*

or 5 M HCl, as shown by Moayed and coworkers.[34,41] A clean anodic limiting current is only observed above the CPT. The complications found by Grimm and Landolt, working with Fe-25Cr, mentioned earlier,[14] may be considered to reflect the same phenomenon occurring imperfectly beneath those salt films.

A remaining challenge in understanding the CPT is the possible influence of the early evolution of pit geometry. Pits are not hemispheres but grow under the metal surface, emerging at numerous points to make a lacy pattern. The development of lacy metal covers over stable pits is now understood in terms of passivation and undercutting near the pit mouth.[41-45] This is conveniently studied by mounting thin foils of stainless steel between glass plates (Figure 13). Figure 14 shows a rationalization of the process (bold lines are passive metal). As the temperature is lowered toward the CPT, the pit geometry becomes ever more convoluted, including concentric shells of lacy metal. A likely "definitive" interpretation of the CPT is that it corresponds to the temperature where the metal cannot achieve the very high anodic current density required to propagate an undercutting event (since this would exceed i_{crit}), and thus pits are denied the chance to shelter their contents by growing under the surface. Repassivation is thus inevitable.

The preceding comments on potential and temperature effects may be combined into a schematic diagram as shown in Figure 15.

EFFECTS OF SULFUR COMPOUNDS ON PITTING

In the 1980s, the remarkably aggressive effects of thiosulfate-chloride or thiosulfate-sulfate mixed solutions were discovered and related to the ability of thiosulfate to generate adsorbed sulfur that activates anodic dissolution of stainless steel (Figure 16).[20,46-50] Another important factor was the tight black cover over the pits, retaining the contents (this material contains metal sulfides and chromium hydroxide). The protective effect of alloyed molybdenum against this activated dissolution was noted[51] (Figure 17) and can be related to an active desorption of sulfur, as proposed by Marcus for nickel and, later, stainless steel.[52]

The lesser effect of H_2S than thiosulfate appears paradoxical, since it is closer to the required oxidation state (somewhere between 0 and –2) required for the activation, but this is a transport effect, not a reaction effect. At the acidic pH values in and near a pit, sulfide is uncharged and will always be depleted inside the pit. Thiosulfate is an anion, and, although it is decomposed by acidic solutions, this is slow enough that there is always enrichment by electromigration into pits.

A special effect is seen when carrying out pitting scans with chloride/sulfide solutions (Figure 18).[53] Small pits show very negative repassivation potentials, close to those seen with thiosulfate as the activator, but above a certain pit size there is little or no activation and the repassivation potential rises to a value similar to that for a pure chloride solution. This is a simple depletion effect: there has to be a
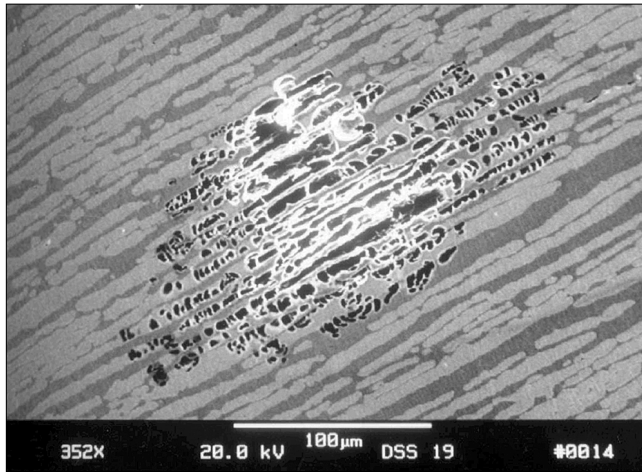
(a)
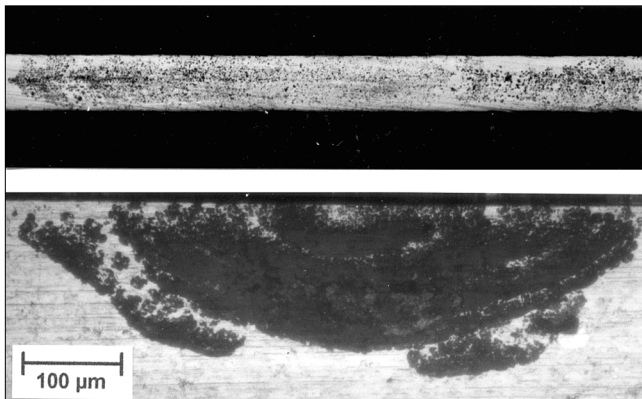
(b)

FIGURE 13. *Examples of lacy metallic covers over pits: (a) duplex stainless steel plate from a potentiostatic experiment, showing reemergence of holes within the austenite (light-etching), which is the less easily passivated phase, and (b) plan view and cross-section of a Type 304 SS foil potentiostatically pitted at high potential but low temperature (10°C) showing that as the CPT is approached the pitting process becomes convoluted and oscillatory, with nested lacy covers. (Figure taken from Reference 45.)*

(a)

(b)

(c)

(d)

(e)

(f)

FIGURE 14. *Schematic of lacy metallic cover formation in pitting of stainless steel. Bold lines indicate passive metal.*

certain minimum limiting diffusion flux of H_2S to the dissolving surface to sustain pitting (for a given alloy, the value of this flux will increase, for example, with molybdenum content).

There is no concrete evidence that thiosulfate or other sulfur anions "break down" the passive film on stainless steel. The few detailed data that exist suggest that thiosulfate simply takes advantage of events that would occur anyway (Figure 19);[54] that is, the pit lifetime and stability are increased, but the pit nucleation frequency may not be. This, however, requires further investigation before it can be taken as a generalization.

There can be little doubt that thiosulfate is a major player in "microbiologically influenced corrosion" (MIC) processes due to sulfate-reducing bacteria.[47] The lifetime of thiosulfate produced by air-oxidation
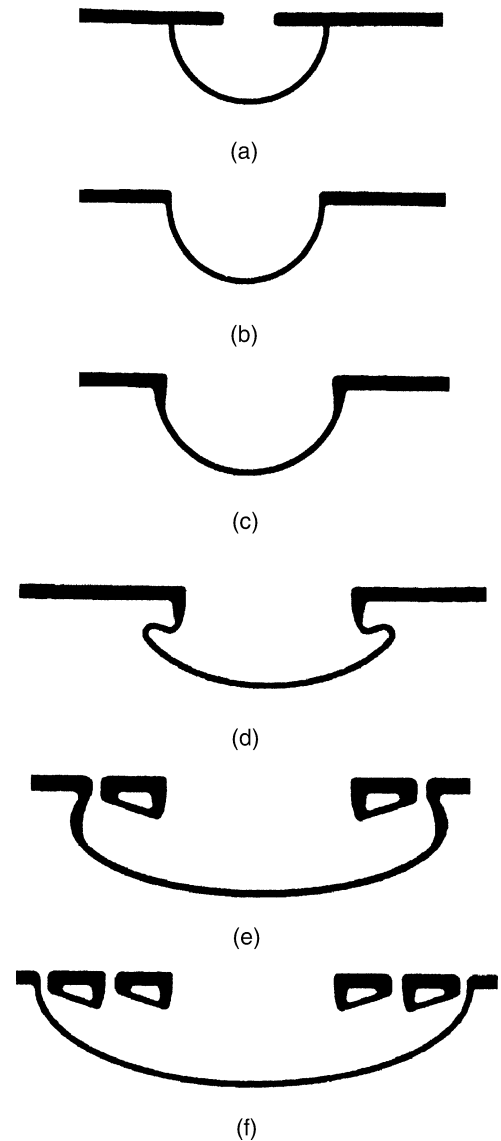
of neutral sulfide solution is measured in days to weeks, and corrosion can occur at very low overall ionic strengths if thiosulfate is present.

OBSERVATIONS ON PIT DYNAMICS

Some of the most fascinating aspects of localized corrosion are not accessible in conventional potentiostatic studies but arise from the mixed-potential nature of natural corrosion processes. The dynamics of pitting at the open-circuit potential are simulated better by galvanostatic than by potentiostatic polarization where the current can become arbitrarily large. In natural free-corrosion of a passive material, the limitation on cathodic current (per corrosion site) causes the potential to drop significantly as corrosion proceeds. In a well-controlled system such as chlo-
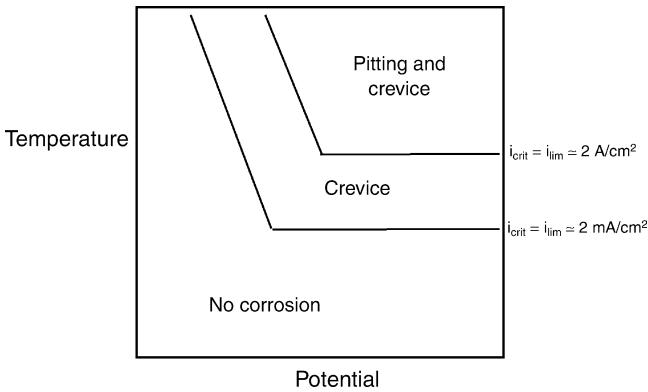
FIGURE 15. *Localized corrosion map, indicating the explanation of the critical temperatures in terms of kinetics within the local environment.*

FIGURE 16. *Results of scratch tests for pitting of a high-purity Type 304 SS in a chloride-free sulfate/thiosulfate solution. Pitting occurs over a range of potentials because thiosulfate must be electro-reduced to activate anodic dissolution in the pit. (Note to those repeating this experiment: commercial Type 304 SS does the same thing but not at room temperature. 50°C is a suitable temperature to display the effect.) (Figure taken from Reference 48.)*
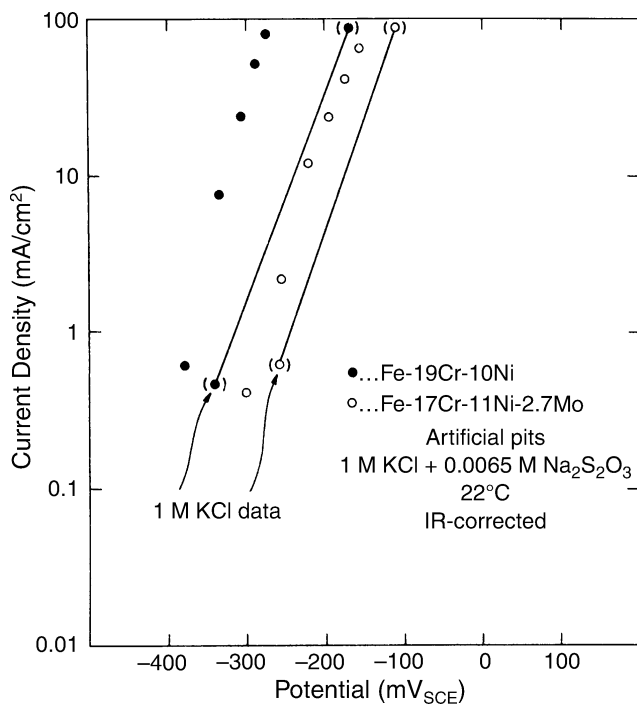

FIGURE 17. *Anodic kinetics of high-purity Types 304 and 316 alloys in nearly-saturated pit solutions as deduced from artificial pit experiments. The solid lines show the data for pure potassium chloride (KCl) solutions. The data points are for solutions containing thiosulfate and show the lesser activating effect of thiosulfate on the molybdenum-containing alloy. (Figure taken from Reference 51.)*

permanently under a constant current. One of the effects of biological deposits is to stabilize propagation of corrosion at constant or decreasing corrosion current, especially if the deposit has an anion-selective character, as shown for inorganic analogs by Suleiman, et al.[55]

The complicated undercut pit shapes observed in potentiostatic pit growth experiments become still more ramified in natural immersion. Pits are very good at "finding" a way to continue propagating, even when the potential or available cathodic current is not high enough to permit propagation as a conventional hemisphere-like cavity.[19] Such "intelligence" of localized corrosion sites is typical of the whole class of autocatalytic reaction/diffusion phenomena that show discontinuous variation of the reaction rate with the concentration of product. For this reason, one has to doubt the long-term reliability of any repassivation potential that is higher than the corrosion potential of the metal in the local environment.

Atmospheric pitting of passive metals is not very well understood, and this lack of understanding is hindering corrosion predictions for nuclear waste containers in several countries. Considerations such as the exhaustion of cathodic current are exacerbated by the large ohmic potential drops that exist in thin liquid layers,[56] and this could provide a fruitful field for modelers.

The ultimate morphology transition in localized corrosion is that from pitting to tunnelling in aluminum. According to the view presented here, this is simply one possible response of the system to a current that is too low to sustain a uniform hemispherical dissolution front (since that process would not

ride/thiosulfate solution, where spontaneous re-passivation is kept to a minimum, a deterministic sequence of initiation and repassivation is observed in galvanostatic experiments.[54] A generation of pits initiates upon first application of the current, then these repassivate one at a time until there is one champion pit remaining. Normally, this pit will repassivate too, and the cycle will repeat itself. But, if there are any major flaws, crevices, or surface deposits present, one of these sites will propagate
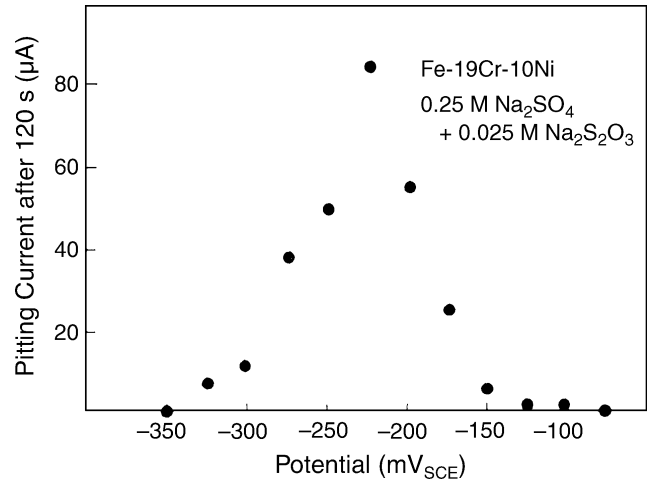
maintain an aggressive enough chemistry to continue the reaction). By splitting into active and passive areas, the metal uses the current available to drive local penetrations at higher velocity (initially very high indeed, because of the microelectrode character of these corrosion sites) and with more concentrated local chemistry.[57] This can be represented graphically as a singularity on a plot of anodic current density vs concentration of dissolution products. Stainless steel does something similar when it is very near its repassivation potential,[19] although the geometry is never as clean as that seen with aluminium. People often ask the wrong question when presented with a phenomenon like tunnelling: the important thought experiment is to imagine a single propagating tunnel, passive on the sides and active at the end, growing under a constant applied current, then to imagine what it might do *other than* continue growing as a tunnel. What can happen? Can the metal repassivate? No—unless it transits to oxygen evolution, it has to use the current that is being applied. Can the tunnel get wider at the end? Can the sides start dissolving? In both cases, no—this would eventually turn into a hemispherical pit that would not be stable because its current density would be too low to maintain the right chemistry. Can the tunnel propagate in any direction other than <100>? Possibly, but <100> propagation has the advantage that the end of the tunnel has no tendency to grow into a wedge shape that would increase its area and eventually turn it into a pit (albeit perhaps not hemispherical).

STRESS CORROSION CRACKING OF STAINLESS STEEL

Chloride-induced stress corrosion cracking (Cl-SCC) is so hard to understand on the atomistic level that attention of SCC mechanicians seems to have moved elsewhere.[(2)] However, one notable success has been the detailed rationalization of the relationship between SCC and localized (pit or crevice) corrosion. This was mainly the work of Tsujikawa and colleagues in Japan.[58] The essence of this approach is so simple, it almost seems like a circular argument until one appreciates that SCC does not grow by simple anodic dissolution. The main features of the argument are as follows:

—SCC initiates from actively growing localized corrosion sites and occurs in the active (albeit slowly corroding) state, in a locally acidic chloride solution.

[(2)] However, in my group, we are confident that dealloying and consequent mechanical fracture are involved, rather than, for instance, hydrogen embrittlement. Recently, we were able to confirm, using strong caustic solution, that the dealloying of austenitic stainless steels does indeed produce a nanoporous, 50-50 Fe-Ni alloy as the de-alloyed product,[59] which was suspected but not proved for similar experiments in acidic chloride,[60] as the layers formed in that environment are very thin owing to simultaneous dissolution of the Ni and Fe from the layer.
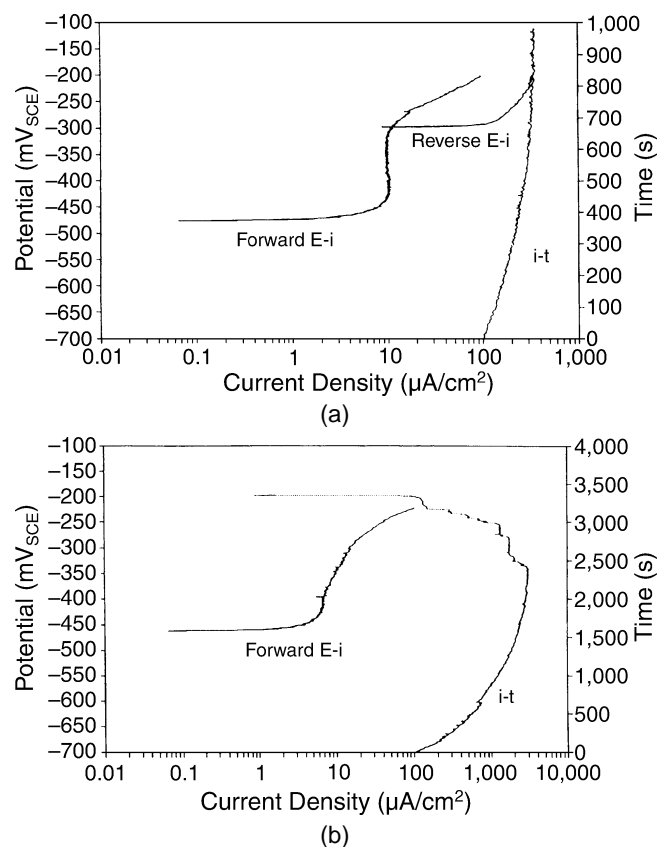

FIGURE 18. *Effect of pit size (as reflected in the time spent at a fixed potential above the pitting potential) on the repassivation potential for pitting of Type 316 SS in a mildly acidic, sour chloride environment. In the upper figure, pitting was allowed to occur for 1,000 s before reversing the potential scan, and the repassivation potential of these small pits was ca. −300 mV. In the lower figure, deterministic repassivation of all initiated pits occurred while the potential was being controlled at −225 mV (i.e., for the large pits grown in this experiment the repassivation potential was more positive than −225 mV). Individual pit repassivation events can be seen in the lower figure; the pits carrying the largest currents repassivated first, not last, as would be expected in a plain chloride solution. (Figure taken from Reference 53.)*

—The lower critical potential for SCC will therefore be the repassivation potential for whatever type of localized corrosion is occurring (more negative for crevice corrosion than for pitting).

—The velocity of SCC, at least for austenitic steels, does not vary much with potential, nor with stress intensity above the threshold, which is very low, nor with the bulk solution composition provided localized corrosion is occurring. The main factors affecting crack velocity are metallurgy (such as nickel content) and temperature.

—Thus, there will be an upper critical potential (blunting potential) where the velocity of the crack equals the velocity of the localized corrosion.

—The crack velocity varies more steeply with temperature (higher activation energy) than the localized corrosion velocity.
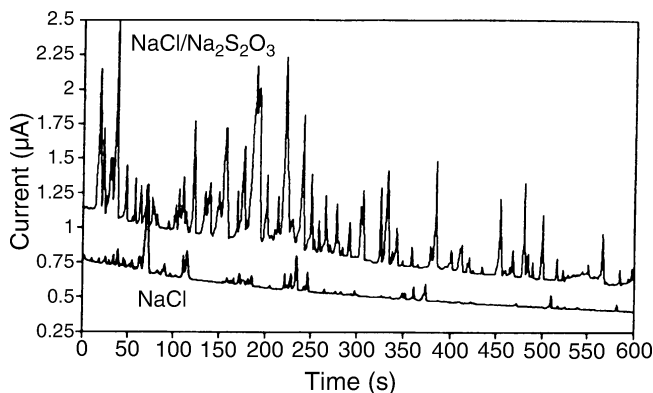
FIGURE 19. *Potentiostatic current decays following a potential step into the metastable pitting region for Type 316L SS in NaCl solutions with and without thiosulfate addition. Close examination revealed that it could not be said with confidence that thiosulfate was increasing the number of pits initiated; the main effect is an increase in pit lifetime. (Note that this was a very poor heat of Type 316L SS and thiosulfate may have a smaller effect on other heats.) (Figure taken from Reference 54.)*
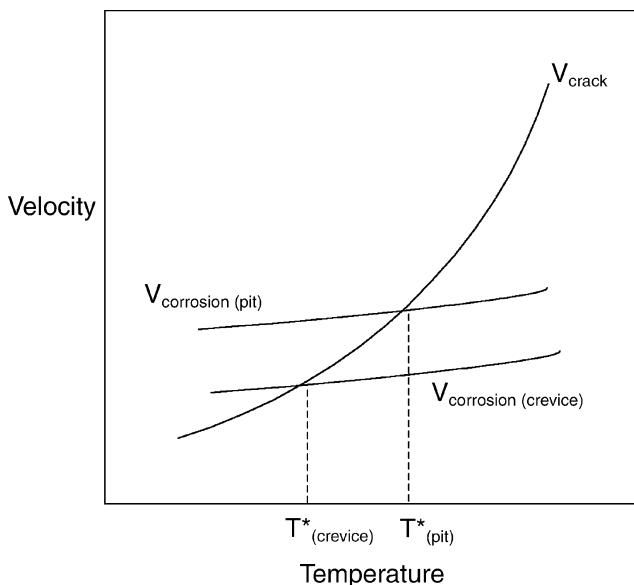

FIGURE 20. *Schematic of the temperature dependences of localized corrosion and SCC for austenitic stainless steel in chloride solutions, based on the work of Tsujikawa. Critical temperatures for SCC arise naturally from such an approach.*

This very simple picture (Figure 20) leads to very useful rationalizations as well as predictions of the effects of alloying elements in newly developed steels.[61] For example, the often-quoted 60°C limit for Cl-SCC arises because that is the temperature at which the tightest commonly encountered localized corrosion sites are dissolving at ~10^{-10} m/s, which is the crack velocity at that temperature. Below this limiting temperature, localized corrosion events never (or very rarely) grow slowly enough to start a crack. This analysis is valid for systems that can be charac-

terized as essentially sodium chloride (NaCl): when the environment can generate highly concentrated magnesium chloride ($MgCl_2$) (which requires a relative humidity in the 30% to 40% range), SCC will occur at room temperature but the conditions will rarely be stable enough for long enough to permit it.[62]

Duplex stainless steels resist SCC better than austenitic steels, even though the individually synthesized phases both crack very rapidly. This is because the ferrite cathodically protects the austenite or displaces it from its optimal cracking potential;[63] thus, cracks start in the ferrite but slow down when they reach the austenite. If the conditions are such that both phases are near their optimal cracking potentials (for example, with extra oxidant present or in developmental high-alloy steels whose phases have very similar electrochemistry), then one can anticipate trouble, and indeed there have been a few failures of duplex stainless steel equipment at temperatures near 100°C.

Sulfide SCC of austenitic or duplex stainless steels is dominated by the kind of H_2S depletion issues discussed earlier.[53] It is quite a challenge for H_2S to maintain sufficient flux to the base of a crack when it is being depleted by reaction with cations in the crack solution, or by adsorption on porous corrosion products. There will generally be two threshold conditions of H_2S concentration for SCC: one where the repassivation potential for pitting moves sharply in the noble direction, thus shutting off the localized corrosion necessary for SCC, and a higher one where stable pitting can be maintained but cannot lead to stable cracking. In every case, the absence of oxygen places clear limits on the corrosion potential that can be reached (in most cases this appears to be close to a H_2S/S^0 equilibrium potential, which is ~120 mV more positive than that of the reversible hydrogen electrode).

FURTHER COMMENTS AND CONCLUSIONS

What do we still need to know about corrosion of stainless steel? It is tempting to say "nearly everything"—after all we still do not understand the microscopic mechanism of Cl-SCC. But, here is a more realistic shopping list, not confined to the topics discussed in this paper:
❖ Long-term prediction of pit or crevice penetration rates, especially in thin-film electrolytes.
❖ Prediction and scientific understanding of SCC thresholds for martensitic and duplex steels in sour oil-and-gas production environments, or for 13Cr-Mo-Ni steels in carbon dioxide (CO_2) environments.
❖ Development of surface treatments designed to inhibit cathodic reactions such as oxygen reduction.
❖ Development of surface treatments for improved cleanability and nonstick properties.

❖ Improved understanding of corrosion processes in nonaqueous electrolytes including concentrated acids.
❖ And more generally, rediction of propagation rates for real stress corrosion cracks in real components.

ACKNOWLEDGMENTS

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