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rent Understanding of Pitting and Crevice Corrosion and Its Application to Test Methods for Determining the Susceptibility to Such Corrosion of Nuclear Waste Metallic Containers

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Center for Materials Science
Materials Chemistry Division
Washington, DC 20234

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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, ***Secretary***
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, ***Director***

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The successful use of metallic containers for nuclear waste in a repository depends on these containers being able to resist corrosive attack by the repository environment for a long period of time (usually set at greater than 1000 years for the whole containment system). The most damaging and prevalent type of corrosive attack that is most likely to breach the container wall is localized corrosion [1]. The main forms of this kind of attack of importance to nuclear waste problems are pitting, crevice corrosion, stress corrosion cracking and intergranular corrosion. This review will only consider pitting and crevice corrosion with the latter two failure modes being considered in a future review. Pitting corrosion is a form of localized attack that produces a penetration into a metal object at highly restricted sites. Usually these sites, called pits, are covered with corrosion products that restrict the flow of ionic species into or out of the pit. Thus, a pit eventually becomes a small crevice -- a crevice being formed by covering part of a metal surface by material that restricts the access of ionic species and oxygen to that surface. Crevice corrosion occurs when such a covered surface is placed in a corrosive environment. The restricted environments and surfaces inside pits or crevices have been called by B. F. Brown "occluded cells" [2]. In an engineered barrier system for managing nuclear waste, it is highly likely that the packing of the backfill against the wall of a canister will put most of that canister's surface in a crevice and produce a very large occluded cell.

In order to assess the susceptibility of various nuclear waste container candidate alloys to pitting and crevice corrosion, it is necessary to use currently available or develop new test methods that can reliably determine the rate of localized attack. Effective test methods for assessing susceptibility to pitting or crevice corrosion are based on a better understanding of the mechanisms of the processes that control these two similar types of corrosion. This review looks at our current understanding of such mechanisms and describes the presently available test methods used to assess pitting and crevice corrosion susceptibility. Some of those test methods have been developed using our current understanding of localized corrosion mechanisms as their basis.

Current Understanding of Pitting and Crevice Corrosion

There have been a number of reviews of theories and mechanisms of pitting and crevice corrosion [3-7]. This discussion will break the subject into two parts -- initiation and propagation processes. It is especially important in the context of assessing the susceptibility of nuclear waste containers to localized attack that the initiation and propagation steps be separated because the proper choice of a test method will depend on which step, initiation or propagation, is rate determining. For example, in a hypothetical situation if the initiation of crevice attack takes a long time, e.g., 50 years, the propagation rate must be slow enough to prevent penetration for as long as 1000 years. Thus, a test that only looks at initiation or only at propagation, would give only incomplete information. Therefore, initiation (or breakdown) and propagation processes will be considered separately because their mechanisms probably differ and because their separation is necessary to develop reliable and effective test methods.

Pit and Crevice Corrosion Initiation

This discussion of initiation will make extensive use of a 1976 review by Kruger [6] by bringing it up to date. Initiation of pitting or crevice corrosion involves the chemical breakdown of a protective or passive film that must be present on a metal or alloy surface in order for it to be used effectively in a corrosive environment. Chemical breakdown (the initiation of pitting or crevice corrosion) can be defined as those processes brought about by chemical alteration of the film or the environment that produce changes in the passive film so that it can no longer effectively prevent damaging anodic currents from flowing [5]. Another way to destroy the effectiveness of the passive film is by mechanical disruption. Mechanical breakdown occurs by the introduction of externally applied stresses; it will be described in a future review.

1. Theories of Initiation or Breakdown

A number of theories or models have been proposed to describe the events leading to pit or crevice corrosion initiation. Most of these were listed by Hoar [8]. In order to be successful, a model must, of course, explain the phenomenology of breakdown. While perhaps not all inclusive and in some cases controversial, the following phenomena are usually considered to be the required characteristics of chemical breakdown which lead to localized attack: (a) a certain critical potential E_p must be exceeded, called by some the critical potential for pitting [9, 10]*; (b) damaging species (examples are Cl^- or the higher atomic weight halides) are needed to initiate and propagate breakdown; (c) there exists an induction time separating the initiation of the breakdown processes by the introduction of conditions conducive to breakdown and the completion of the process when pitting or crevice attack commences; and (d) breakdown occurs at highly localized sites.

Many models for initiation have been developed that can satisfy the above requirements. They can be divided into three groups: (a) adsorbed ion displacement; (b) ion migration or penetration; and (c) breakdown-repair. As Hoar [8] has pointed out, there are common elements in all of the models, and if a true model for breakdown is ever achieved, it probably will contain elements of all three groups. The individual groups will be discussed in terms of how well they satisfy the phenomenological requirements.

a. Adsorbed Ion Displacement Models

Two mechanisms have been suggested under this general model. First, there is the mechanism suggested by Kolotyrkin [13] and Uhlig [14,15]. This model considers the passive film to be an adsorbed film (probably a monolayer) of oxygen. Breakdown occurs when a more strongly adsorbing damaging anion displaces the oxygen forming the passive film. Once the Cl^- ion is adsorbed at the surface, breakdown commences because the theory surmises,

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*The situation is more complex. Pourbaix [11] has pointed out that there exists a potential E_{prot} which he calls the protection potential. This potential which is more active (negative) than E_p is the potential below which breakdown once initiated can be stopped. Work by Pessel and Liu [12] indicates that when E_p is determined in a way that eliminates the time for breakdown to occur, $E_p = E_{prot}$.

the bonding of the metal ions to the metal lattice is weakened. When other anions are present, they can compete with the Cl^- for sites and inhibit breakdown [14,15]. Direct evidence that this occurs has been provided by Rozenfeld and Maksimchuck [16] using radioactive Cl^-. The model explains the critical pitting potential as that potential above which Cl^- adsorbs on the surface under consideration. The effectiveness of ions such as Cl^- in promoting breakdown is explained by their being more readily adsorbed than oxygen in the competition for surface sites. The effect of damaging ion concentration on induction times can perhaps be explained by this mechanism, but such important influences on induction time as thickness of the passive film [17] and heat treatment of the passive film [17,18] cannot be readily accounted for by this model. Finally, this mechanism is consistent with localized attack since adsorbed ion displacement will probably occur at discrete sites, defects, inclusions, etc., where displacement may be more likely.

The second model that can be considered as falling under the general heading of an adsorbed ion displacement model is that described by Hoar and Jacob [8]. It has, however, elements in common with the ion migration models also. In this model, a small number (3 or 4) of halide ions jointly adsorb on the surface of the passive film around a lattice cation. The probability of formation of such a high energy complex is small and thus requires a high activation energy for formation. Once formed, however, the halide ions will readily remove the cation from the passive film lattice as a soluble complex (this model assumes a three-dimensional passive film). The film is thus made thinner at the site where the complex first formed and the stronger anodic field at the thinned site will rapidly pull another cation through, where it will meet more halide ions, complex with them, and thereby enter the solution. Thus, once started, the passive film is locally thinned and breakdown proceeds, using Hoar's word "explosively."

This model like the Uhlig one requires a critical potential where adsorption takes place. It also requires strongly adsorbing anions. Because of the difficulty of forming the transitional complex, an induction time is required, and in fact, it was developed to explain the dependence of the induction time on Cl^- concentration, temperature, and potential. Also, it is consistent with the localized nature of breakdown. This model does not appear to be applicable to all systems because Ambrose and Kruger [18] have shown that incorporation of Cl^- in the passive film lattice rather than the formation of a complex on the outside of the film accelerates breakdown for passivated iron. Hoar [19] has also found that the proper functional dependence of induction time with temperature found for stainless steel, which was the basis for his model, does not hold for iron. For this metal he proposes a penetration model.

Another model that uses a transitional complex is that of Foley [20]. He and his co-workers have pointed out that breakdown must involve the formation of metal-anion complexes. The solubility of these complexes controls pit initiation. If the complex is stable and insoluble, initiation is inhibited. On the other hand, if the complex is transitory and easily dissociated, corrosion is enhanced and pitting is initiated.

Finally, the chemical model of Heusler and Fischer [21] which postulates that initiation is started by the displacement of oxygen or hydroxyl ions in the passive layer by chemisorbed chloride ions at local sites belongs under the adsorbed ion displacement heading. This displacement reaction results in the formation of two-dimensional nuclei of a chloride salt. Their experimental results suggest continuous growth and disappearance of these two-dimensional chloride islands. Such growth and currentless chloride catalyzed dissolution of two-dimensional islands can take place on successive underlying monolayers of the oxide until the metal surface is reached, at which time the initiation stage is over. Essentially, this model assumes that localized chemical thinning of the passive layer is responsible for the initiation of pitting.

b. Ion Migration or Penetration Models

The theoretical models that can be grouped under this heading all require the penetration of damaging anions through the passive film, the breakdown processing being complete when the anion reaches the metal-film interface. Most of these models consider the passive film to be three-dimensional. The models differ widely, however, with respect to the mode of penetration proposed.

At one extreme is a model assuming the existence of pores in the passive film. This model is quite old and was suggested by Evans [22] and co-workers. More recently, Richardson and Wood [23,24] have revised this pore mechanism and conclude that breakdown of the passive film does not occur at all because there always exist pores or defects in the film that allow instantaneous penetration and hence instant localized corrosion. One consequence of this is that there is no induction time for the breakdown processes to take place because there are no breakdown processes. Richardson and Wood account for incubation by asserting that during the beginning stages of pitting, the currents are so low at the small bare metal sites that it appears the pitting has not been initiated, although it actually has been going on from the instant that the surface was exposed to damaging anions. In this way, it satisfies the phenomenological requirement for the existence of an induction period. The other phenomena this model must contain are also satisfied. Thus, since the pores, bare or "weak spots," are discrete sites, attack will be localized. The critical potential is the potential for adsorption at the bare metal at the base of the pores, and the role of the damaging anion is the same, and as mysterious, as it is for the other models.

At the other extreme of the types of penetration models are those models involving migration of the damaging anion through a lattice, via defects, or via some sort of ion exchange process. The processes which involve ion migration in a lattice can occur in a variety of ways. Hoar, et al [25] suggest anion entry without exchange to produce "contaminated" passive films. The site where this occurs becomes a path of high conductivity where high cation currents and hence the initiation of pitting are possible. Pryor and co-workers [26,27] also propose the production of an anion contaminated film but suggest that cation vacancies are created which lower ionic conductivity and promote breakdown. Another ion migration scheme can involve exchange of $O^{=}$ or OH^{-} with the damaging anion [17]. Equation (1) shows that such a process can also create anion vacancies that will further enhance the migration of damaging anions to the film-metal interface.

$$Cl^{-}_{solution} + \square_{O}{}^{=} + 2OH_{lattice} = Cl^{-}_{lattice} + 2\square_{OH^{-}} + 2OH^{-}_{solution} \qquad (1)$$

The anion lattice migration models have no difficulty in satisfying the phenomenology of breakdown. The critical potential is, as with all the models, the potential required for adsorption, although in this case, it is on the outer interface of the passive film. The induction time is the time required for the migration of the damaging anion through the passive film, and since this migration may be via discrete defects, the localized nature of breakdown would be expected. The special role of certain damaging anions is not accounted for any better than it is by the other models thus far considered.

c. Breakdown-Repair

This group of theoretical models which involves chemically induced mechanical disruption of the passive film is perhaps the newest. One version was briefly described by Hoar [8]. He postulated that the adsorption of a damaging anion on the surface of the passive film lowers the interfacial surface tension (surface free energy) at the solution interface until "peptization" occurs. This "peptization" results from the mutual repulsion of the adsorbed anions. When the repulsive forces are sufficient, the passive film cracks and damaging anions can attack the metal exposed unless conditions exist where rapid repair of the film can occur (repassivation).

Sato [28] has extended this concept of chemical-mechanical breakdown by providing a more detailed examination of the model. He has suggested that high fields could lead to mechanical rupture of thin films by electrostriction pressures exceeding the compressive fracture strengths of the film. The so-called film pressure this generates is given by:

$$p - p_o = \frac{\varepsilon(\varepsilon - 1)E^2}{8\pi} - \frac{\gamma}{L} \qquad (2)$$

where p = film pressure, p_o = atmospheric pressure, ε = film dielectric constant, E = electric field, γ = surface tension, and L = film thickness.

It is possible that those ions considered to be "aggressive" in promoting localized corrosion attack increase film pressure by decreasing the surface tension term in Equation (2) through adsorption. A recent paper by Yahalom and Pozvansky [29] gives results that indicate that this is so. They found that halides decrease the solid/liquid surface energy. E_p decreases linearly with log C_{Cl^-} and the addition of a surface active agent also decreases E_p. They suggest that lowering the solid/liquid surface energy lowers the stress for the brittle fracture of the passive film. Unlike the other theories we have considered, this theory does not consider the critical potential for breakdown to be related primarily to adsorption but instead to be the "critical potential above which the film pressure exceeds the critical compressive stress of film breakdown" [28]. Also, this model differs from the other models described in that, although as with the others, the special role of aggressive anions such as chloride is not clear, this model goes further and would appear to rule out any special role at all. This is so because zero charge potentials are similar on mercury and probably are likewise similar on oxides as well [30]. The existence of an induction period is also difficult to explain using the mechanical breakdown model. Finally, the localized nature of attack is consistent with the model if one mode of breakdown involves rupture at discrete sites as Sato does suggest. Sato points out in his description of his mechanical breakdown theory that whether a pit nucleates or dies depends not only on breakdown but also on film reformation. This concept is, of course, the basis upon which all models in the group are based. Videm [31] first proposed that it is the interplay between the breakdown (although he does not specifically say so, this could be mechanical as Sato has suggested) and repassivation that determines whether a passive film will suffer permanent breakdown that leads to pitting. Videm proposed that the critical pitting potential is determined by the relative rates of breakdown and repassivation.

Two other models rely on a dynamic breakdown-repair mechanism. First, there is the localized acidification model proposed by Galvele [3]. He assumes that a transient breaking of the passive layer occurs through mechanical or electrochemical means; hydrolysis then occurs during the reaction between the exposed metal and the environment. This reaction produces localized acidification at the site of the cracked film. The amount of acidification necessary to prevent repassivation varies for each metal or alloy. If the acidification is sufficient to prevent repassivation, pitting is initiated. In this model the induction time is the time needed to achieve a critical pH in a broken passive film. The pitting potential is that potential needed to cause the current flowing to the initiating pit to reach a value where a critical pH is reached that renders repassivation impossible.

The last model using a breakdown-repair mechanism is the thermodynamic model of Vetter and Strehblow [32]. They postulate a certain relation between pit nucleation and the disorder of the passive layer which may be of mechanical origin, for example, stresses. These stresses lead to frequent rupture of the passive film. In nonaggressive environments the breaks in the film are rapidly repaired. In the presence of aggressive species such as chloride ions, pit initiation occurs when the repair process results in the formation of a nonprotective salt at the site where the film breaks. Such a salt forms at a potential determined by thermodynamics. Below this potential, presumably E_p, thermodynamics favor oxide formation and pitting is not initiated.

In the Vetter and Strehblow model and in all of the breakdown-repair models, the special role of the aggressive anions is that they influence the rate of repassivation. Recent direct measurements of repassivation [33,34] have verified this. The critical potential can influence a number of factors, adsorption of the aggressive anion as in other mechanisms, the rate of repassivation, the formation of nonprotective layers, and the mechanical properties of the film.

The mechanism supports the existence of an induction period, usually to build up critical acidity and/or concentrations of aggressive anions. Finally, because attack occurs at rupture sites on the passive film, the initiation of localized attack would be expected to occur at discrete sites.

2. Comparison of Theoretical Initiation Models with Experimental Results

It is evident from the discussion of the various theoretical models that even some of the widely different models have elements in common. For example, virtually all of them require the existence of an adsorption step. There is, however, a high probability that no one model is applicable to all systems. Thus, it will be very difficult to match experimental results to models in an orderly way. Instead, our approach will be to select only a few results described in the literature to emphasize contrasting points of view. It is anticipated that by doing so, a clearer definition of the problems will be achieved and experimental work will be stimulated to provide new insights which may result in more effective test methods. For a more comprehensive comparison of experimental results and initiation models, see the recent review by Janik-Czachor, Wood and Thompson [35], Brit. Corros. J., 15, 154 (1980).

a. Kinetics of Initiation -- The Induction Period

The only kinetics that need to be considered in chemical breakdown, as defined earlier, are the kinetics of the processes occurring during the induction or incubation period that takes place prior to the significant increase in current that marks the onset of pitting or crevice attack. A number of conflicting ideas, experiments, and explanations of these experiments exist to explain this induction period. Three representative groups will be described. A representative from the group of experiments such as those of Uhlig [14,15] and Rozenfeld [16] which use the competitive adsorption model for interpretation is not included because no induction periods were reported.

Breakdown-Repair. A very extensive study of the breakdown on pure Al has been made by Videm [31]. His main conclusions were as follows:

(a) He found, as Bogar and Foley [36] had also shown for an Al alloy, that above E_p, there exists an incubation period before pitting starts, when Cl^- is added to solution containing a filmed Al surface. The induction time decreased exponentially with potential, and a ten-fold increase in chloride concentration reduced the time to initiate a pit by ten-fold as well.

(b) Because he could not detect Cl^- by autoradiography, except at sites where pitting attack had taken place, and because he could not detect impedance changes after Cl^- soaking, he concluded that theories for initiation of pitting of Al requiring contamination of oxide films by gradual chloride pick-up and subsequent change in conductivity are not valid.

(c) He was able to measure regular current pulses during anodic polarization which he ascribed to the development of local defects. Recent studies of electrochemical noise by Bertocci and Kruger [37] using more sensitive techniques than Videm have bolstered his results by showing that the magnitude of current fluctuation increased markedly when Al is above E_p and in the presence of chloride ions (fig. 1). Videm and Bertocci, as well, found the pulses (electrochemical noise) both with and without the presence of Cl^- in the experimental solution, but the nature of the pulses changed markedly and abruptly when pitting was initiated at the end of the induction period. This result led Videm to conclude that the Richardson and Wood [23] suggestion that there is no pit initiation step because pitting starts immediately at small flaws in the passive film, is invalid. A recent review [35] points out, however, that the change in the nature of the current fluctuations when pitting is initiated may bolster the Richardson and Wood model because the pulses that are observed during the induction period indicate flaws and the change in their nature is an artifact introduced by the potentiostat.

(d) The role of the chloride is not promoting breakdown per se, but in preventing repair during a dynamic breakdown-repair type of mechanism. Similar conclusions were reached for Al by Zahavi and Metzger [38].

These results of Videm's thus point to a nonpenetration dynamic breakdown and repair theory. It does not explain, however, how a system predisposed to pit reaches the stage where there is sufficient chloride available at the initiation sites to stop repassivation effectively. For crevice attack where the crevice helps concentrate Cl^-, his results would be understandable.* In the absence of a crevice, however, it is difficult to see why at some definite time prior to pitting the Cl^- ions should suddenly start to prevent repassivation unless they concentrate in the film or somehow locally in the environment. Also, the localized acidification mechanism of Galvele [3] described earlier might be operative.

Transitional Complex Formation. An experimental representative of this group is that of Hoar and Jacob [8], whose model was described earlier. Their experimental data for austenitic stainless steel showed that $1/\tau$, where τ is the induction period, was an approximate measure of the rate of breakdown. A plot of log τ vs log C_{Cl^-} showed that the breakdown rate is proportional to the n-th power of C_{Cl^-} with n having values between 2.5 and 4.5. They found an activation energy of 60 kcal/mole and τ to be dependent on potential. Their interpretation

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*Wilde's [39] admonition that the kinetics of pitting corrosion and crevice corrosion are different and that one must disentangle the two to assess susceptibility to localized attack is pertinent to this point.

of the values found for n was that 2.5 to 4.5 halide ions form a "transitional complex" which once formed (because of the high activation energy, a difficult and seldom event), will proceed to break down the film in the way described in the section on models. Because of the high activation energy and the requirement for 2.5 to 4.5 halide ions to form a complex, Hoar and Jacob rule out an ion migration model for stainless steel. However, for other systems, their model may not be valid. For example, Engell and Stolica [40] found a value of 1 for n for mild steel, and the induction time potential independent. This could mean a penetration model where individual aggressive anions were penetrating independently of each other. Foster and Hoar [19] and also Ambrose and Kruger [18] propose a penetration model for the passive film on iron. Other values of n have, however, been found. For Al, Bogar and Foley [36] found values of n between 4 and 11 while Videm found a value of 2. Obviously, one must be careful in using a simple interpretation such as Hoar's and Jacob's to explain the meaning of n.

Penetration. All of the penetration models explain in a very direct way the existence of an induction period. This period is the time required for the damaging anion to travel through the passive film. An experiment directed at providing a test of this idea was given by McBee and Kruger [17] who measured the time to breakdown as a function of passive film thickness. They found that the thicker the passive film, the longer the time to breakdown. They were not able, however, to establish a functional relation between thickness and breakdown time, since three functional relationships fitted the data equally well. To show further that penetration is involved in the breakdown of the passive film on iron, Ambrose and Kruger [18] showed that by removing part of the passive film by cathodic reduction and then regrowing the film in the presence of Cl^-, one could repassivate, but the time for breakdown was shortened. They interpreted this as evidence for the penetration model because the regrowth step incorporated Cl^- ions. These ions, therefore, had a shorter distance to penetrate, and the time for breakdown was shortened. Finally, Ambrose and Kruger showed that annealing the passive film on iron at 65 C for one hour and then bringing the system back to room temperature increased the induction time over 100-fold. Therefore, they reasoned the defects in the film whereby penetration proceeds were removed by the annealing. Similar results for Ta were found by Vermilyea [41], but opposite results were found for stainless steels by Okamoto [42]* (annealing shortened the induction time). These results plus others [18] [42] which show that longer passive film growth times lengthen the induction period, do not rule out the transitional complex model because the production or reduction of defects in the film can also occur on the film surfaces and thereby affect the adsorption of damaging anions at that surface.

Two main experimental observations exist that create problems for the penetration model. First, micro-breakdown events [31,44] as indicated by small current or potential pulses (fig. 1) may continuously exist throughout the induction period. If so, why is penetration needed? There exists contradictory evidence of Cl^- entry into the film lattice. Ellipsometric spectroscopy [17], impedance measurements [26,45], and autoradiography [46] have indicated gradual Cl^- entry. Other work, however, using autoradiography [31], impedance measurements [31,47], and Auger electron spectroscopy [48] show no Cl^- uptake by the film.

b. Critical Potential for Breakdown

There are vast numbers of experiments and discussions in the literature on the factors or underlying causes of the existence of a critical potential for breakdown, E_p. A discussion of its practical significance [27,49,11] and methods of measurement [50,12] will be given in the section on test methods. Here we will detail briefly only those ideas or findings that relate to its role in initiation of breakdown. An incomplete listing of different explanations of the origin of E_p follows:

E_p Determined by Potential of Zero Charge. Almost all of the models require as their first step the adsorption of damaging anions. Roughly, the potential above which such adsorption takes place is the potential of zero charge (pzc). Thus, since the adsorbed ion displacement models require the damaging anion to adsorb and thereby displace the ions forming the passive film, such an explanation of E_p would be reasonable, and the effect of such variables as the nature of the metal, concentration of anions, and temperature all affect E_p and pzc [51,52]. The transition

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*If the films on stainless steel are amorphous [43], the annealing could have caused crystallization producing more diffusion paths. On the other hand, if the films are crystalline, annealing could destroy diffusion paths by grain growth and destruction of lattice vacancies.

complex model also could use the relation of pzc to E_p, not for a bare metal, but for the passive film-solution interface. Likewise, for the penetration models, Ambrose and Kruger [18] have suggested the relationship of pzc to E_p. Because it is difficult to measure the pzc for solid electrodes [51], especially when adsorption may coincide with the initiation of breakdown processes, there have been no good experimental verifications that E_p is related to the pzc. Galvele [53] has pointed out that E_p and pzc may be related if E_c is the potential to initiate pitting, but they are not related if E_p is the potential to maintain pitting.

A major problem with relating pzc to E_p is that the pzc for many anions, both aggressive and nonaggressive alike, are similar on mercury and probably are similar on oxides as well [30], whereas the values of E_p can vary a great deal.

E_p Determined by Film Pressure to Fracture Film. Sato [28] has identified E_p with the critical potential above which the film pressure exceeds the critical compressive stress of film mechanical breakdown. The film pressure, p, resulting from both electrostriction and interfacial effects is given in Eq. (2). Using the above assumption, Sato has been able to derive the relationship between the E_p and the concentration of anions in solution as follows:

$$\frac{dE_p}{d\ln a_{MA}} = \frac{8\pi kT\Gamma_{A^-}}{\varepsilon(\varepsilon+1)E} \qquad (3)$$

where a_{MA} is the activity of the salt MA, Γ_{A^-} is the adsorption density of A^-, k is the Boltzman constant, T the temperature, E the electric field strength, and ε the film dielectric constant.

He was able to calculate from Eq. (3), using the results of Leckie and Uhlig [15] for co-existing anions, that the density of adsorption of the aggressive Cl^- ion on passive stainless steel is of the same order as that for the inhibitive OH^-, NO_3^-, and SO_4^{2-} ions. One problem with the relation of E_p to film pressure is that the special role of aggressive anions such as Cl^- is uncertain because they have about the same polarizability as oxygen ions and only slight changes in dielectric strength (a few percent) might occur if they were to replace the oxygen ions. This would be particularly true at the low concentrations of Cl^- to be expected in passive films undergoing breakdown [54].

E_p is Determined by Repassivation Kinetics. This concept of E_p is based on kinetic considerations. Some studies [31,55,38,42] have found that a competition between repassivation and breakdown of films on Al is important in determining initiation of final breakdown. Videm [31] proposed that the value of E_p is determined by the relative rates of these two processes. He based this on his experiments that showed a narrow potential region where repair and breakdown were competitive. Below this region, repair predominated and above it, breakdown was the major process. Because potential may affect repassivation kinetics [33,34] and because, as Videm and others [53,38,42,55,56] suggest, initiation of localized attack depends on a dynamic balance between breakdown and repair, the kinetic control of E_p must definitely be considered. More quantitative details are still lacking, however, and the problem remains of finding a way to concentrate damaging anions before final breakdown occurs when no crevice or "occluded cell" situation exists. Galvele's [3] local acidification model may provide a way for this to happen.

E_p is Determined by the Potential of Formation of an Unprotective Film. One possible factor determining E_p which may not apply to all cases may be that it is the potential above which an unprotective film may form. The thermodynamic model for breakdown [32] described earlier suggests this. Ambrose and Kruger [18] found that this may be the case for iron. They found that the E_p they measured in pH 8.4 borate solutions containing Cl^- was both equal to the pzc for iron found by Lorenz and Fischer [57] and the equilibrium potential for the reaction that produces in a series of steps the nonprotective γ-FeOOH [58]. It was proposed that γ-FeOOH was formed after penetration by Cl^- had produced an ion conductive path for Fe^{2+} which would produce the nonprotective γ-FeOOH above E_p. The role played by E_p in producing a nonprotective film in the presence of Cl^- is shown dramatically in fig. 2. Whether this sort of explanation of E_p can apply to a large variety of situations remains to be shown.

c. Alloy Composition, Structure, and Environmental Factors

It is not possible within a limited space to discuss the many complex and contradictory results concerned with the effect of alloy composition and structure and environmental factors that influence breakdown initiation processes. An excellent review has been given by Smialowska [4]. This discussion will concentrate on how some of these factors relate to the theoretical models for breakdown.

Alloy Composition. Kolotyrkin [5] points out in his review of pitting that the tendency to breakdown decreases with an increase in the content of N, Ni, Cr, and Mo, especially for the latter two. The main effect of these beneficial alloying elements is to shift E_p in a noble direction. This explains phenomenologically why they are beneficial but does not actually tell us how they work. One way in which they can retard initiation processes is by producing a passive film that is more difficult to penetrate because it provides fewer diffusion paths. Hoar [58] has suggested that some of these beneficial alloying elements can do this by producing amorphous (glassy) films. McBee and Kruger [43] have found experimental evidence for this when Cr is added to Fe and also have found reduced rates of penetration [59]. Another way, however, in which these alloying elements can affect breakdown is by affecting repassivation kinetics. Mo is known to be beneficial in retarding breakdown leading to pitting [60]. Measurements by Ambrose and Kruger [55] indicate that its addition to an alloy does increase the rate of repassivation.*

Alloy Structure. Only the surface structure of alloys will be considered here. Three kinds of possible variations in surface structure have been studied. First, Kruger has looked at the role of crystallographic orientation on breakdown tendency for iron [62]. As Fig. 3 shows, the tendency to pit goes up as the surface approaches the {100} orientation. He also found that pitting density varied with crystallographic orientation [63]. Another example is the single crystal work by Smialowska and colleagues [64,65] on Fe-16Cr. They found that nucleation occurred at crystal subboundaries as well as at other sites where there were not necessarily any metal inhomogeneities.

The second surface variation can occur by the introduction of defects by abrasion, cold work, or other deformation processes.

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*More recent work by Kodama and Ambrose [61] found that the addition of Mo affects the propagation stage of pitting more profoundly than the initiation stage.

Contradictory results have been found. Thus, Rozenfeld [66] found that removing cold work by annealing an 18Cr-9Ni-Ti steel increased the number of pits while Randak and Trautes [67] found that cold work increased the number of breakdown sites for an 18Cr-8Ni steel.

Finally, surface heterogeneities play a big role in initiating breakdown. Smialowska, Janik-Czachor, and co-workers [65,68,69] have found extensive evidence for the nucleation of pits at inclusions such as sulfides or chromium oxide for a number of alloys. Bond and co-workers [70] showed that very small amounts of segregated metallic impurities in quite pure aluminum single crystals could produce breakdown nucleation sites.

The obvious, but sometimes contradictory, effect of surface structure on breakdown can be explained by all the theoretical models discussed because it is reasonable to expect adsorption, penetration, complex formation, or repassivation kinetics to be affected by surface heterogeneities.

Environmental Factors. These factors can include solution composition (including pH) and temperature. There are large numbers of experiments in the literature [4,5] and the results are contradictory. Generally, however, breakdown tendency increases with temperature and concentration of damaging anions while it is not strongly dependent on pH [71]. The nature of the anions in solution play a large role [15] especially if competitive anion adsorption situations are possible. There is some controversy as to what constitutes a damaging anion. Thus, Hoar [72] considers the ClO_4^- ion as damaging as Cl^-, whereas Uhlig [15] has found it to be inhibitory. With regard to models, again all models will depend on environmental considerations. A detailed examination of how all the various and contradictory results in the literature best fit the various models is outside the scope of this discussion. For such a discussion, see references 3, 4, and 35.

Pit and Crevice Propagation

After pitting or crevice corrosion is initiated by the breakdown of a passive film on a metal or alloy surface, the damaging stage of those two localized corrosion failure modes, propagation, commences. If the rate of propagation is very rapid, initiation would be the stage that would control the life of a nuclear waste container. As stated at the beginning, it is a requirement of an effective test method to determine whether initiation or propagation is rate determining. This section describes our current understanding of the factors that control the mechanism and hence rate of propagation.

1. Theoretical Models of Pit and Crevice Corrosion Propagation

As can be inferred from our discussion of the theories of initiation, there is not always a sharp separation between propagation and initiation theories. There are models in the three groups of models described for initiation or breakdown that must of necessity relate to propagation processes as well. Thus, Kolotyrkin [5] and Rosenfeld [81] explain both stages using adsorbed ion displacement models. The version of the ion penetration or imigration model requiring pre-existing flaws as espoused by Richardson and Wood [24] has been characterized as being equally applicable to propagation as it is to initiation [35]. In fact this characterization has been used to argue that no initiation stage exists [35]. Finally, the localized acidification [3] and the thermodynamic versions [32] of the breakdown-repair models have difficulty in separating initiation from propagation, and their proponents deal extensively with the propagation stage.

In this section we will emphasize the theoretical aspects or mechanisms that apply most directly to propagation of pits and crevices. Since the geometry of crevices differs greatly from pits and crevice corrosion starts at lower potentials [3], the theory of crevice corrosion propagation will be treated separately.

a. Theories of Pit Propagation

The theories of pit propagation are, of necessity, less atomistic in nature and are more concerned with geometrical and mass transfer considerations. We will consider both theories that combine the initiation and propagation stages and those that clearly only deal with the propagation stage.

In 1967, Rosenfeld and Danilov [73] invoked the adsorbed ion displacement model to explain the initiation of pits at sites, where the oxygen-metal bonds were supposedly weaker than on most of the metal surface, by the displacement of oxygen ions with chloride ions. This displacement of oxygen by chloride ions leads to a penetration of the passive film at highly localized sites. This event creates local anodes and cathodes and the concentration of aggressive anions (e.g., chloride ions) is enhanced at the positive anodic sites. This situation creates favorable conditions for raising the potential in the newly started pits and thereby further stimulating the anodic reactions (metal dissolution) taking place in the new pits. These pits become covered over with corrosion products and thereby become small crevices where Rosenfeld suggested the mechanisms for crevice corrosion become operative. We will describe those mechanisms in our discussion of crevice corrosion.

Galvele's localized acidification theory [3] provides a great deal more detail to the Rosenfeld picture just described. The initiation stage described by the localized acidification theory has been discussed earlier so we will begin in our description of Galvele's theory at the point in time after a pit has been initiated. Galvele has used the diagram (a simplified Pourbaix or potential-pH diagram) given in fig. 4 to describe events that take place at the beginning of the propagation stage. In fig. 4, $\underline{a}$ represents the pH of the bulk environment and $\underline{b}$ the pH in the starting pit where conditions for the metal dissolution reaction

$$Me = Me^{Z+} + Ze^{-} \qquad (4)$$

becomes thermodynamically favorable. The hydrolysis reaction

$$Me + ZH_2O = Me(OH)_Z + ZH^{+} + Ze^{-} \qquad (5)$$

only takes place between $\underline{a}_1$ and $\underline{a}_2$ in fig. 4. When the potential is above $\underline{a}_2$, the localized acidity produced by reaction (5) will promote dissolution. Potentials between $\underline{a}_1$ and $\underline{a}_2$ will promote repassivation. A somewhat similar description of the role of local acidification on pit propagation has been given by Pourbaix [9].

An important aspect of Galvele's mechanism is that it provides insights into the effect of potential on the rate of metal dissolution in pits. The rates of reactions (4) and (5) and the hydrogen evolution reaction

$$2H^{+} + 2e^{-} = H_2 \qquad (6)$$

are potential dependent. If the hydrolysis reaction producing $Me(OH)_Z$ is rapid, reaction (5) will give the rate of proton production, the higher the potential the higher the rate. When the potential is low, however, reaction (6) is favored and protons are consumed. When the potential is at a value where the rates of reactions (4) and (6) are equal, it is the corrosion or open-circuit potential in an acidified solution close to the anode, called E_c^* by Galvele. At E_c^*, rate of the proton production reaction (5) is equal to the rate of the proton consumption reaction (6), and no acidification will take place. Below E_c^* passivity conditions exist and any passive film that is disrupted will be reformed rapidly. Above E_c^* repassivation is nonexistent or ineffective, and the pit will propagate. This treatment of E_c^* by Galvele suggests a somewhat, but not completely, similar explanation by Pourbaix of his protection potential, E_{prot}. The various potentials used to characterize pitting phenomena will be described more fully in the section on test methods.

Vetter and Strehblow [32] in the exposition of their mechanism of pit growth (and initiation) questioned the local acidification mechanism just described. Their calculations indicated that no significant changes in solution composition could take place during initiation or when very small pits were growing. (A newer calculation by Galvele [74] indicates significant changes of pH but insignificant increases of chloride ions during the early stages of pitting.) The theory of Vetter and Strehblow was described briefly in the discussion of initiation. Their theory is an elaboration of propagation ideas developed earlier by Franck [75].

The ideas of Vetter and Strehblow on initiation have already been discussed. Their picture of pit growth starts with their attempts to resolve the problem of the simultaneous existence of active pitting sites and passive regions on the same surface. This requires a potential difference between the surfaces in pits and the rest of the surface and indeed potential drops of tenths of volts have been observed. However, Vetter and Strehblow have shown experimentally [76] that such large differences cannot exist in small pits. Based on calculations, they dismiss the cause of this potential difference as being due to large differences in pH between the environment in the pit and that outside, as suggested by Galvele [3] and others. Instead they use Franck's proposal [75] that a highly resistive surface layer, probably a salt, must exist on a growing pit's surface.* This salt

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*Strehblow [77] recently included the possibility that local acidification due to hydrolysis may occur in the pit along with the formation of a salt film especially in cases where a dense film may not form, e.g., for aluminum.

layer was said by Vetter and Strehblow to be formed by the cations of the metal and the aggressive anions. They hypothesized that it is dense, poreless and contiguous to the pit solution which is not saturated with the salt. The current flows through this layer in the same manner as the current has been proposed to flow through an oxide film, as an ionic current produced by a high electric field ($\sim 10^6$V/cm). A key point in their mechanism is that the rate of pit growth (corrosion) is equivalent to the rate of salt film dissolution. At steady state the dissolved metal ions are replaced by the anodic ionic current which is equal to the steady state corrosion rate (corrosion current density). Since the thickness of the salt layer determines the field strength which sets the ionic current, it is regulated by the process to set the steady-state value of the corrosion current density. Since many workers have found pits with hemispherical shapes [75-79], the corrosion current density must be constant over the whole surface of such pits, indicating a very uniform salt layer in the pit. More recent ideas by Strehblow [77] indicate that since repassivation of pits can take place when the potential is lowered below E_{prot} that repassivation is closely related to the removal of accumulated aggressive anions into the bulk electrolyte, a diffusion-controlled process. This bolsters the idea that aggressive anions in the pits are essential for stable pit growth.

The final model type for pit growth to be described is one that considers diffusion-controlled or mass-transfer processes as being of great importance. Kaesche [78] in considering the pitting of aluminum in a NaCl solution used a mass transport model. He assumed the following: (a) the base of the pit was active and (b) hydrolysis of the Al^{3+} ion lowered the pH in the pit which caused a buildup of an $AlCl_3$ layer at the base of the pit because of the dissolution of the $Al(OH)_3$ formed during hydrolysis. Using these assumptions, he combined a one-dimensional solution to the mass transport equations for Al^{3+}, Cl^- and Na^+ ions with the condition of electroneutrality to determine the limiting current density for aluminum ion dissolution at the base of a pit. He calculated that the limiting current density, i_L, for Al^{3+} in a single pit was

$$i_L = \frac{ZFKD}{\delta} \qquad (7)$$

where Z = 3 (for Al^{3+}), F is the Faraday constant, D is the diffusion constant for Al^{3+}, δ is the thickness of the diffusion layer and K is a constant that has the dimensions of concentration and is determined from model equations as a function of bulk concentrations of NaCl.

Beck [79] modified this model in order to treat the pitting of titanium because the Kaesche model did not reflect the phenomenology of titanium pitting. Beck spelled out the following assumptions for his model for titanium:

(a) Base of pit is active.
(b) Titanium tetrahalide (TiX_4) is formed at base of pit.
(c) Covalent TiX_4 diffuses away from the surface.
(d) TiX_4 is hydrolyzed in solution to TiO_2, X^-, and H^+ by first-order reaction with rate constant, k (sec^{-1}).
(e) Bulk solution has concentration, C^o of HX.
(f) Rate of dissolution of Ti is limited by mass transport of X^- to base of pit.
(g) One-dimensional mass transport for TiX_4, X^-, and H^+ through diffusion layer of thickness δ.
(h) Electroneutrality.

A mathematical treatment using these assumptions lead to an expression similar to Eq. (7) but with K replaced by a factor R that depends on the regeneration of halide ions by hydrolysis within the diffusion layer. R is the ratio of the experimentally measured current density at a particular halide concentration to that calculated from the simple expression for the limiting current density. The model predicts that if hydrolysis is too rapid a passive oxide layer would form too close to the pit's metal surface and block the surface. Beck suggests that this will happen for iodide. For bromide the hydrolysis rate will be in the right range and it will be too slow for chloride solutions.

b. Theories of Crevice Corrosion Propagation

The propagation of crevice corrosion differs from pitting corrosion mainly because of two reasons: (a) the geometry of a crevice is usually different from that of a pit, being much flatter and shallower and (b) the restriction of mass transfer of reactants is much more effective for a crevice than for a pit. In an admirable and quite useful effort to develop a mathematical model for crevice corrosion, Oldfield and Sutton [81] have described rather completely the mechanisms of crevice corrosion propagation. To do this they have incorporated the earlier mechanistic ideas of Rosenfeld [81], Karlberg and Wrangler [8] and Fontana and Greene [83].

Oldfield and Sutton divide the processes controlling crevice corrosion into four stages with the first two stages being involved essentially in the initiation of breakdown of passivity and the latter two being involved in the actual removal of metal within the crevice. Their four stages are as follows:

Stage 1. During this stage the normal corrosion reactions that take place on an uncreviced surface take place outside and inside a crevice. Assuming a NaCl solution containing dissolved oxygen, the reactions at the anodes and cathodes of a metal surface bearing passive film will be

Anodic reaction: $Me = Me^{Z+} + Ze^-$ (8)

Cathodic reaction: $H_2O + 2e^- + 1/2\ O_2 = 2OH^-$ (9)

The overall reaction when these half reactions are combined

$$2Me + \frac{Z}{2} O_2 + ZH_2O = 2Me(OH)_Z \quad (10)$$

leads to the thickening of the passive film. If the diffusion of oxygen into the crevice is severely limited by a deep tight crevice, the crevice solution eventually becomes depleted in oxygen because of reaction (9), and the first stage is at an end.

Stage 2. After the depletion of the oxygen in the crevice solution, the anodes and the cathodes of the metal surface become localized with the cathodic reaction taking place outside of the crevice and the crevice reaction inside. The production of an increase in the concentration of metal ions by the anodic reaction inside the crevice and their participation in a hydrolysis reaction ($Me^{Z+} + ZH_2O = Me(OH)_Z + ZH^+$) causes the precipitation of metal hydroxides and a lowering of the pH. In order for electroneutrality to be maintained and because of the mass transport associated with carrying the current during the reduction in pH, cations move out of and anions move into the crevice. In this way the concentration of chloride ions is built up in the crevice solution thereby increasing its corrosivity. The rate of this increase in crevice solution corrosivity depends on the magnitude of the corrosion current and the volume of the crevice (and hence its average gap).

Stage 3. When the concentration of Cl^- and the pH of the crevice solution reach values where repassivation becomes slow or not possible, stage 3 commences. This stage is the point in the process where there is a complete breakdown of passivity. The crevice solution composition in which this occurs was called by Oldfield and Sutton the "critical crevice solution" (CCS). This solution can be defined by its pH and chloride concentration. They stated that the value of the passive current (the corrosion current before the breakdown of passivity) and the CCS are factors that are important in determining an alloy's resistance to crevice corrosion.

Stage 4. During this stage, which begins with the complete breakdown of passivity within the crevice, propagation, i.e., rapid dissolution of the alloy inside the crevice, takes place. Outside the crevice the metal dissolution reaction is, of course, balanced by rapid oxygen reduction. There may also be some hydrogen evolution occurring in the highly acidic solution inside the crevice.

Using these four stages, Oldfield and Sutton have built a mathematical model that emphasizes the importance of the CCS and the passive current and use these factors to characterize an alloy's resistance to crevice attack, crevice geometry and the chloride concentration in a bulk. Using the model they are able to predict whether the pH will reach a limiting value controlled by mass transport or go beyond the limiting value to a critical value where breakdown and rapid corrosion takes place. A complete discussion of their model is beyond the scope of this review.

2. Factors and Processes Involved in Pit and Crevice Corrosion and Their Implications for Test Method Development

A brief listing of the factors as suggested by the theories and mechanisms discussed above will now be given. A good starting point is fig. 5 from the paper by Oldfield and Sutton [80]. It is given for crevice corrosion only but, with the exception of crevice-type and crevice geometry, the same factors apply to both forms of localized corrosion. Our listing will not include all of the items in fig. 5, but it will add some not in that figure.

a. Alloy Composition and Passive Film Characteristics

As mentioned in the section on pit and crevice initiation, the constituents of an alloy and especially their effect on the nature of a passive film are of crucial importance. Test methods used for a given alloy must assure that the test environment has a composition that includes major and minor constituent ions that may be present in the crevice or pit solutions.

b. Electrochemical Reactions

All electrochemical reactions, anodic and cathodic, should be considered in test designs. In crevice corrosion situations, cathodic reactions may play a bigger role than hitherto expected. Another group of electrochemical reactions that is usually neglected because it is of a transient nature is repassivation. Because many models emphasize the importance of repassivation in pitting or crevice attack, test methods that measure it are of great value.

c. Bulk Solution Composition

Many of the models indicate that except for the effect of the bulk solution on the pit or crevice environment, the bulk environment is of secondary importance. This is especially so if a test environment is sought that simulates propagation processes.

d. Bulk Solution Temperature

In the corrosion of containers for nuclear waste containers, temperature is perhaps the most important factor here. It affects passive film characteristics, the kinetics of corrosion, the rate of repassivation and the composition of the pit or crevice environment. It should always be a parameter in a test program that seeks to predict long-term susceptibility.

Pit and Crevice Environment

As stated above, most pitting and crevice corrosion mechanisms involve a change in the local environment. It is of crucial importance to characterize this environment for a given bulk environment-alloy system and to determine whether this local environment is the best test environment to use in the development of an accelerated test method.

Testing Techniques

Tests designed to determine the susceptibility of alloys to localized corrosion, specifically pitting and crevice corrosion, often include natural exposure tests. These tests involve placing metal coupons or assemblies (see fig. 6b and c) in the environment, i.e., seawater, and either monitoring the sample *in situ* or leaving it there over a long period of time (greater than one year). After the samples are retrieved, they are weighed and examined. The weight lost of the sample is then used to determine the corrosion rate. The Multiple Crevice Assembly with 40 small crevices on it, developed by Anderson [84], is generally used to study crevices. The large number of crevices is desirable in a statistical approach to the results.

Natural exposure tests are impractical for metallic containers in nuclear waste repositories in that information is needed about the localized corrosion resistance of alloys over 1000 years. In this situation accelerated testing technique, capable of determining pitting and crevice corrosion rates of selected alloys at various temperatures, are needed. Corrosion rates, as previously mentioned, are dependent on both initiation time and propagation rates of pits and/or crevices; therefore, techniques that can separate the two are desirable. Unfortunately, most techniques involve both, but if the experiments are carefully designed this conflict can be greatly reduced or eliminated.

Because of the requirement that nuclear waste containers resist localized corrosion for very long periods, evaluations of their susceptibility must, of necessity, be carried out using accelerated tests. This discussion will only deal with such tests. While most accelerated testing techniques cannot produce absolute numbers for corrosion rates of a particular alloy, these methods can rank alloys as to their susceptibility to localized corrosion and can describe mechanisms involved with initiation and propagation of the pit and/or crevice [85]. To evaluate the suitability of alloys for application as containers of nuclear waste, rates for pit or crevice initiation and propagation are needed and accelerated tests that only rank alloys are not enough.

Tests to Evaluate Susceptibility to Pitting and Crevice Corrosion

1. Ferric Chloride Solution - ASTM G 48-76

This is the standard test method for crevice corrosion resistance of stainless steels and related alloys. The ferric chloride solution seeks to simulate crudely the pit or crevice environment. The crevice design consists of two TFE-fluorocarbon blocks on either side of the sample and is held together with two rubber bands at right angles to each other. Metal coupons (for pits) and crevice samples are immersed in 10 percent $FeCl_3$ at a controlled temperature [86]. The $FeCl_3$ solution is a highly corrosive environment similar to that found in the pit environment which accelerates the corrosion rate of alloys susceptible to localized corrosion. Samples are weighed and optically examined for pits and crevices. Those alloys that have low corrosion rates and exhibit little or no evidence of pitting are considered resistant to localized corrosion.

Another approach or test method to determine crevice corrosion susceptibilities is the use of the crevice corrosion temperature by Garner [86]. In this test method the critical temperatures of various alloys are determined using $FeCl_3$ solutions. After the crevice assembly has been immersed in 10 percent $FeCl_3$, the temperature is increased by 2.5 C every 24 hours from -2.5 C up to a temperature where crevice corrosion can be observed. This temperature is called the crevice corrosion temperature (CCT). Garner's results showed an increase of the CCT of stainless steels with the addition of 6 percent Mo and that these metals would be essentially free of crevice corrosion in ambient sea water.

The ferric chloride solution is not an ideal accelerated test for several reasons. Since ferric ions are always present in the crevice, the cathodic reaction for the corrosion process can occur. This may suggest possible susceptibility of stainless steel and iron alloys but is an unnatural crevice environment and therefore of little value for other alloy materials such as those of titanium. It is also difficult to reproduce the exact crevice geometry from test to test. Even for stainless steel tests, the ferric chloride test represents propagation conditions only and ignores the initiation process necessary to develop the cathodic reduction of oxygen outside the crevice.

2. Electrochemical Techniques

Polarization curves are obtained to (a) acquire general information on the localized corrosion process, (b) determine critical potential values such as critical pitting potential, critical crevice potential, protection potential, and the corrosion potential, and (c) suggest the composition of the local environment conditions such as pH and chloride content. The effect of chloride and pH content can be seen by comparison of the various concentrations on the polarization curves. Three methods are most often used in these studies and will be discussed separately.

a. Potentiodynamic Techniques

Potentiodynamic anodic polarization of an alloy gives the current-potential relationship for the alloy in a given environment by scanning at a selected rate over a range of potentials. When an alloy sample is immersed in an aqueous solution, oxidation and reduction occur on its surface. Although the alloy can function as a cathode or an anode, corrosion of the alloy generally results from anodic currents. The corrosion potential, or open circuit potential, is the potential, relative to a reference electrode, at which the rate of oxidation is equal to the rate of reduction. In other words, the magnitude of the anodic current is equal to the cathodic current. The corrosion potential (-163 mV) is shown in fig. 7 at A. Potentials less than E_{corr} (lower than A in fig. 7) are in an active region, and potentials greater than E_{corr} are considered increasingly noble potentials. The general corrosion rate can be determined from this by extrapolating a straight line through the cathodic portion of the curve (in the active region) to E_{corr}. That intersection defines the corrosion rate of the alloy and is 6.7×10^2 na/cm^2 for 304 stainless steel in this example.

The corrosion rate just mentioned does not consider localized corrosion and, therefore, is not particularly useful if pitting or sites for crevice corrosion develop. Under localized corrosion conditions, the corrosion rate of the alloy will increase greatly at highly localized sites. Potentiodynamic anodic polarization scans can give qualitative information of the alloy such as its passivation tendencies and effects of inhibitors, under different environmental conditions. Critical potentials and potential regions of the scan, however, can only indicate the relative susceptibility of an alloy to pitting and/or crevice formation because scanning over a potential range does not always allow for induction times to be exceeded so that pitting is initiated at the correct E_p. Also, the potential region of the alloy's passive film and its current density can be roughly determined.

A potentiodynamic anodic polarization curve is shown in fig. 7 from A to B. The potential of the sample was scanned slowly in the anodic direction from the corrosion potential to B. Pits and crevices are initiated at potentials more noble than the critical pit or crevice potential, E_p (see fig. 7). This potential range is called the pitting region. At potentials above E_{prot} the alloy is susceptible to pitting. At potentials lower than the protection potential, E_{prot}, pits and crevices are repassivated. At potentials lower than the protection potential, E_{prot}, pits and crevices are repassivated. A large passive region, between A and E_p, is also desirable in that it indicates the oxide film is stable over a wide potential range. Pitting and crevice corrosion can occur simultaneously unless the alloy sample is carefully prepared. If the critical crevice corrosion potential is desired, then a crevice assembly is needed (see fig. 6d and e). However, crevices should be avoided in pitting experiments (fig. 6a).

Defranoux [90] and Wilde and Williams [49,91] have studied pit initiation on stainless steel and nickel alloys in chemical and marine environments. Specifically, they were comparing results of accelerated testing by polarization techniques to natural exposure (weight-loss) tests and found that accelerated testing can represent the relative susceptibilities of different alloys to pit corrosion. However, these results were meaningless if crevices were present. Their observations suggested that the propagation mechanisms of both pitting and crevice attack are identical but the initiation mechanisms are different. Since the initiation in crevice corrosion was found to have faster kinetics [92], the critical pitting potential can be related to the breakdown of passivity by pit initiation only when no crevices are present. Unlike pit initiation, crevice initiation [93] results from differential aeration or a depletion of the cathodic reactant which fosters the breakdown of the passivity in the crevice.

Pit and crevice propagation, however, have been observed to follow the same mechanism. It involves increasing anodic dissolution in regions of limited diffusion. Therefore, the experimental designs of differentiating pits from crevices are not as critical when studying propagation effects of localized corrosion. One method of determining the relative amount of propagation of pits and/or crevices in alloys is by comparing the area in the hysteresis loop formed during cyclic or pitting polarization curves.

Cyclic or pitting scans can be obtained by reversing the potential sweep in the cathodic direction at a particular potential or current (B in fig. 7). As the pits repassivate during the reverse scan, the current is reduced and a hysteresis loop emerges. The protection potential, E_{prot}, is determined by the intersection of the forward and reverse scan. Pitting characteristics of the alloy are represented by the shape and position of the hysteresis loop. A rule of thumb is that the difference potential, $E_p - E_{prot}$, is related to the crevice corrosion resistance of the alloy and is used to represent the area of the hysteresis loop. In fig. 7 the sample was severely pitted before the potential was reversed. Not surprisingly, the material did not repassivate quickly and indicated high susceptibility to crevice corrosion under these severe conditions.

An example of the application of cyclic scans to crevice corrosion susceptibility can be found in the study of crevice corrosion of Hastelloy C, Incoloy 825, and Carpenter 20Cb3, combining the polarization measurements with weight-loss data [49]. An artificial crevice assembly was used in the tests, and the alloys were subjected to potentials large enough to break down the passivity through crevice initiation. It was found that under increasing anodic conditions, premature breakdown of passivity occurred when a crevice was present. In the absence of a crevice, no breakdown of the passivity would occur (no hysteresis). The cyclic polarization results can be seen in fig. 8 and agree well with crevice corrosion weight-loss data of these alloys exposed to seawater for two years. The weight loss for Hastelloy C, Incoloy 825, and Carpenter 20Cb3 is 0.16, 4.1, and 26.1 mg/cm^2, respectively. The cyclic potentiodynamic anodic polarization curve for Hastelloy C exhibits no hysteresis loop (note reversibility of the curve). The curve for Incoloy 825 has a small amount of hysteresis (very little crevice corrosion) while Carpenter 20Cb3 exhibits severe crevice corrosion.

There are several problems involved with potentiodynamic and cyclic potentiodynamic anodic polarization curves. The presence of a crevice makes it very difficult to detect pitting susceptibility. Any pitting values for E_{prot} and E_p obtained in the presence of a crevice would be suspect. This is illustrated in fig. 9 for Fe-30Cr-3Mo in nitrogen saturated 1 M NaCl at 25 C [49]. There was no pit initiation, and the major sites of dissolution were the grain boundaries where chromates and molybdates were formed. A photomicrograph of the surface confirmed that no pits were present. However, the cyclic polarization of the alloy containing a crevice assembly resulted in a pronounced hysteresis loop indicating initiation of crevice corrosion.

Critical values such as E_p and E_{prot} found through potentiodynamic scans are very sensitive to the conditions under which the experiments are conducted. The critical pitting potential can differ widely depending on the potential scan rate as seen in fig. 10 [94]. When the potential is more noble, the initiation time is shorter for pit formation. Therefore, a rapid increase of current can be measured when there is a short induction time which corresponds to fast potential scanning rates, thereby giving too low values for E_p. Thus, for long term situations like nuclear waste containment a test should not ignore long induction times, e.g. one year, a small fraction of the 1000 years. The protection potential, E_{prot}, is not a value unique to the alloy and environmental conditions but rather reflects the experimental conditions necessary to repassivate the pits depending on the amount of pit propagation before the reverse scan begins [49]. This can be seen in fig. 11 where the amount of pit propagation was increased after pit initiation had occurred. There was a large difference in E_{prot} particularly after the pit growth was close to 1 A/cm^2 before reversing the scan.

b. Potentiostatic Techniques

The potentiostatic technique can be used in studies of either initiation or propagation mechanisms and involves monitoring the current or current density versus time at a constant applied potential [50,95]. Often potentiodynamic or cyclic polarization scans are taken first to determine E_p and E_{prot} values. For comparison a cyclic polarization curve of the potential versus the log of the current is shown in fig. 12(a) with the critical pitting and protection potentials labeled. Standard mathematical practice is to plot the dependent variable (in this case log i) as the ordinate with the independent variable (the potential) as the abscissa. However, ASTM specification G-3 calls for data to be presented in the reverse way with the potential as the ordinate and the log i as the abscissa (fig. 7). This allows the longer axis of most x-y recorders to be used for recording the current or current density.

There are two variations of potentiostatic measurements that are commonly used. One, primarily associated with initiation studies, measures the change in current density over time at potentials greater than and less than the critical pitting potential, E_p. A new sample is used with each curve. This variation is illustrated in fig. 12(c) in which E_2 is equal to E_p. When $E < E_p$ as with the potential E_1, the current decreases with time since the alloy's surface is passive. At potentials greater than E_p, pitting is initiated; thus the current increases. Propagation studies involve activating the alloy's surface to form pits by applying a potential greater than E_p, then quickly shifted it to values less than E_p. The results of this procedure can be seen in Fig. 12(d). Propagation of already existing pits at $E > E_{prot}$, continues and is shown by an increase of the current with time. However, at $E < E_{prot}$, pits are repassivated and the current decreases with time.

The potentiostatic method of current versus time plot at constant potential can be determined on the clean surface of the alloy. This gives a reliable value of E_p but is very time consuming since the induction time can be very long. Activated surfaces can, however, give reasonably good values of E_{prot} which some believe is the true E_p [12].

c. Galvanostatic Techniques

The galvanostatic technique measures potential versus time at constant current. Generally measurements are made as the potential decreases in time until a constant potential is reached. This potential is the protection potential, E_{prot}, and is shown in fig. 12(b). This technique can take on various forms in that it can involve two dissimilar metals in a solution or the two metals may be in two different solutions which are electrically connected by a salt bridge.

Galvanostatic measurements of potential versus time at constant current are very quick and easy but the periodic oscillations of the potential make interpretations of the data very difficult. Also, the maximum potential is often unmeasurable without an oscillographic device since the localized corrosion can occur within seconds.

3. Modified Electrochemical Techniques

a. Corrosion Behavior Diagram Technique

Corrosion behavior diagram techniques are useful as a qualitative approach for comparing various alloys in a specific environment [96]. The CBD technique is particularly valuable for determining the primary passive potentials, E_{pp}, and critical anodic current density I_c, in self-passivating samples. Both E_{pp} and I_c values arise when the cathodic curve intersects the anodic curve in the active region. This is a theoretical curve since experimentally only the net current can be measured. Self-passivation can occur in potentiodynamic scans in that an initial delay before data collection is generally present and the scanning rate is usually 1 mV/s or less. There is no initial delay in the CBD technique because the run begins immediately when the sample is immersed and the scanning rate is 10 mV/s or greater.

Figure 13 shows a CBD plot. The forward scan (scan 1) is shown as a long dash, short dash line. At an experimentally set potential or threshold current the scan is reversed (scan 2) and is indicated by a solid line. After a time delay scan 3 (dashed line) is resumed from the initial potential of scan 1 in the forward direction to a final potential. The passive film stability is indicated by lower current dips during the second scan. The rule of thumb suggests the plot be linear over several decades for low current dips. However, if the second scan shows great curvature, one can assume poor passive film stability. The alloy is said to have less corrosion resistance the closer the third scan comes to retracing the first scan.

b. Scratch Method

The scratch test technique, suggested by Pessall and Liu [12], involves scratching the alloy surface at a constant potential and measuring the current or current density as a function of time. This technique is based on the concepts demonstrated in fig. 14 and suggests a critical potential, E_s, that usually results in values between E_{prot} and E_p. The figure illustrates how the authors expect the potential dependences of repassivation time and induction time for an alloy in a particular environment to relate to a critical potential value, E_s. Smooth surfaces and rapid stirring would lead to greater induction times to break down the protective film on the alloy. If this film is removed by scratching the alloy surface below E_s, the alloy would repassivate as shown in fig. 14.

The critical potential, E_s, can be determined by the current versus time curves at various potentials. When the potential is below E_s, the current observed upon scratching returns to the original values. However, when the potential is above E_s there is little if any repassivation and the current remains constant or increases. Figure 15 illustrates the current transients above and below E_s. A major advantage of the scratch method is that it eliminates the induction time for localized corrosion to be initiated. The results obtained by Pessall and Liu are dependent on the alloy and the environment and can be characterized by a critical potential, E_s, above which pits will nucleate and below which pits do not nucleate ($E_s = E$). However, this value is usually less noble than E_p values obtained by potentiodynamic anodic polarization scans. In other words E_s separates pitting tendencies from repassivation tendencies. Their results also indicate that the protection potential is the same as the critical potential E_s. Therefore, only one critical potential E_s, exists. E_s can also be determined by galvanostatic techniques; however, the results are difficult to interpret in that large oscillations of the potential occur.

c. Tribo-ellipsometry

Tribo-ellipsometry is a technique developed to bypass the initiation phase by abrading off the surface oxide and to measure the repassivation of the exposed surface by ellipsometry to determine the film growth kinetics [97,98]. The electrochemical cell with the retracting abrasion wheel is shown in fig. 16. The initial phase of repassivation is usually completed in less than 50 milliseconds so rapid withdrawal of the abrasive wheel is desired. This equipment is designed so that ellipsometric measurement of film growth kinetics can begin within 10 milliseconds of cessation of abrasion. Results of low carbon steel in nitrate, nitrite, and buffered borate solution revealed significant oxide film growth had occurred before the ellipsometric measurements were taken. However, this technique showed that in nitrite solution the rate of repassivation was greater and that after film rupture in the nitrate solution, the anodic current went into metal dissolution. Therefore, tribo-ellipsometric measurements indicate film repair mechanisms as well as metal dissolution kinetics.

d. Pit Propagation Rate (PPR) Curves

Another technique to determine the rate of pit or crevice propagation by avoiding long initiation times is the PPR curve technique [99]. Figure 17 describes the PPR technique. It involves the following steps:

(1) Alloy sample is immersed in the solution for one hour at E_{corr}.

(2) Scan at 36 V/hr (10 mV/sec) to a preselected potential between E_p and E_{prot} (0.25 V in fig. 14) and hold this potential for 10 minutes. Since this potential is below E_p, the current should give the rate of general corrosion in the passive state.

(3) Continue the scan beyond E_p until a current density of 10 mA/cm^2 (10^7 nA/cm^2) is reached.

(4) Decrease the potential in a single step to the preselected potential between E_p and E_{prot} (0.25 V in fig. 14) and hold this potential for 10 minutes. The current density is a measure of the general corrosion and the rate of pit growth.

(5) Decrease the potential in a single step to the original free corrosion potential, E_{corr}, to repassivate the pits. Hold this potential for 5 minutes.

(6) Repeat (2) to ensure the current under passive conditions have not changed significantly.

(7) Reduce the potential to E_{corr}.

The general corrosion portion of the current is subtracted from the total current found in (4) to obtain the shaded area in fig. 17 which is the average pitting current. The area due to pitting is determined by microscopic examinations. Therefore, the pit propagation rate is the average pitting current by the pitted area, and Syrett [100] refers to this as the "average pit current density." Syrett's results of 316L and 3 Mo TRIP in arterial Tyrode's solution show similar pit propagation rate behavior where as cyclic polarization scan results indicated significant differences in that E_p - E_{prot} might not be a good indication of crevice or pit propagation. Also, cyclic polarization scans showed little difference of E_{prot} for cold worked and as cast 3 Mo TRIP but PPR curves demonstrated distinct differences (fig. 18).

The scratch test and pit propagation rate curves avoid the initiation time by removing the passive film or initiating pits at noble potentials. Pessall and Liu [12] found light, small scratches to give greater reproducibility. However, they assume the film will be broken in the sites that are favored for pitting sites. The PPR curves scan to potentials greater than the film breakdown potential to initiate pits, but this value is dependent on the scan rate and surface effects of the alloy. Nevertheless, both of these techniques along with rotating ring disk electrode methods offer reasonably good quantitative information concerning propagation rates. Initiation time can be estimated by studying passive film techniques that shed light on the mechanisms of film breakdown.

e. Electrochemical Noise Measurements

This technique described by Bertocci and Kruger [37] examines events leading to film breakdown, in particular the dynamic breakdown-repair process preceding actual film breakdown. This process can be accomplished by detecting and analyzing the fluctuations from the average values of the current and electrode potential. Either voltage fluctuations under galvanostatic conditions or current fluctuations under potentiostatic conditions can be monitored. The potentiostatic method was found to be preferred when passive films are studied in that distinct energy conditions can be maintained at the electrode/electrolyte interface. In studies of amorphous and crystalline Fe-Ni-Cr alloy it was found that the amorphous compound resisted film breakdown better because its homogenous film inhibited the dynamic breakdown repair process to a greater extent. The electrochemical noise technique is mainly useful for the detection of the onset of pitting and for the determination of E_p (see fig. 1).

f. Rotating Ring-Disk Electrode

Rotating disk and rotating ring disk electrodes can be used to study corrosion phenomenon [101-104] and determine instantaneous corrosion rates [106]. These corrosion rates were measured at open circuit as a function of rotation speed and temperatures. The RRDE collection experiment involved locating the potentials of oxidation of the copper (I) product at the ring and monitoring the partial anodic current in the dissolution of copper at the disk. The ring current can detect directly surface alteration without the averaging necessary in integral techniques such as various potentiostatic methods. For further information about RDE and RRDE techniques and results concerning corrosion mechanisms, see references 101 through 105. Recent discussions with Ambrose [106] suggest a more appropriate technique for determining propagation rates would involve a ring-ring electrode since a ring disk electrode would probably have current transients depending on the location of the pits.

Standard testing procedures for cyclic potentiodynamic polarization measurements for localized corrosion [107] and pitting or crevice corrosion of metallic surgical implant materials [108] are available by the American Standard Testing Measurements organization.

Significance of Current Understanding to Testing--Concluding Remarks

The current understanding of the mechanisms of pitting and crevice corrosion we have described, incomplete and controversial as they are, nevertheless provide valuable insights into test methods that could be useful in assessing the life of metallic containers for nuclear waste. Out of our understanding of localized corrosion processes, four significant aspects can be identified that appear to be of the utmost importance for the development or choice of more reliable test methods:

1. The Existence of an Induction Period

The existence of an induction period, whatever the processes are that control it, is by its very existence a measure of the time for pitting or crevice corrosion to initiate. Thus, a test that can measure the induction period will also measure the time for initiation to take place. While such tests exist (one simply holds a specimen above E_p by means of a potentiostat and measures the time required to observe a rapid increase in anodic current), induction times can be too long (greater than a year) to be measured in a reasonable test period. To our knowledge, there is no way one can extrapolate test data to get a measure of the induction time and, hence, the time for the initiation of localized corrosion. This implies that there is no way to develop an accelerated test to measure, by extrapolation or otherwise, the time required for localized corrosion initiation. This is, however, not so for the propagation process. Once pitting or crevice corrosion is initiated, test methods, such as the PPR method described earlier, can give a value for the rate of propagation. This value, as imperfect as it may be, can then be used to estimate the time required for penetration of the container wall.

A question must now be posed, what does one do if the rate controlling step is initiation and not propagation? The only course of action that we can suggest is the one that proposes the use of tests that eliminate the initiation stage and measures the propagation rate only. If this propagation rate is unacceptably high, critical potential measurements, which determine conditions where initiation is not possible or, at least, probably occurs after an acceptably long induction period, must be used as a testing procedure. If one can be assured that the potential of the alloy used in the environment in which the container will be emplaced is less than the critical potential determined for that environment, our current understanding would imply that the time for initiation would not be exceeded during the required containment period.

2. The Existence of Critical Potentials

The importance of the existence of critical potentials, especially when initiation processes control container life, has been discussed in item 1. The major mechanistic and, therefore, testing problem associated with critical potentials is that the literature is in a confused state providing many "critical" potential values and procedures for their determination. In defining many of these values, concepts of initiation and propagation have been intertwined. For instance, the critical potential, E_p, in potentiodynamic scans is supposed to represent the value at which pits nucleate. Yet, this value is dependent on the scan rate and therefore does not give a true representation of initiation time for that or other potential values. The protection potential is the potential below which repassivation occurs during the experimental conditions. Therefore, a better understanding of the localized corrosion process is needed to define more clearly the important critical potentials and how they may be obtained experimentally. With this in mind, it should be possible to develop accelerated test methods that reflect real time values for the initiation time and propagation rates for the localized corrosion of alloys in a specific environment.

3. The Role of Repassivation

One key element in determining critical potentials is the presence or absence of a repassivation process and, quantitatively, the rate of such a process. As pointed out earlier, some of the definitions of a critical potential make E_p the potential below which repassivation takes place at a high rate. Some theoretical models reserve for it an important role in breakdown, i.e., initiation, processes. Propagation proceeds when repassivation can no longer choke off initiation. Test methods such as the scratch test, triboellipsometry, and others, therefore, evaluate the possibility for breakdown of passivity and propagation of localized corrosion of a given alloy in a relevant environment (discussed in item 4) at a given potential by measuring the rate of repassivation. If this rate is coupled to E_p, i.e., a high rate below E_p, a low rate above, its importance to testing for container life is evident.

4. The Role of the Local Environment

Since most pitting and crevice corrosion mechanisms involve a change in the local environment in a pit or crevice, it is reasonable to assume that this environment should be the most relevant test environment. Such an assumption should, however, be established. The first task in establishing the validity of the local environment as a test medium, actually an accelerated test medium, is to characterize the local environments that develop in pits and/or crevices for a given alloy in a given ambient environment. Once the composition of these environments is known and the validity of their use as test media is established, it would seem reasonable to assume that such environments would be the most relevant ones to use to measure critical potentials, pit or crevice propagation rates, or repassivation rates.

In summary, a better understanding of the mechanisms of localized corrosion can be used to suggest currently used tests or new tests to be developed that can provide useful estimates of metallic nuclear waste container life.

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Figure Captions

Figure 1 Noise current spectra of 6061 Al in borate buffer + 0.01 M NaCl. Potentiostatic conditions. Reference: SCE. Averages over 64 spectra. (1) -700 mV, (2) -650 Mc, (3) -650 mV after 10 min, (4) -600 mV. From Bertocci and Kruger [37].

Figure 2 The effect of potential on film growth in the absence and presence of chloride ion (10^{-2} M) in boric acid-sodium tetraborate buffer solution (pH = 8.4). Potentials were above E_a^2 (at -0.11 V). Film thickness was measured by ellipsometry. E_a^2 is defined as E_p in the text. From Ambrose and Kruger [18].

Figure 3 Stereographic triangle showing the effect of orientation of iron grains on tendency of pit. From Kruger [62].

Figure 4 Schematic potential-pH diagram. a, pH of the bulk solution; a_1-a_2, passive zone; a_2, pitting potential; b, pH of the locally acidified zone. From Gravele [3].

Figure 5 Factors affecting crevice corrosion. From Oldfield and Sutton [80].

Figure 6 Pit and crevice corrosion assemblies. (a) artificial pit, ref. 87; (b) and (c) natural exposure tests, ref. 49; (d) Stern-Makrides assembly, ref. 88; (e) artificial crevice assembly, ref. 87. Other designs can be found in references 85, 86, and 89.

Figure 7 "Cyclic" potentiodynamic anodic polarization of 304 stainless steel in a ground water type environment at 26C. Scan rate 0.5 mV/sec (1.8 V/hr). Saturated calomel electrode used as reference electrode.

Figure 8 "Cyclic" potentiodynamic anodic polarization curve of three alloys containing a synthetic crevice at 25C, aerated in 3.5 w/o NaCl solution. (a) Hastelloy C; (b) Incoloy 825; (c) Carpenter 20Cb3. From Wilde [49].

Figure 9 "Cyclic" potentiodynamic anodic polarization curves for Fe-30Cr-3Mo alloy in nitrogen saturated 1 M NaCl at 25°C. Sweep speed 0.17 mV/sec. From Wilde [49].

Figure 10 Effect of potential scan on the value of E_p for 304 stainless steel in 0.1 M NaCl. From Leckie [107].

Figure 11 "Cyclic" polarization behavior of 430 stainless steel in 1 M NaCl demonstrating the striking effect of pit propagation on E_p. From Wilde [49].

Figure 12 A schematic representation of (a) a "cyclic" potentiodynamic anodic polarization curve; (b) a galvanostatic curve; (c) a potentiostatic curve with a passivated surface; (d) a potentiostatic curve with an activated surface. From S. Smialowska and M. Czachor [50].

Figure 13 A corrosion behavior diagram plot of 304 stainless steel, forward scan (– - –), reverse scan (solid line), third scan after a time delay (dashed line). From EG&G Princeton Applied Research [97].

Figure 14 Potential versus time plot of scratch test illustrating the critical potential, E_s, as it relates to the repassivation time and the induction time. From S. Smialowska and M. Czachor [50].

Figure 15 Scratch test current-time curves for specimen held potentiostatically above E_p (pitting or breakdown) and below E_p (repassivation). From J. Kruger [98].

Figure 16 Electrochemical cell used in tribo-ellipsometry studies of repassivation kinetics. From J. R. Ambrose and J. Kruger [99].

Figure 17 Schematic of potential-time and current-time cycles used to determine the pit propagation rate curves. From Syrett [101].

Figure 18 Effect of cold work on PPR curves for 3Mo TRIP. From Syrett [10].

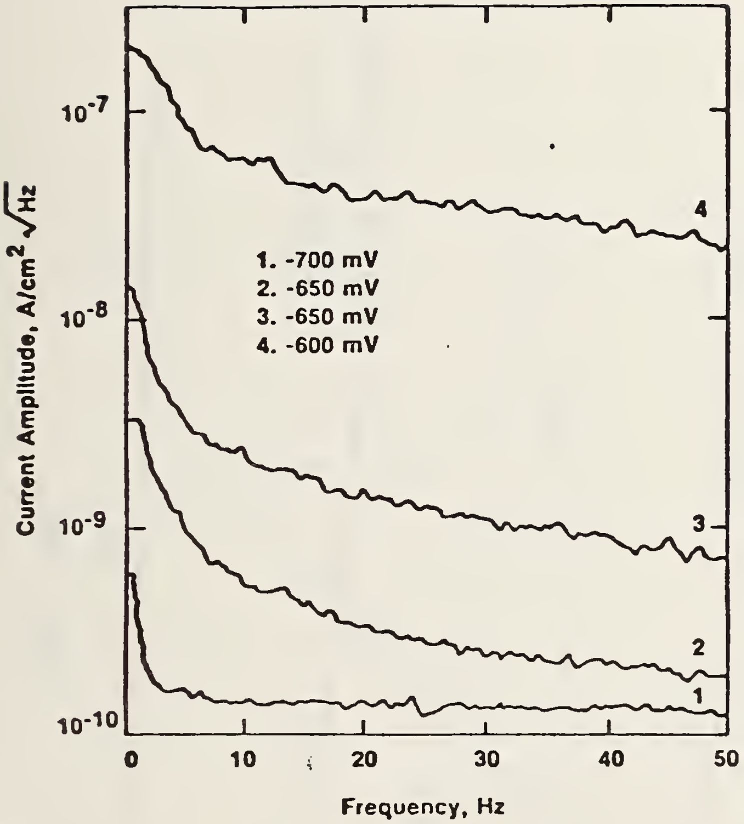

Current Amplitude, A/cm^2 $\sqrt{Hz}$
10^{-7}
10^{-8}
10^{-9}
10^{-10}
0
10
20
30
40
50
Frequency, Hz
1. -700 mV
2. -650 mV
3. -650 mV
4. -600 mV
4
3
2
1

Fig. 1

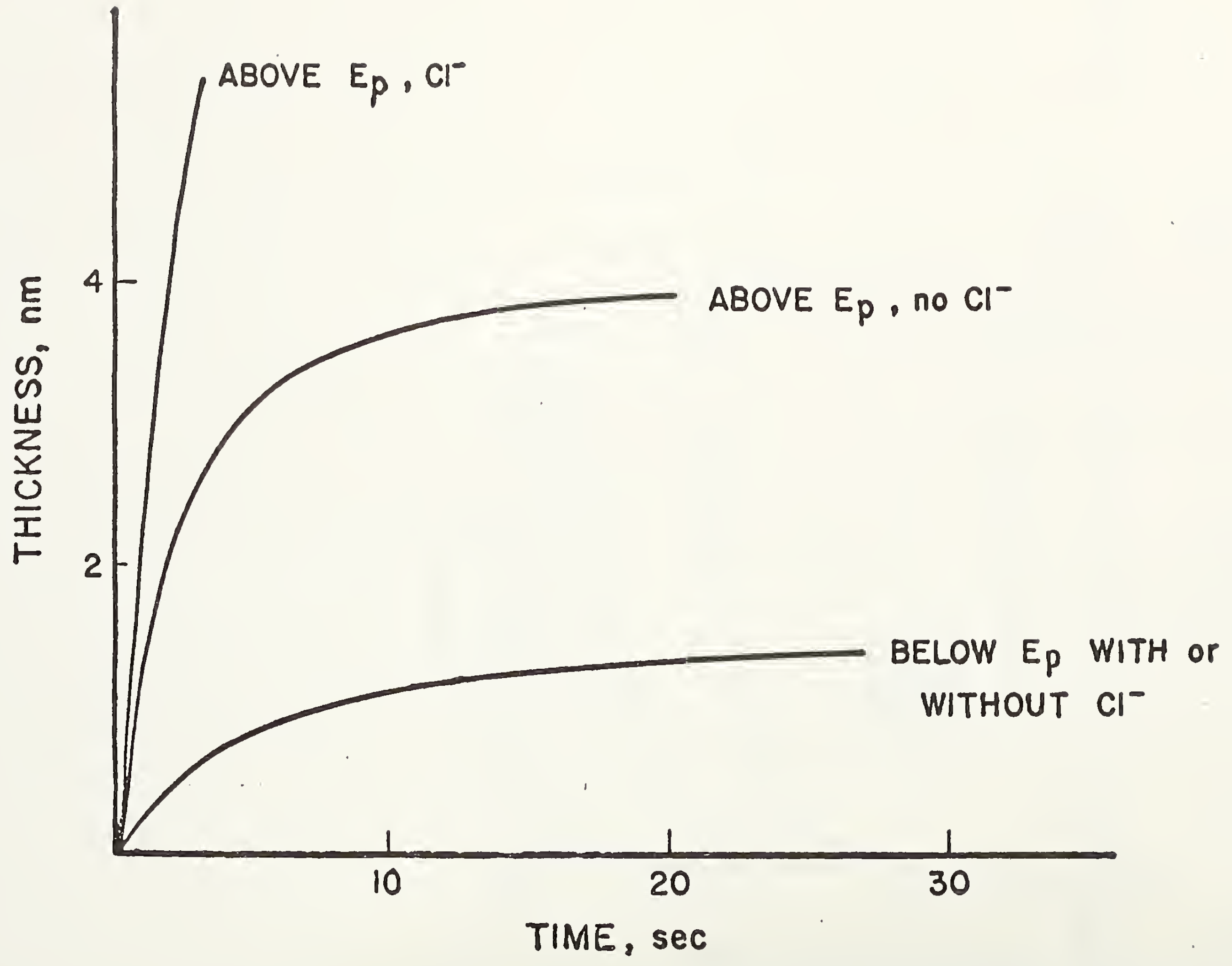

ABOVE E_p , Cl^-
ABOVE E_p , no Cl^-
BELOW E_p WITH or WITHOUT Cl^-
THICKNESS, nm
4
2
10
20
30
TIME, sec

Fig. 2

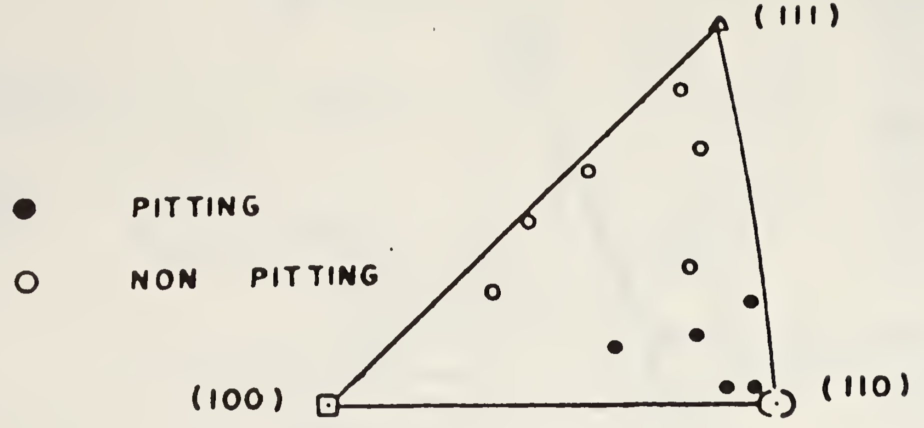


Fig. 3

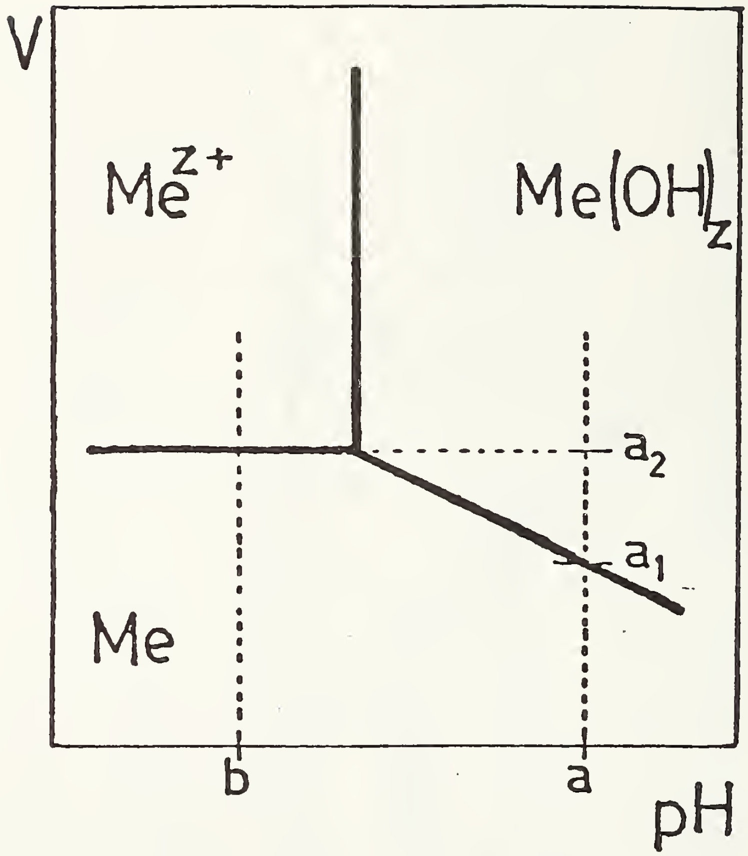


Fig. 4

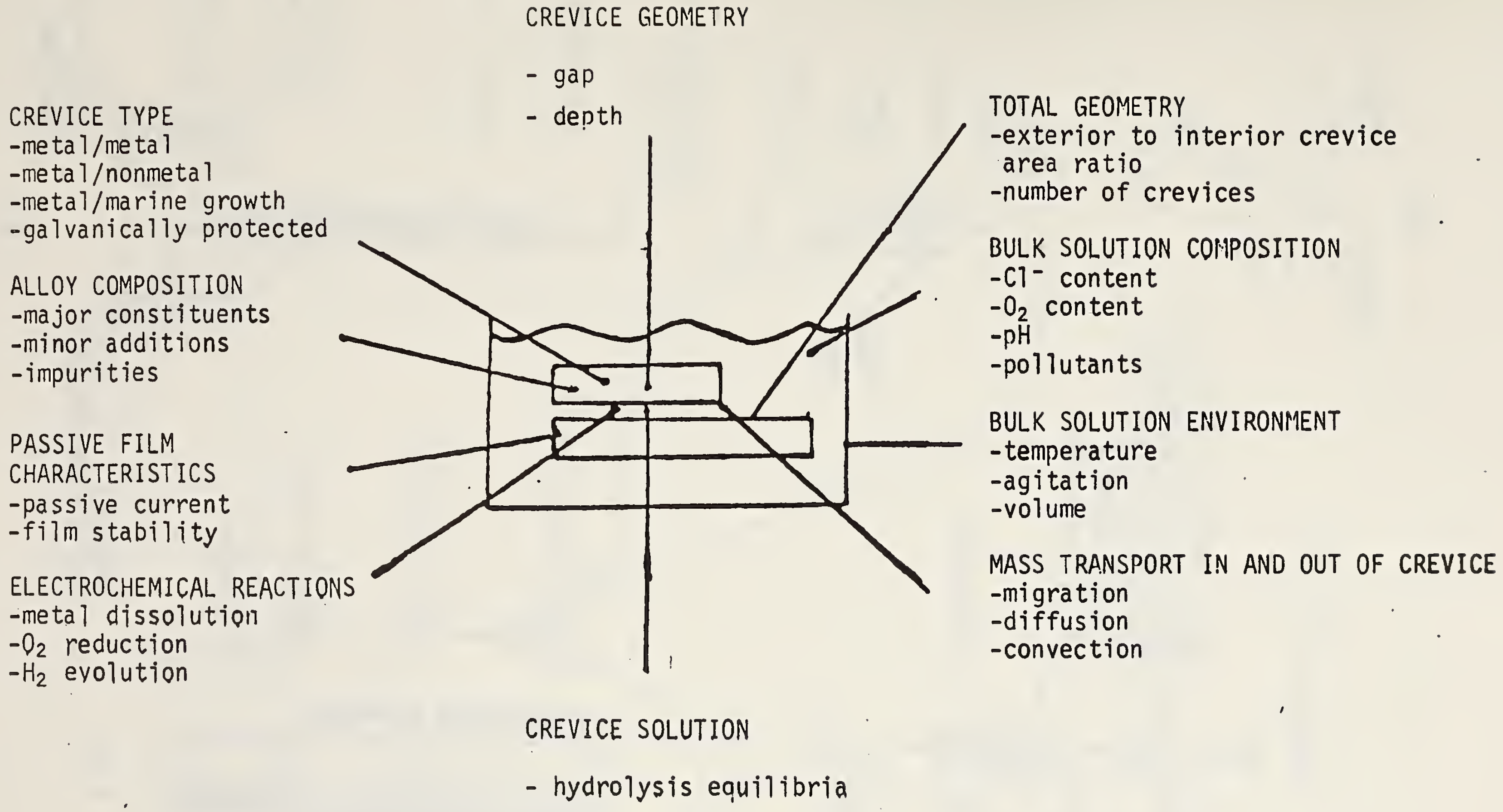

CREVICE GEOMETRY
- gap
- depth
CREVICE TYPE
-metal/metal
-metal/nonmetal
-metal/marine growth
-galvanically protected
ALLOY COMPOSITION
-major constituents
-minor additions
-impurities
PASSIVE FILM CHARACTERISTICS
-passive current
-film stability
ELECTROCHEMICAL REACTIONS
-metal dissolution
-O_2 reduction
-H_2 evolution
TOTAL GEOMETRY
-exterior to interior crevice area ratio
-number of crevices
BULK SOLUTION COMPOSITION
-Cl^- content
-O_2 content
-pH
-pollutants
BULK SOLUTION ENVIRONMENT
-temperature
-agitation
-volume
MASS TRANSPORT IN AND OUT OF CREVICE
-migration
-diffusion
-convection
CREVICE SOLUTION
- hydrolysis equilibria

Fig. 5

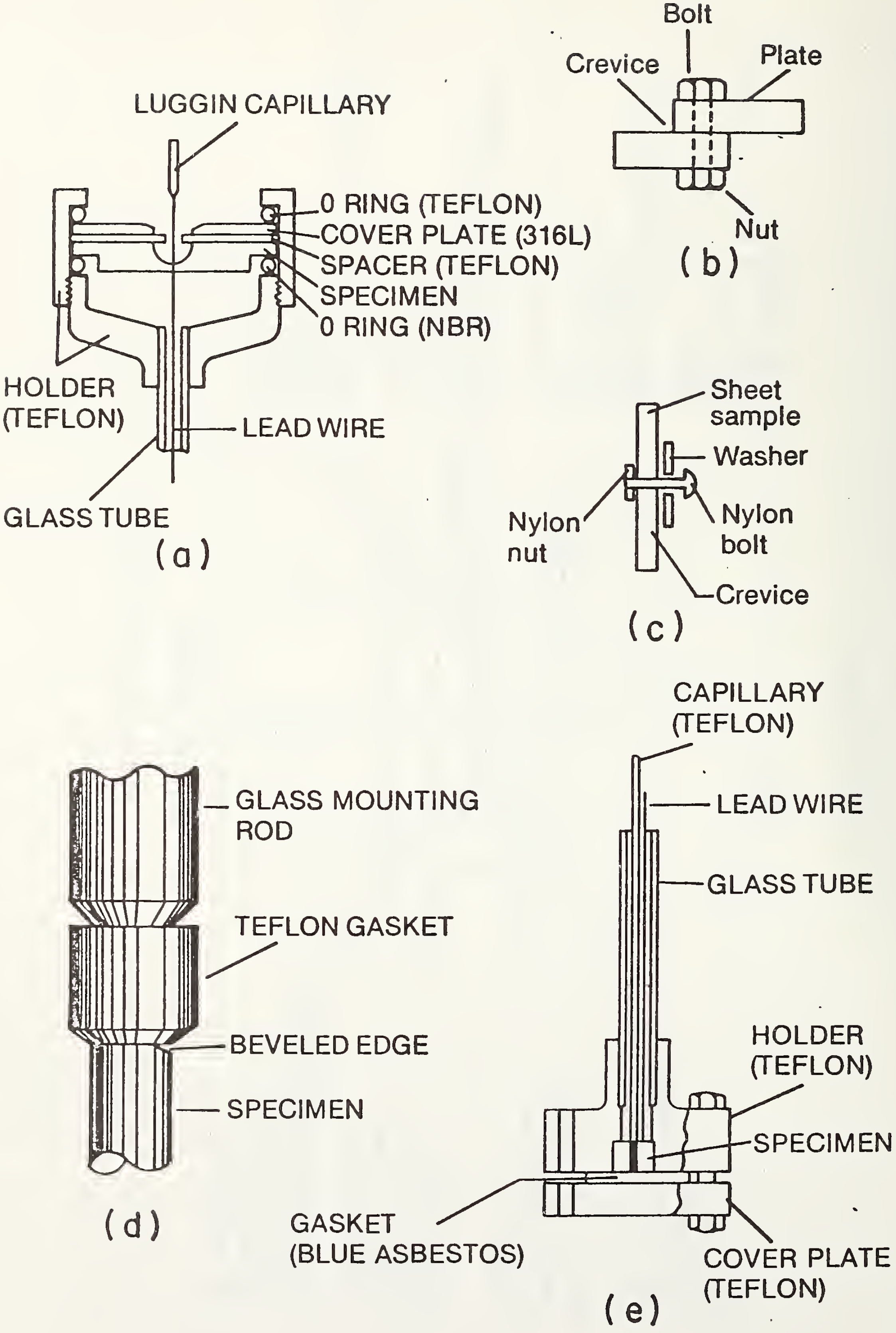

LUGGIN CAPILLARY
0 RING (TEFLON)
COVER PLATE (316L)
SPACER (TEFLON)
SPECIMEN
0 RING (NBR)
HOLDER (TEFLON)
LEAD WIRE
GLASS TUBE
(a)
Bolt
Crevice
Plate
Nut
(b)
Sheet sample
Washer
Nylon nut
Nylon bolt
Crevice
(c)
GLASS MOUNTING ROD
TEFLON GASKET
BEVELED EDGE
SPECIMEN
(d)
CAPILLARY (TEFLON)
LEAD WIRE
GLASS TUBE
HOLDER (TEFLON)
SPECIMEN
GASKET (BLUE ASBESTOS)
COVER PLATE (TEFLON)
(e)

Fig. 6

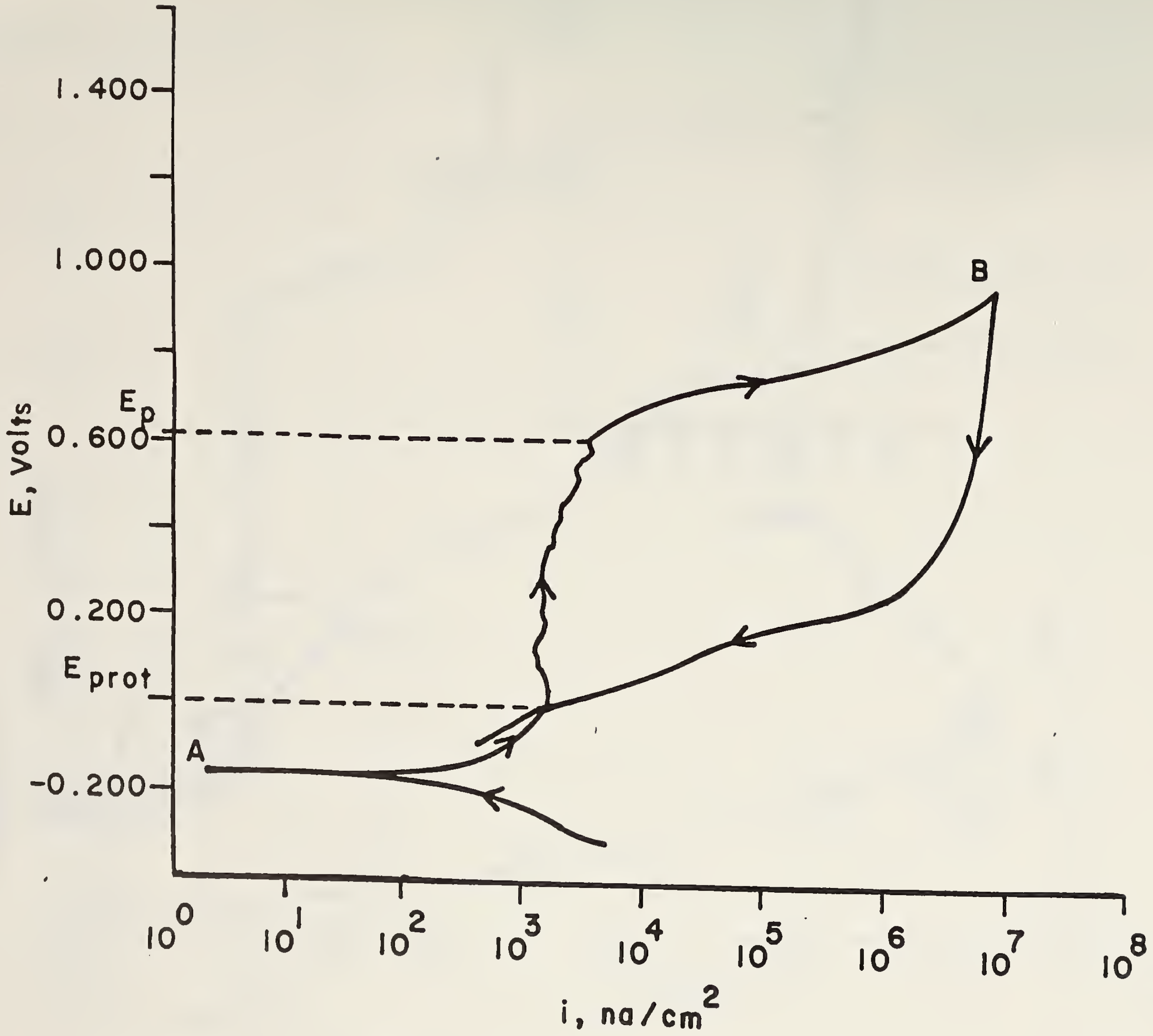

1.400
1.000
E, Volts
E_p
0.600
0.200
E_{prot}
-0.200
A
B
10^0
10^1
10^2
10^3
10^4
10^5
10^6
10^7
10^8
i, na/cm^2

Fig. 7

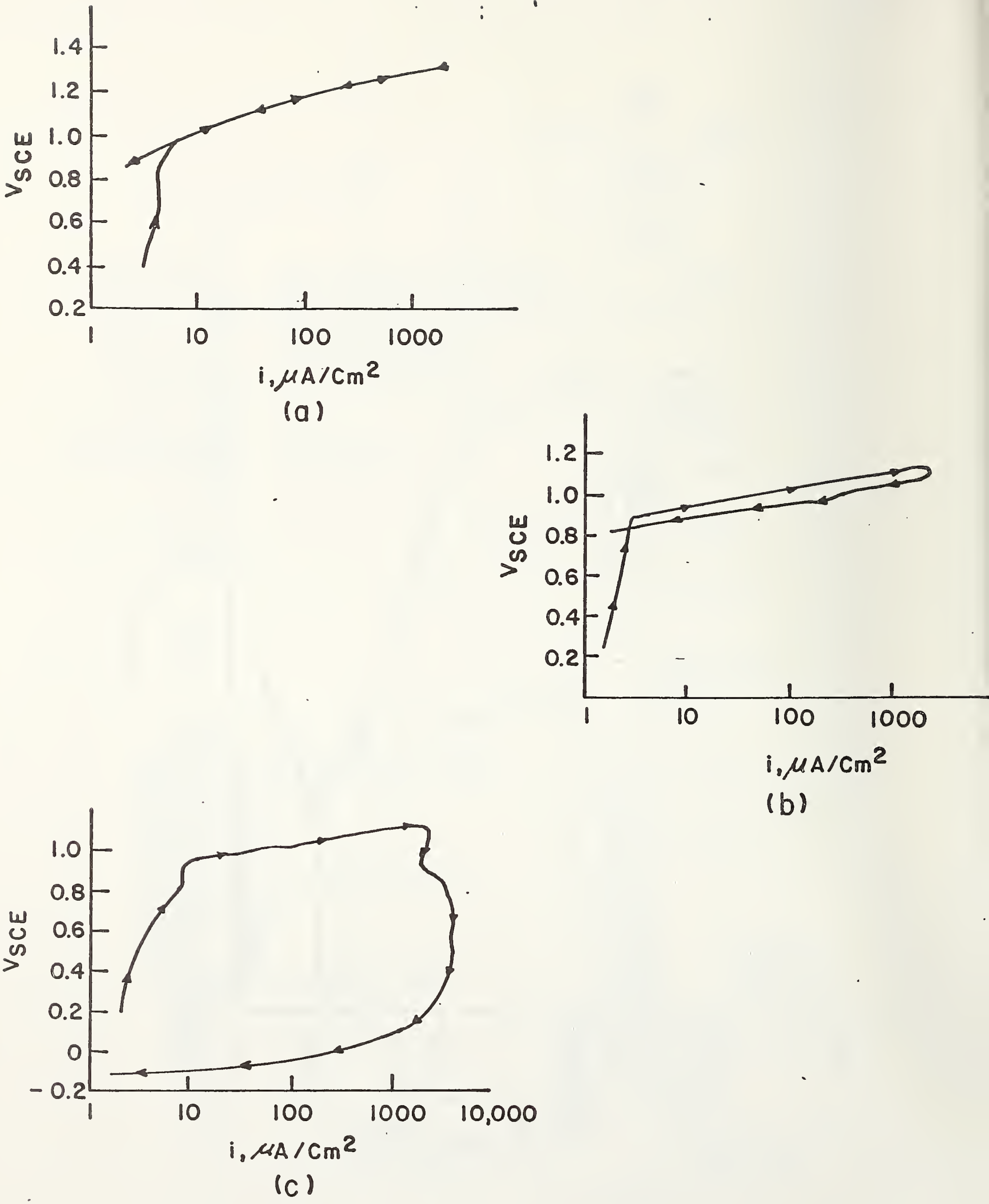

1.4
1.2
1.0
0.8
0.6
0.4
0.2
VSCE
1
10
100
1000
i, μA/Cm2
(a)
1.2
1.0
0.8
0.6
0.4
0.2
VSCE
1
10
100
1000
i, μA/Cm2
(b)
1.0
0.8
0.6
0.4
0.2
0
− 0.2
VSCE
1
10
100
1000
10,000
i, μA/Cm2
(c)

Fig. 8

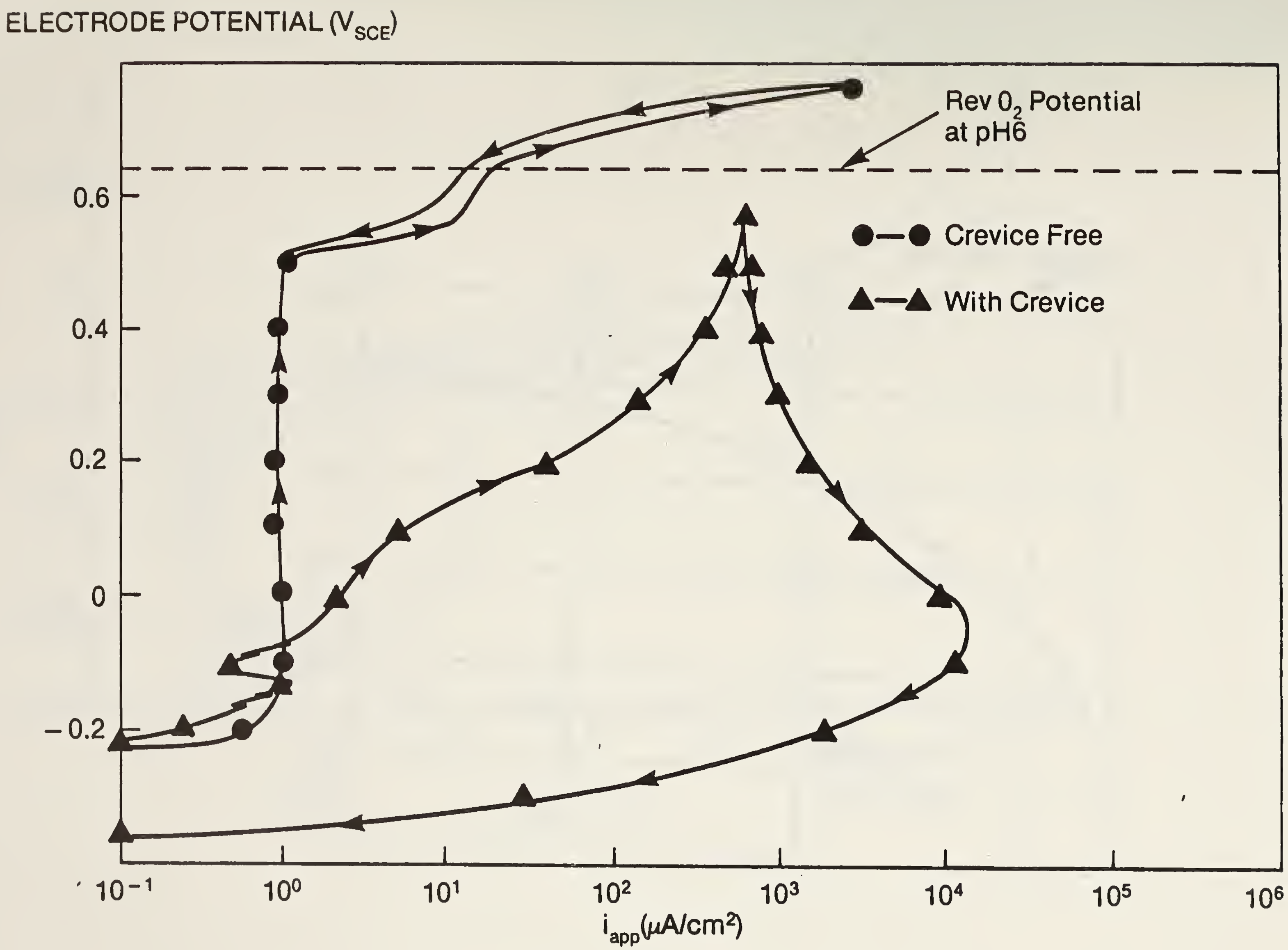

ELECTRODE POTENTIAL (V_{SCE})
Rev 0_2 Potential at pH6
Crevice Free
With Crevice
0.6
0.4
0.2
0
−0.2
10^{-1}
10^0
10^1
10^2
10^3
10^4
10^5
10^6
i_{app}(μA/cm^2)

Fig. 9

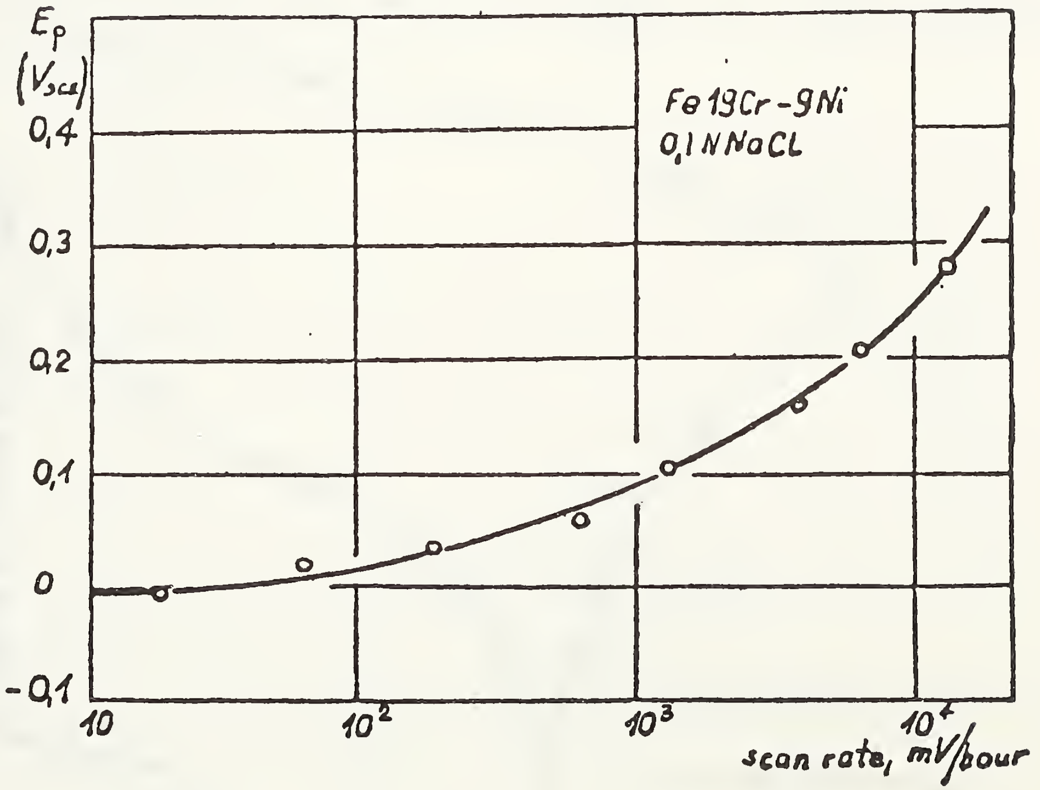

E_p
(V_{sce})
0,4
0,3
0,2
0,1
0
-0,1
10
10^2
10^3
10^4
scan rate, mV/hour
Fe19Cr-9Ni
0,1 N NaCL

Fig. 10

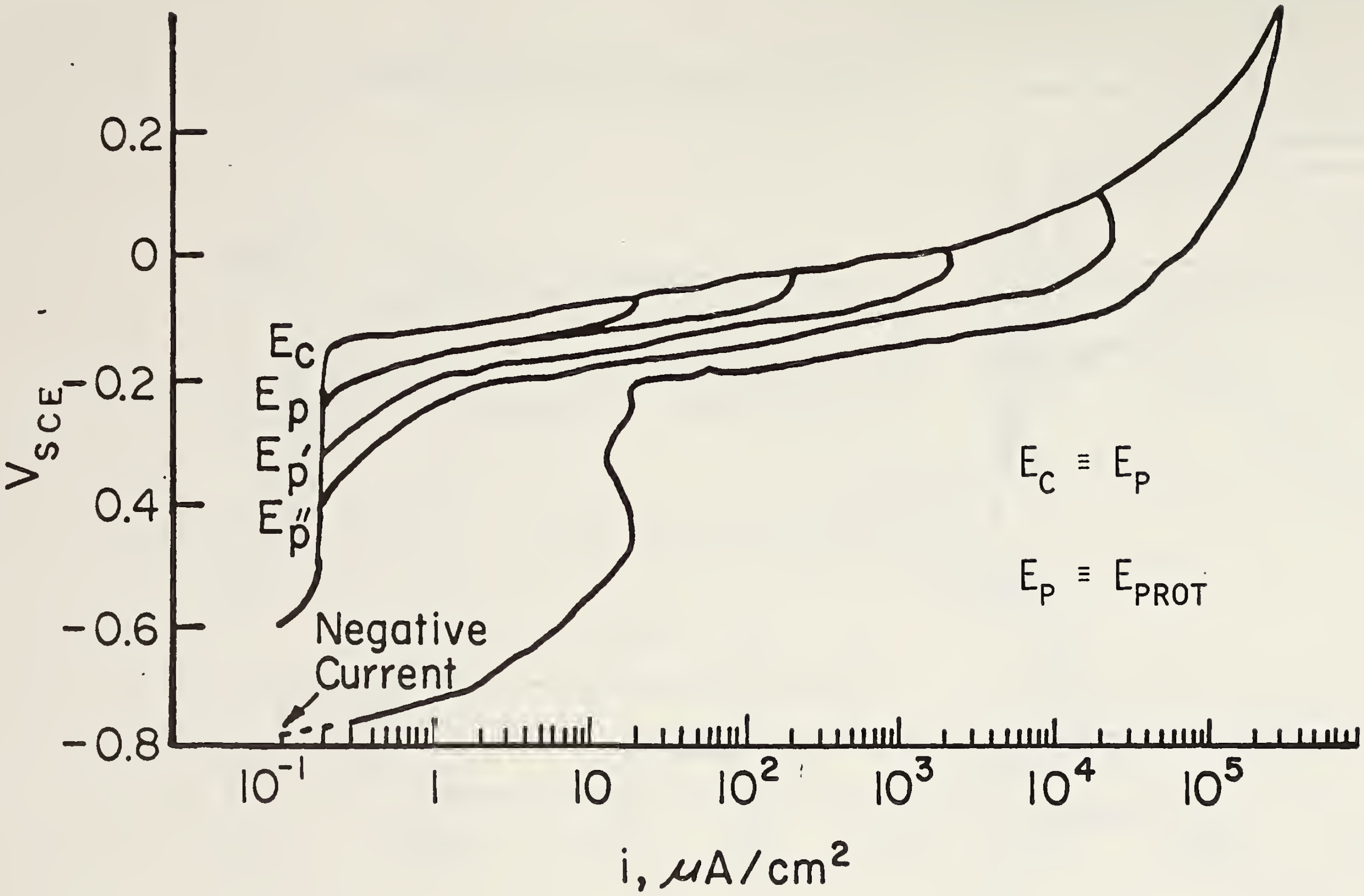

V_{SCE}
0.2
0
−0.2
0.4
−0.6
−0.8
E_c
E_p
E_p'
E_p''
Negative Current
$E_C \equiv E_P$
$E_P \equiv E_{PROT}$
10^{-1}
1
10
10^2
10^3
10^4
10^5
i, μA/cm²

Fig. 11

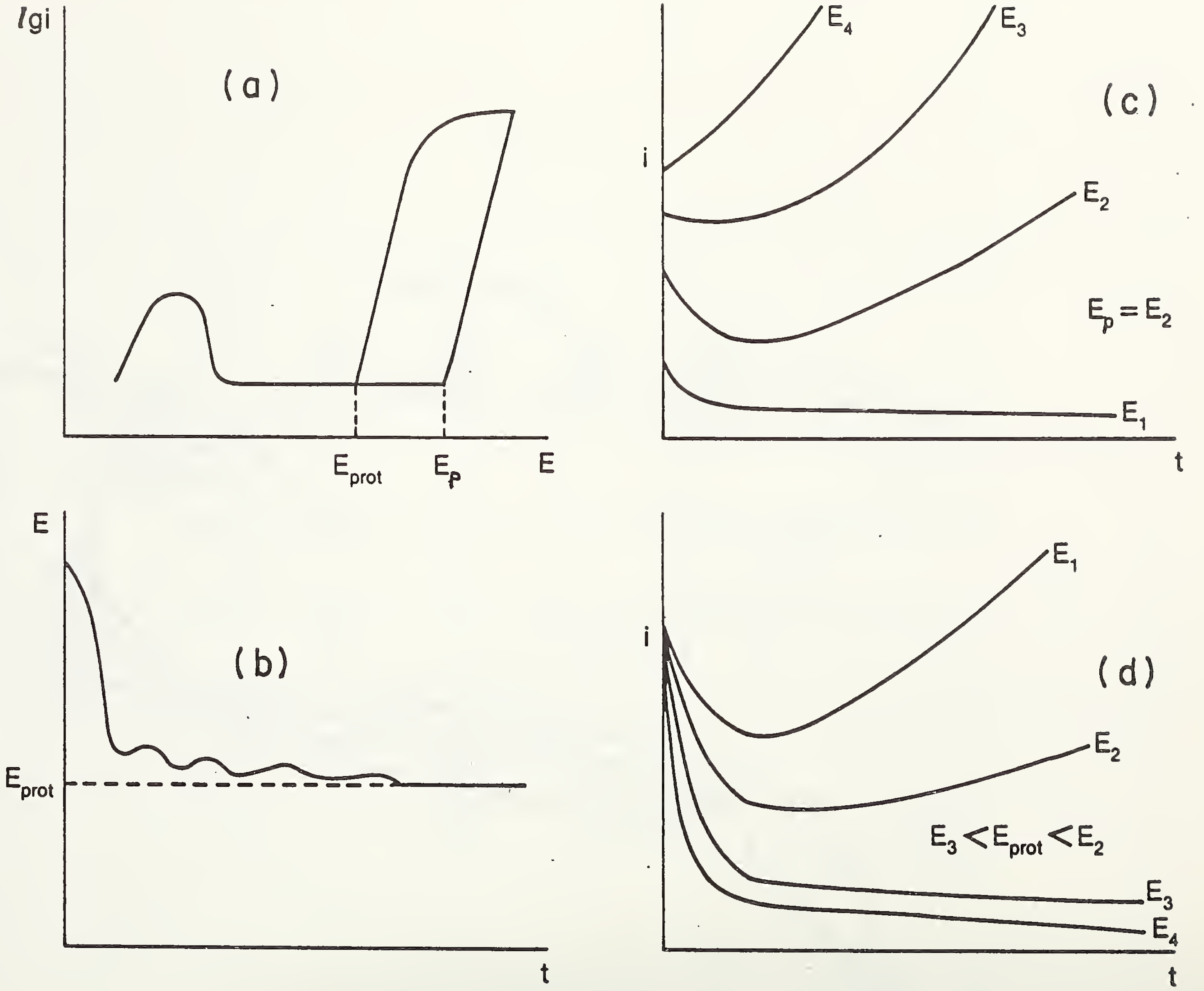

lgi
(a)
E_{prot}
E_p
E
E
(b)
E_{prot}
t
i
E_4
E_3
(c)
E_2
$E_p = E_2$
E_1
t
i
E_1
(d)
E_2
$E_3 < E_{prot} < E_2$
E_3
E_4
t

Fig. 12

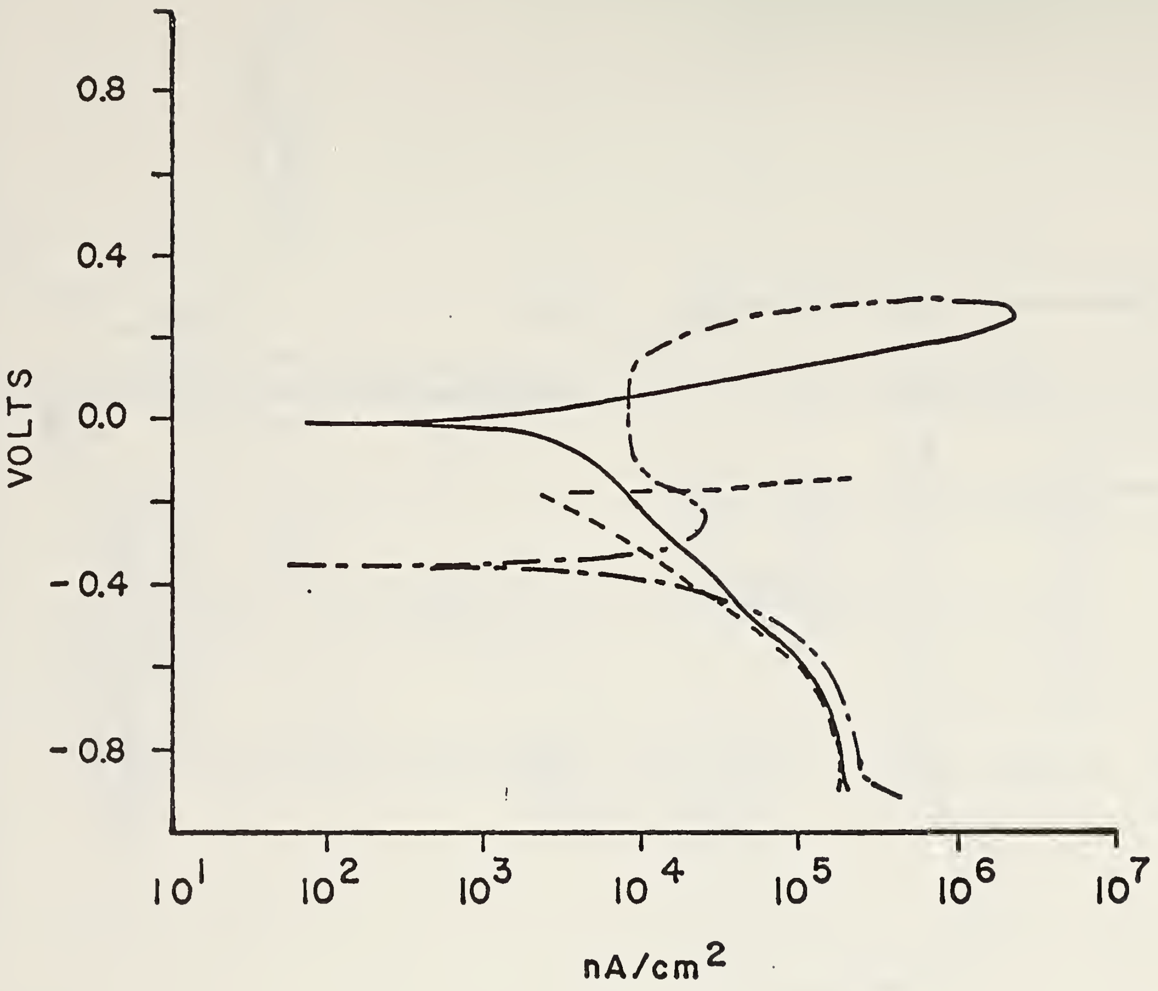


Fig. 13

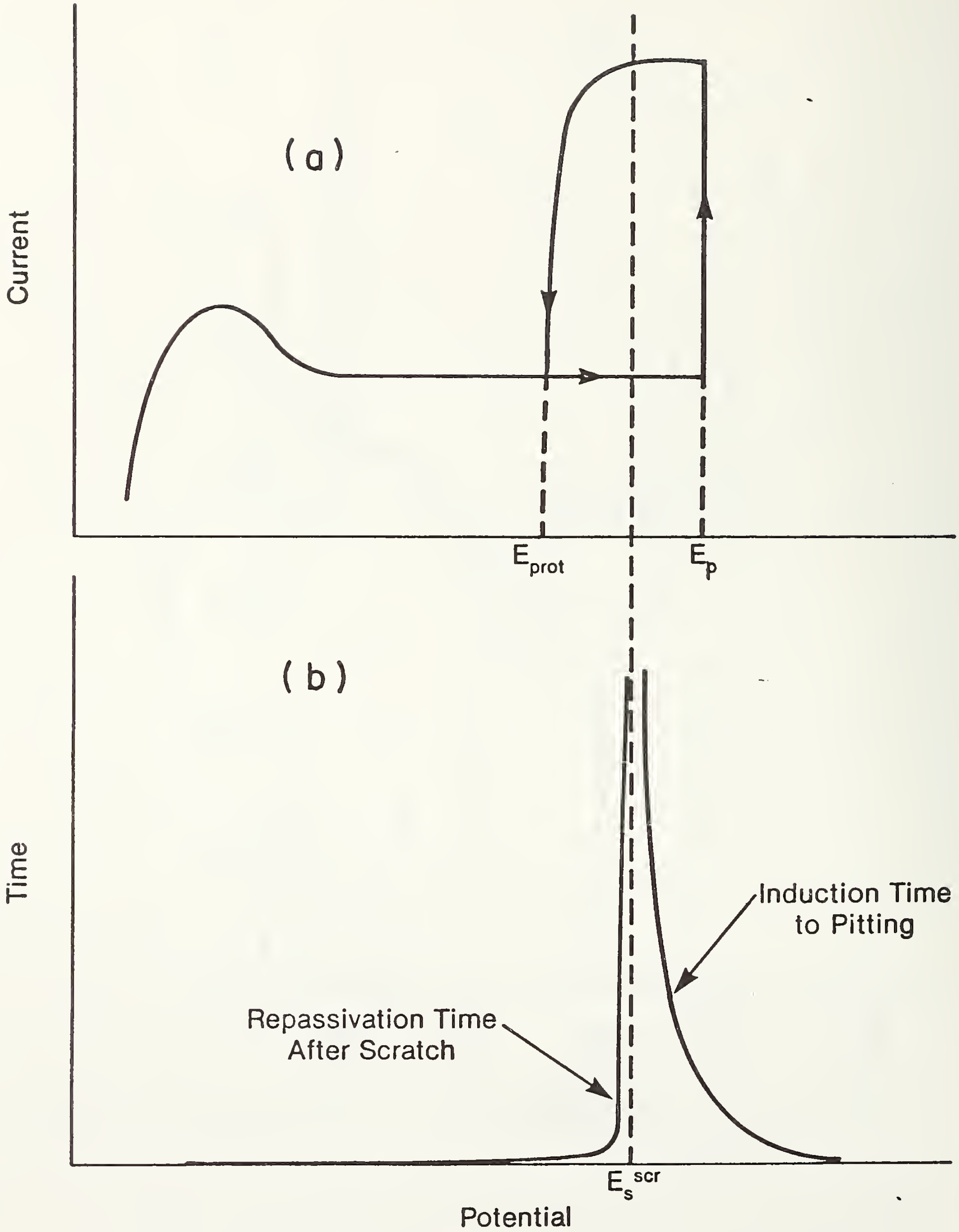

(a)
Current
E_{prot}
E_p
(b)
Time
Induction Time to Pitting
Repassivation Time After Scratch
E_s^{scr}
Potential

Fig. 14

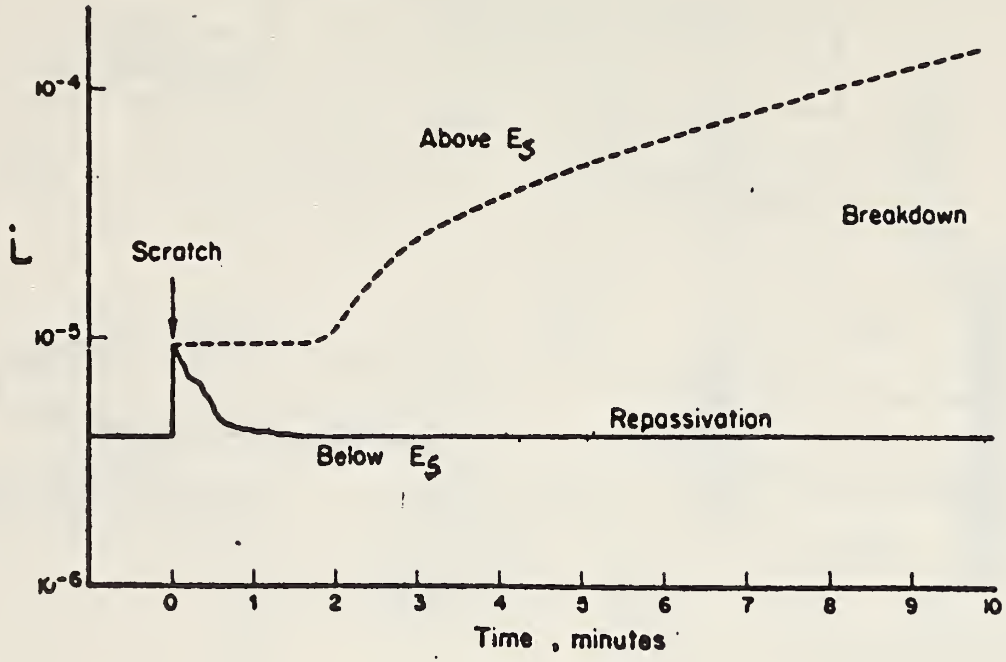

10^{-4}
10^{-5}
10^{-6}
i
Scratch
Above E_S
Breakdown
Repassivation
Below E_S
0
1
2
3
4
5
6
7
8
9
10
Time , minutes

Fig. 15

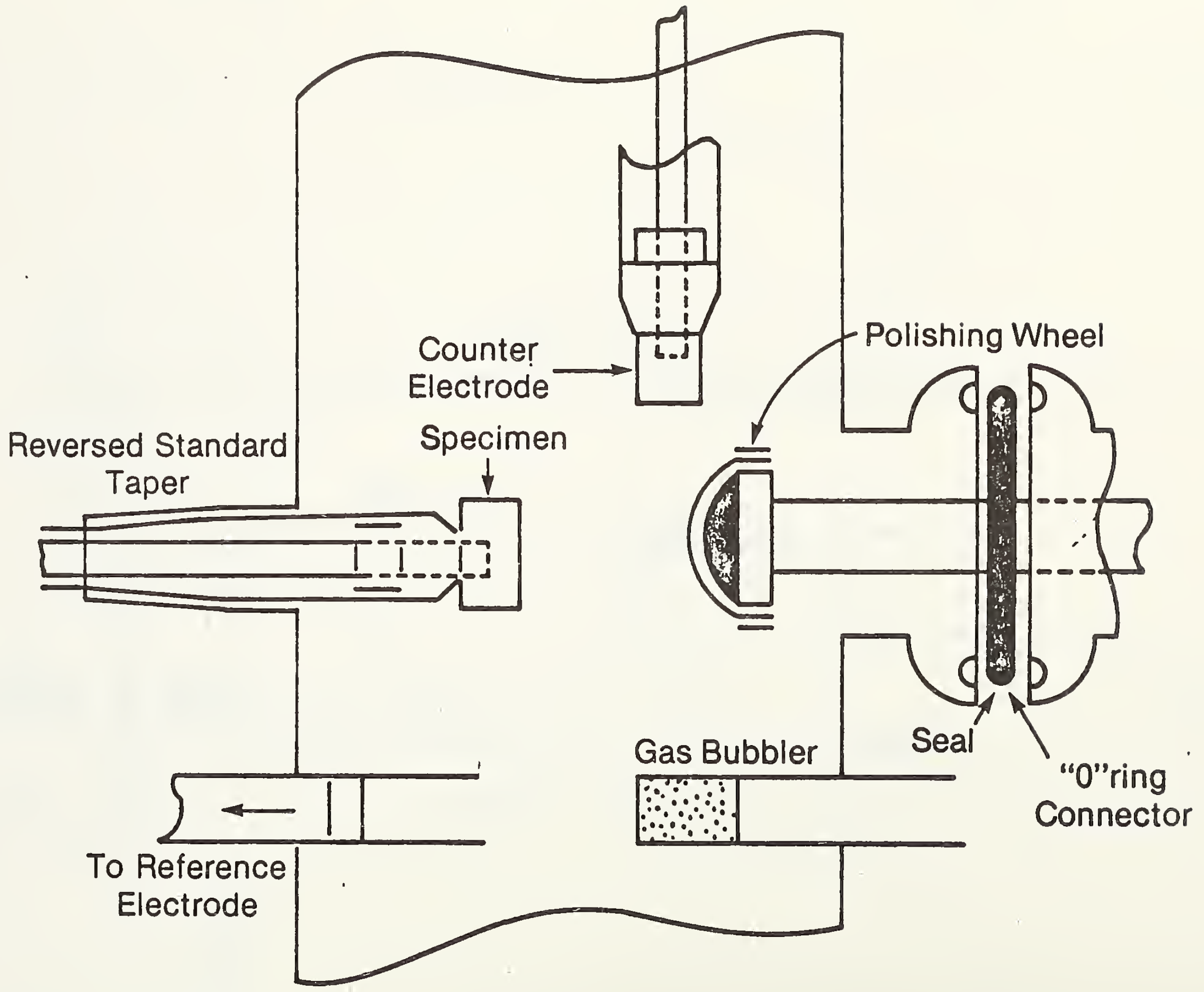

Polishing Wheel
Counter Electrode
Reversed Standard Taper
Specimen
Gas Bubbler
Seal
"0"ring Connector
To Reference Electrode

Fig. 16

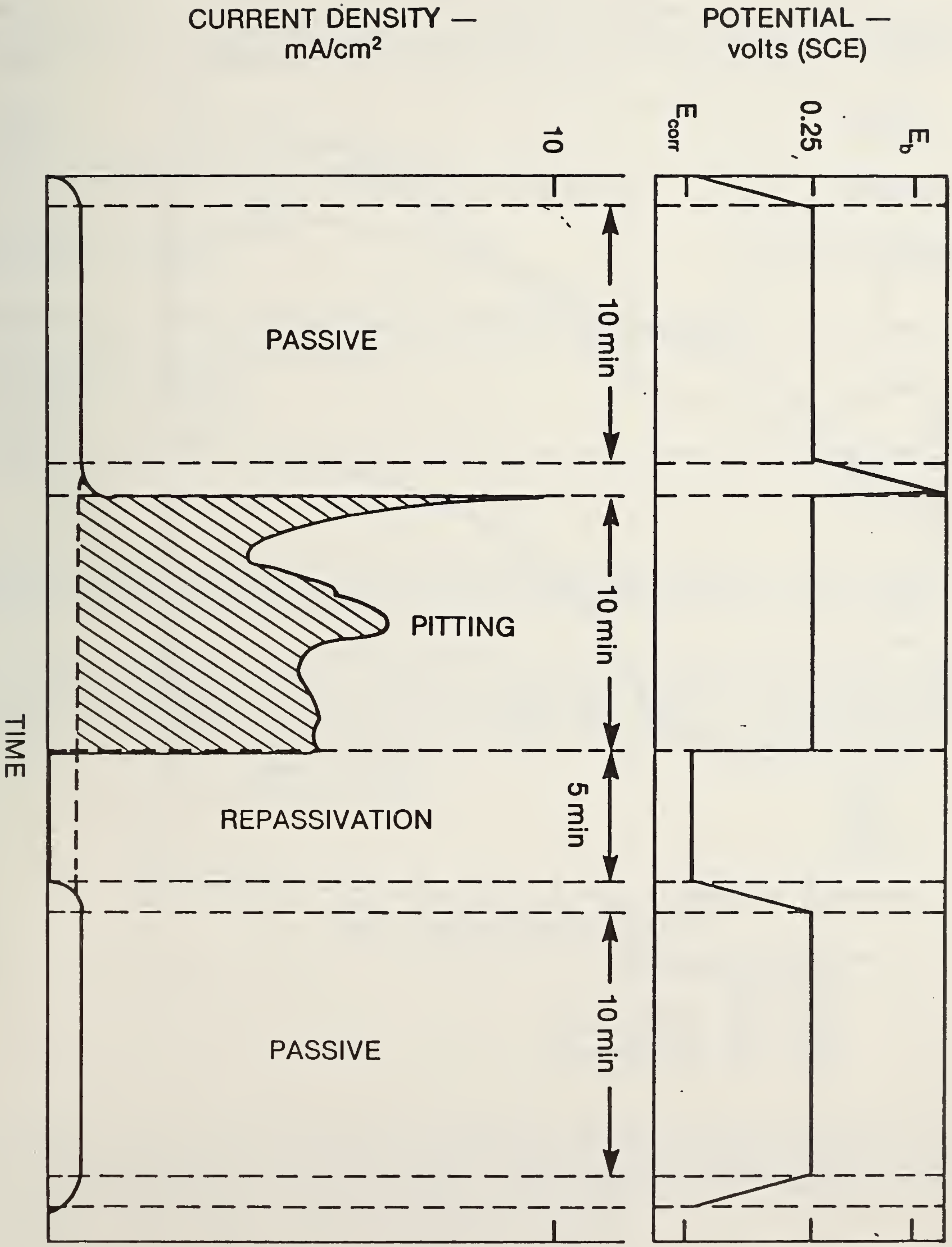
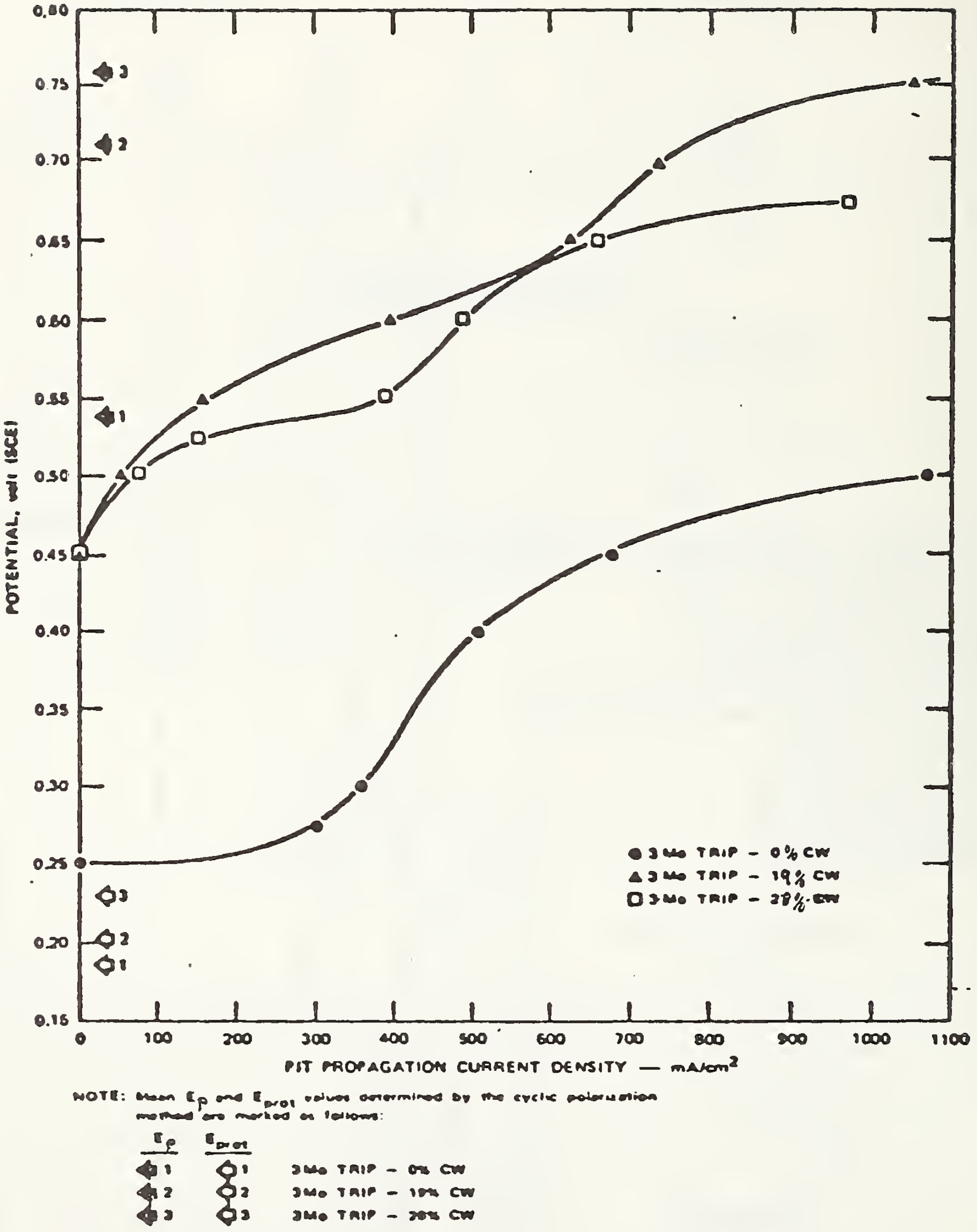

CURRENT DENSITY — mA/cm²
POTENTIAL — volts (SCE)
10
E_{corr}
0.25
E_b
PASSIVE
10 min
PITTING
10 min
REPASSIVATION
5 min
PASSIVE
10 min
TIME

Fig. 17



NOTE: Mean E_p and E_{prot} values determined by the cyclic polarization method are marked as follows:

E_p	E_{prot}	
1	1	3Mo TRIP – 0% CW
2	2	3Mo TRIP – 19% CW
3	3	3Mo TRIP – 28% CW

Fig. 18

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5. AUTHOR(S)

Jerome Kruger and V. Kay Hardman

6. PERFORMING ORGANIZATION *(If joint or other than NBS, see instructions)*

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11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

Localized corrosion is the most damaging and prevalent type of corrosion that can affect metallic containers used in nuclear waste repository sites. Mechanisms of pittin and crevice corrosion and the techniques used in elucidating these mechanisms are discussed in this review which includes a literature survey.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

Accelerated testing; crevice corrosion; electrochemical techniques, localized corrosion, localized corrosion mechanism; pitting

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