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The Resistance of Titanium to Pitting, Microbially Induced Corrosion and Corrosion in Unsaturated Conditions

La résistance du titane à la corrosion par piqûres, à la corrosion d'origine microbienne et à la corrosion dans des conditions non saturées

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ABSTRACT

Titanium and its alloys (Grades-2, -12, -16) are candidate materials for Canadian nuclear waste containers on the basis of their apparent immunity to many localized corrosion processes. This simplifies markedly the effort needed to justify the use of these materials and to develop models to predict the lifetimes of containers. Here we review the pitting, microbially influenced corrosion (MIC), and corrosion under unsaturated conditions, of titanium. For all these processes, the properties of the passive oxide film are paramount in determining the metal's resistance to corrosion. A review of these oxide properties is included and the conditions to which the metal must be exposed if localized corrosion is to occur are defined. Since these conditions cannot be achieved under Canadian waste vault conditions, it can be concluded that pitting and MIC will not occur and that corrosion under unsaturated conditions is extremely unlikely.

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RÉSUMÉ

Le titane et ses alliages (nuances 2, 12 et 16) sont des métaux retenus pour la fabrication des conteneurs de déchets nucléaires canadiens en fonction de leur immunité apparente à un grand nombre de phénomènes de corrosion localisée. Cela simplifie énormément les travaux nécessaires pour justifier l'utilisation de ces métaux et pour élaborer les modèles destinés à prévoir la durée de vie des conteneurs. Nous examinons ici la corrosion par piqûres, la corrosion d'origine microbienne et la corrosion dans des conditions non saturées du titane. Dans le cas de tous ces phénomènes, les propriétés de la pellicule d'oxyde passif sont primordiales quand il s'agit de déterminer la résistance à la corrosion du métal. On a fait un examen de ces propriétés et on a défini les conditions auxquelles le métal doit être exposé pour que la corrosion localisée se produise. Puisque ces conditions ne peuvent être réunies dans les conditions de l'enceinte canadienne de stockage des déchets, on peut en conclure que la corrosion par piqûres et la corrosion d'origine microbienne ne se produiront pas et que la corrosion dans des conditions non saturées est extrêmement improbable.

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1. INTRODUCTION

Two classes of material have been considered when choosing possible container materials for nuclear fuel waste disposal: corrosion-allowance materials possessing slow, but predictable, general corrosion rates; and corrosion-resistant materials possessing very low passive corrosion rates, but potentially susceptible to localized corrosion processes (Johnson et al. 1994a). Our choice of titanium as the primary corrosion-resistant candidate material is based on a combination of industrial operating experience (Ikeda and Shoesmith 1996), the known properties of the material and its ready availability (Grover 1990).

A titanium (Ti) waste container should be easy to fabricate, weld and examine non-destructively. The alloys of Ti used when corrosion resistance is of paramount importance are alpha or near-alpha phase materials containing very little beta phase and only small quantities of impurities and/or alloying additions. This compositional and microstructural simplicity effectively eliminates the possibility of significant metallurgical phase transitions over the long disposal period required. It also avoids the formation of complex unstable structures due to mechanical and thermal treatments such as cold working or welding. Table I lists the grades of titanium eligible within these restrictions. Of these grades, ASTM Grades-2 (Ti-2), -12 (Ti-12) and -16 (Ti-16) have been investigated within the scope of the Canadian Nuclear Fuel Waste Management Program (CNFWMP).

The major attraction of Ti from the corrosion viewpoint is the durability of the passive oxide film over a wide range of conditions, including hot saline solutions (Schutz and Thomas 1987). This durability makes Ti alloys the materials of choice for many seawater

TABLE I

ASTM NOMINAL MAXIMUM COMPOSITIONS (WEIGHT %)

FOR VARIOUS GRADES OF TITANIUM

Grade	N	C	H	Fe	0	Mo	Ni	Pd
1	0.03	0.10	0.015	0.20	0.18			
2	0.03	0.10	0.015	0.30	0.25			
3	0.05	0.10	0.015	0.30	0.35			
4	0.03	0.10	0.015	0.50	0.40			
7	0.03	0.10	0.015	0.30	0.25			0.2
11	0.03	0.10	0.015	0.20	0.18			0.2
12	0.03	0.10	0.015	0.30	0.25	0.3	0.8	
16	0.03	0.10	0.01	0.30	0.25			0.04-0.08

applications and attractive candidates for use in a Canadian nuclear waste disposal vault where saline conditions are anticipated and where Ti will be passive for the range of redox conditions anticipated, Figure 1. Those alloys of titanium commonly used in industrial applications in which corrosion resistance is a primary requirement are expected to be potentially susceptible to only a small number of corrosion processes.

Under waste vault conditions only crevice corrosion and hydrogen-induced cracking (HIC) are expected to be capable of producing any significant corrosion damage (Johnson et al. 1994b). Extensive discussions of these processes and approaches to modelling and preventing them under waste vault conditions have been published elsewhere (Shoesmith et al. 1995a,b). Providing these processes can be limited or avoided the attainment of long container lifetimes ($>10^5$ a) is feasible since only very slow passive corrosion will be feasible (Shoesmith et al. 1995c).

To fully justify such long lifetimes it is necessary to demonstrate that alternative localized corrosion modes can be confidently dismissed. Previously, brief summaries in support of the resistance of Ti to pitting and microbiologically influenced corrosion (MIC) were given (Shoesmith et al. 1995a). While crevice corrosion was assumed to initiate on emplacement of the container in the vault and either to propagate indefinitely to failure or lead eventually to failure by HIC, this was sufficient. To claim that localized corrosion can be avoided indefinitely (Shoesmith et al. 1995c), a more detailed justification is required.

Here, we review the properties of the oxide film protecting Ti from localized corrosion processes and then discuss how these properties are important in preventing pitting, MIC and localized corrosion in unsaturated environments under waste disposal conditions.

2. DISPOSAL ENVIRONMENT

During the lifetime of the containers, the vault environment will evolve from an initial period of warm, oxidizing conditions to an indefinite cool and anoxic period, as illustrated in Figure 2. The range of container temperature cooling profiles is calculated for the borehole emplacement design (Johnson et al. 1994b). For the in-room vault design, temperatures would be lower (Johnson et al. 1996). The major source of oxidant in a conceptual Canadian disposal vault is the O_2 trapped in the pores of the compacted buffer and backfill materials surrounding the container. While only schematic in form, the O_2 concentration profile (Figure 2) illustrates the expected rate of consumption of oxygen in the vault by reaction with minerals, oxidizable organic material and corrosion of the container. For the in-room emplacement configuration, Kolar and King (1996) have calculated that this oxygen will be consumed in ~670 a. A similar rate of consumption would be expected for the borehole emplacement design.

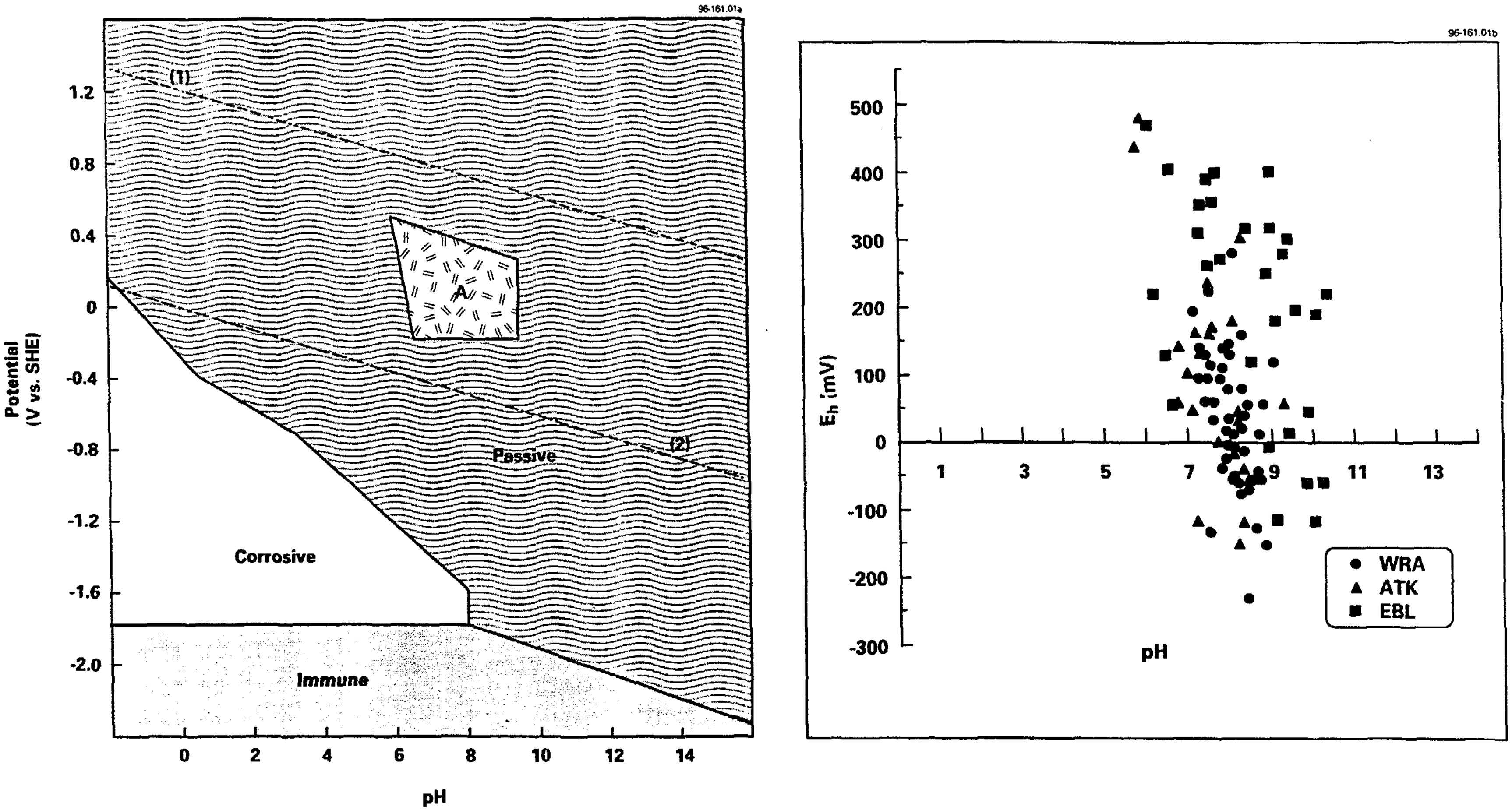

FIGURE 1: A. Partial Potential/pH Diagram for the Titanium/Water System. The two dashed lines represent the stability lines for water; (1) H_2O/O_2 equilibrium, (2) H_2/H_2O equilibrium. The area (A) shows the range of sampled E_h and pH values for actual Canadian groundwater sites.

B. Values of E_h - pH Sampled in Actual Groundwaters from Sites on the Canadian Shield. WRA - Whiteshell Research Area; ATK - Atikokan; EBL - East Bull Lake.

While the profile for the chloride concentration at the container surface is also schematic, it indicates that this concentration could increase as groundwaters entering the vault interact with the rock-mass pore fluids. In the recently published postclosure assessment, a reference chloride concentration of 6000 $\mu g \cdot g^{-1}$ was assumed (Johnson et al. 1994b) but more recent groundwater analyses suggest concentrations as high as 125 000 $\mu g \cdot g^{-1}$ could be established after ~10^6 a (M. Kolar, unpublished data, 1995).

One additional feature of vault conditions could affect the corrosion performance of the container. Initially, high temperatures could lead to the redistribution of water in the compacted buffer and to the establishment of unsaturated conditions close to the container, Figure 2. Eventually, as containers cool, the buffer in contact with the container will resaturate with water. To date, it has proven difficult to predict this period of slow resaturation, and present estimates range from <100 a to >1000 a (Andrews et al. 1986, Pusch et al. 1985). In Figure 2 the shaded area depicts an arbitrary period of unsaturation of 500 a.

3. PASSIVE FILM PROPERTIES

It is generally acknowledged that the protectiveness of the oxide film is the key feature which confers on Ti its ability to resist localized corrosion processes. Under waste

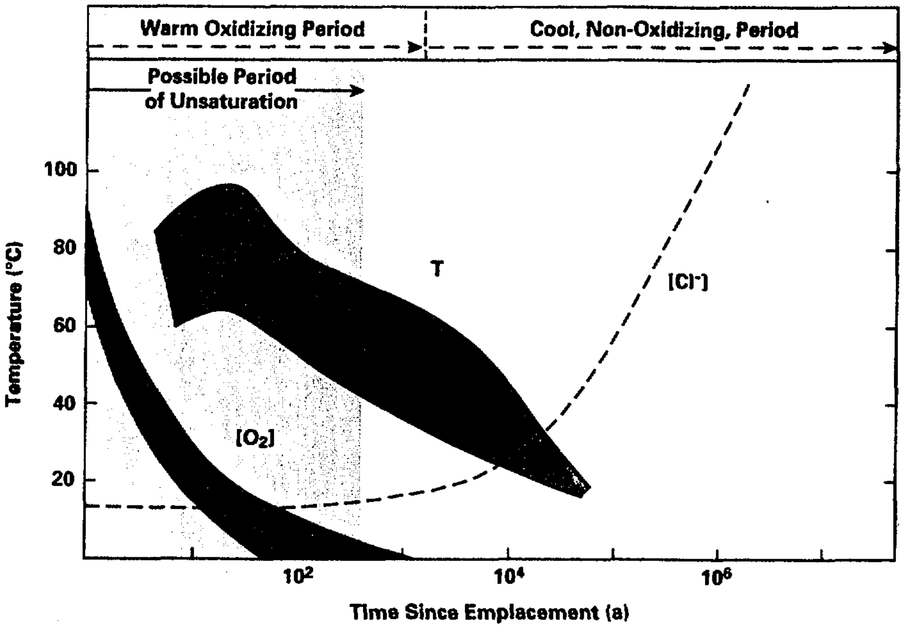

FIGURE 2: Expected Evolution in Environmental Conditions Within a Canadian Waste Vault. The possible period of unsaturation is assumed in this figure to last 500 a.

disposal conditions the variables most likely to affect the properties of this film are the following:

(1) redox conditions, which will be controlled by the concentration of available oxidants and can be expressed as a corrosion potential (E_{CORR});

(2) temperature, which will not exceed 100°C and will generally be much lower, Figure 2;

(3) pH, which should remain within the neutral range 6 to 10 (Figure 1) unless localized corrosion sites are established where acidic conditions can prevail;

(4) groundwater salinity which could eventually attain a chloride concentration of 125 000 $\mu g \cdot g^{-1}$ (M. Kolar, unpublished data, 1995).

Here, we discuss a number of pertinent oxide properties and how they are likely to be affected by variations in these parameters. Subsequently, we discuss the significance of these changes in determining the susceptibility of titanium and its alloys to corrosion by pitting, by MIC and under unsaturated conditions.

Figure 3 summarizes the changes expected in passive oxide properties as a function of potential, pH and temperature. Here, only a brief summary is given, a more detailed discussion, complete with references, being available in Appendix A.

The passive oxide grown under open circuit conditions at room temperature may be amorphous or crystalline depending on the conditions of growth. The thickness and degree of crystalline order may vary spatially and a small degree of non-stoichiometry (in the form of oxygen vacancies (O_V^{II}) and Ti^{3+} interstitial ions (Ti_I^{III})) gives the oxide n-type semiconducting properties. Anodic polarization leads to oxide thickening by a high field ion conduction (HFIC) process and a decrease in the number density of defects (N_P). Amorphous films recrystallize to anatase over the potential range 4 to ~7 V (vs. SCE) and cracks and faults begin to appear in the oxide. The amount of water absorbed by the oxide, which generally leads to an improvement in passivity, does not increase with increasing applied potential. Films grown potentiostatically at high potentials ($\geq$8 to 9 V), and subsequently examined in NaBr solutions, show an increase in pit generation rate without a corresponding increase in pit repassivation rate. For these high anodic potentials the breakdown of the film leads to recrystallization and a more rapid thickening of the film with potential than at lower potentials.

The effect of temperature on films grown either electrochemically or on open circuit is similar in many respects to that of potential. A similar breakdown/recrystallization process to yield anatase/rutile occurs in the temperature range 50°C to 70°C but, in contrast to the effect of potential, is accompanied by the absorption of water. For T > 70°C, the rate of film thickening increases as observed at high potentials, but the amount of absorbed water also increases markedly. Subsequent examination at room

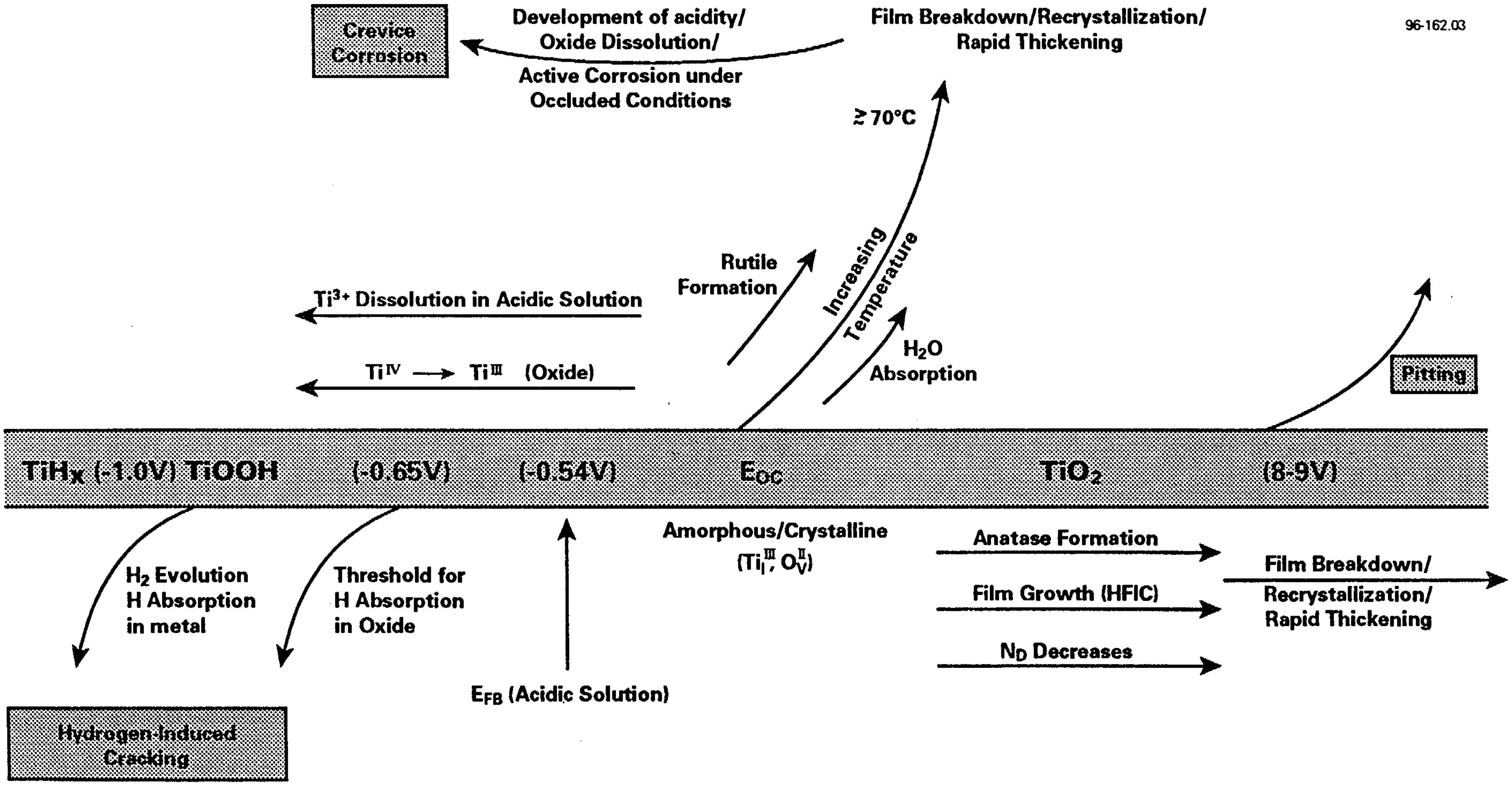

FIGURE 3: Summary of the Changes Expected in Passive Oxide Properties as a Function of pH, Potential and Temperature.

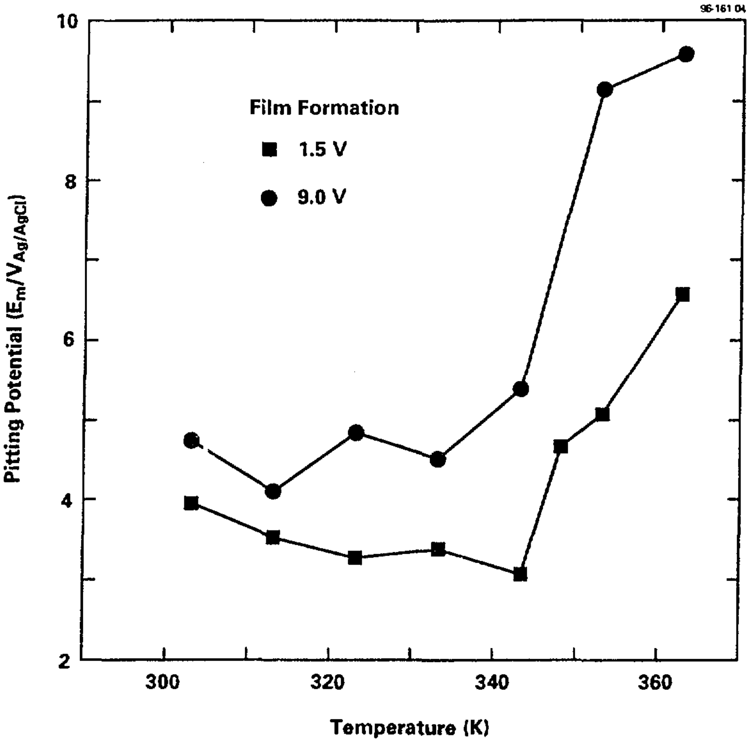

FIGURE 4: The Median Value of Pitting Potential, Determined in 2 mol·L $^{-1}$ NaBr at 303 K, as a Function of Film Formation Temperature (from Shibata and Zhu 1994a).

temperature in NaBr solutions shows this absorption of water improves the passivity of the oxide as indicated by a marked increase in pitting potential, Figure 4 (from Shibata and Zhu 1994a).

Polarization to cathodic potentials leads to a combination of reductive transformations within the oxide and the absorption of hydrogen once the potential is sufficiently negative of the flatband potential (E_{FB}) for surface degeneracy to be established. For $E < -1.0$ V (vs. SCE), hydrogen evolution occurs and the formation of surface hydrides is observed. Measurements of the amounts of hydrogen absorbed suggest a potential threshold of ~ -0.6 V (vs. SCE) above which no absorption occurs.

The pH has no effect on oxide stability for $E \gtrsim -0.3$ V but, for sufficiently acidic conditions, an active region and an active to passive transition are observed between ~ -0.7 V and -0.3 V. At room temperature in chloride solutions, a pH ~ 0 is required before active conditions can be established. For a temperature of 70°C, a pH < 1 is required. On open circuit, dissolution of the oxide film in acidic solutions is slow and chemical in nature, and in solutions of $pH > 1$ is extremely slow. Cathodic polarization in acidic solution leads to reductive dissolution of the oxide. Whether or not this leads to its total dissolution is unclear.

To avoid the two processes most likely to lead to localized corrosion, crevice corrosion and HIC, practical operating guidelines have been established. For crevice corrosion, it is accepted that attack will not occur on titanium alloys below a temperature of 70°C, regardless of solution pH or chloride concentration. For HIC a number of criteria must be simultaneously satisfied: a source of hydrogen atoms must be present; the temperature must be in excess of 80°C; and either the pH must < 3 or > 12, or the potential at the surface must be <-0.7 V (vs. SCE) (Schutz and Thomas 1987).

In our recent studies we have confirmed the validity of these guidelines. Using a galvanic coupling technique we showed that crevice corrosion does not initiate on Ti-2 until $T \gtrsim 70^{\circ}C$ (Noël et al. 1996a). However, in view of the oxide properties discussed above, it is clear that T alone cannot account for crevice initiation since, if conditions inside the crevice were not different to those outside, then the oxide film present at 70°C would be more resistant to the initiation of localized corrosion than those present at lower temperatures due to its higher water content. However, our experiment indicates that oxide dissolution within the crevice occurs prior to initiation, and pH monitoring within the crevice shows a $pH \sim 1$ is established prior to initiation (Yao et al. 1991). The need for such a low pH is consistent with that required for active conditions to be achieved (Watanabe et al. 1989). Clearly, a combination of low pH (~ 1) and high T ($\gtrsim 70^{\circ}C$) is required to breach the oxide within the occluded geometry afforded by the crevice.

Our measurements of the amount of hydrogen absorbed as a function of applied potential in acidic chloride solutions ($pH = 1.0$) at 95°C also support the concept of a threshold for hydrogen absorption around -0.6 V (vs. SCE). Above this potential no absorption is observed, whereas for $E <-0.6$ V, hydrogen is absorbed and surface hydrides eventually formed (Noël et al. 1996b).

We can conclude that if the oxide on titanium is to be breached and localized corrosion to initiate then either a combination of high T ($>70^{\circ}C$) and low pH (≤ 1) or cathodic polarization to <-0.7 V (vs. SCE) is required. It should be noted that a potential <-0.7 V is a severe restriction since polarizations to potentials significantly less than this produce only thin, innocuous surface hydride films. A more realistic threshold to produce severe damage by embrittlement would be a potential <-1.0 V (Schutz and Thomas 1987).

4. CORROSION UNDER UNSATURATED CONDITIONS

A period of unsaturation at the container surface (Figure 2) could leave the container exposed to a moist oxidizing environment. The nature of corrosion processes which might occur during this phase are difficult to specify. In the absence of a condensed water film oxidation of the container should be very slow. If a vapour phase exists and condensation of a thin liquid film occurs then the rapid gas phase supply of oxygen and the radiolytic formation of acidity and oxidants in the condensed film could lead to aggressive conditions. In the absence of a liquid transport medium the formation of mineral or corrosion deposits could occur, and localized under-deposit conditions could be established.

The oxide film on Ti has been shown to provide an excellent barrier to corrosive attack by most gases in wet and dry conditions, including O_2, N_2, dry HCl, SO_2, NH_3, HCN, CO_2, CO and H_2S (Schutz and Thomas 1987). No significant corrosion attack has been observed in oxygen or sulphur-bearing gases below 300°C, and Ti is the preferred metallic material for handling wet chlorine and bromine environments. The outstanding resistance of Ti alloys to rural, marine and urban atmospheric environments has been documented (Covington and Schutz 1981). Titanium alloys are widely used in hydrogen-containing environments and in the presence of traces of moisture or oxygen the surface oxide film is a highly effective barrier to hydrogen absorption (Cotton 1970, Covington 1979).

This practical experience gives us confidence that Ti waste containers will not sustain significant damage if exposed to moist oxidizing conditions in the early emplacement period. However, a number of additional scenarios merit evaluation.

(1) Sufficiently oxidizing and acidic conditions might be established in either condensed water droplets or a thin film of condensed water on the container that oxide dissolution could occur and an oxygen concentration cell be established at this local breakdown site. For this to be feasible, pH values of ~1 would be required for expected vault temperatures of ~90°C (Section 3).

(2) The presence of a mineral deposit on the surface of a container otherwise covered by a thin film of condensed water could establish a crevice. The rapid vapour phase transport of oxygen to the container surface and its absorption into the liquid film could then sustain the crevice propagation process. While crevice corrosion seems impossible in the absence of bulk water it would only be feasible anyway if $T \gtrsim 70°C$ (Section 3). This would mean that, if damage due to crevice corrosion were to be sustained, then the process would have to initiate within the first 200 a, the time required for even the hottest container to cool to <70°C (for the borehole emplacement vault design). Indeed, fully 60% of the containers would have cooled to below this threshold in 30 a, Figure 5 (Shoesmith et al. 1996).

(3) The production of reductants such as H atoms could lead to the reduction of the passive film ($Ti^{IV} \rightarrow Ti^{III}$) which would then either dissolve in an acidic environment or become permeable to the absorption of hydrogen leading eventually to embrittlement and failure of the container by HIC (Section 3).

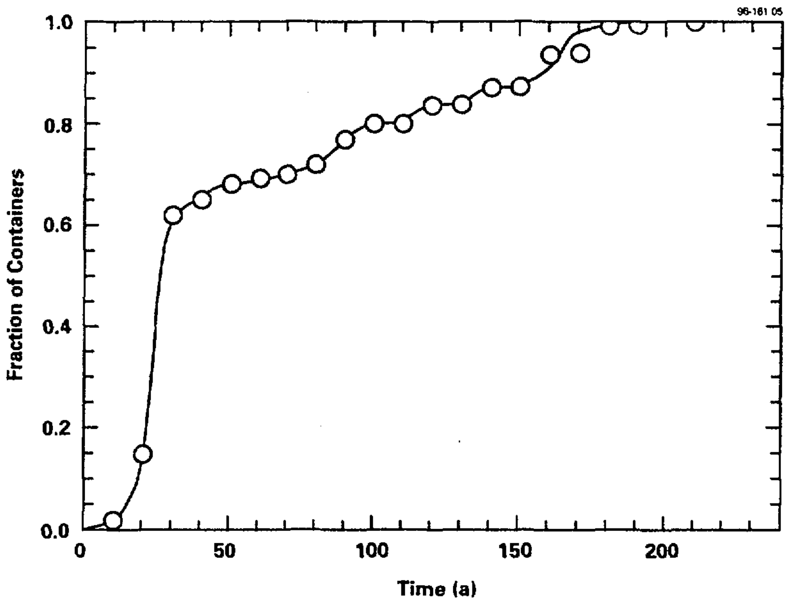

FIGURE 5: Cumulative Fraction of Titanium Containers Cooling to 70°C as a Function of Time after Emplacement in a Canadian Nuclear Fuel Waste Disposal Vault (from Shoesmith et al. 1996).

While oxidizing conditions could be maintained by oxygen trapped in the vault on closure, the development of acidic conditions is not so readily envisaged. The most likely possibility would appear to be the radiolysis of moist air leading to the fixation of N and the production of N-acids, N-oxides and NH_3 (Reed and van Konynenburg 1991, Jones 1959). The amount of nitric acid formed depends on the rate of radiolytic production of NO_2 and the amount of available H_2O,

$$NO_2 + OH \text{ (from water)} \rightarrow HNO_3 \tag{1}$$

and the yield should be a maximum at ~50% relative humidity. For lower relative humidities, HNO_3 decomposes to NO_2 and H_2O. Although suppressed in favour of the formation of N-acids and N-oxides when O_2 is present, the formation of NH_3 is possible.

A number of factors will severely limit the possibility of localized corrosion processes. The availability of water at the container surface will probably be too low for N-acid production to be significant and almost certainly too low to support the continued propagation of crevice, or underdeposit, corrosion. Also, any acidity produced may be neutralized by proton adsorption on the cation-exchanging clay surrounding the container. The ability of gamma radiation to destroy oxygen concentration cells by producing oxidants within crevices (Shoesmith et al. 1995a) would stifle localized corrosion. Finally, even without these influences, the resistance of Ti to corrosion in oxidizing acids, specifically HNO_3, is well documented. Ti has excellent corrosion resistance to HNO_3

over the full concentration range at temperatures below boiling and to NH_3 whether in wet or dry conditions (Schutz and Thomas 1987).

The radiolytic production of H_2 under moist vapour conditions will not be sufficiently extensive to lead to film reduction and, hence, hydrogen absorption. The production of hydrogen in atomic form would need to be sufficient to polarize the titanium surface to potentials negative of the threshold for hydrogen absorption, ~-0.6 to -0.7 V (vs. SCE). Polarization to such negative potentials inevitably requires either the galvanic coupling of titanium to a base material such as carbon steel or the application of a potential during cathodic protection (Schutz and Thomas 1987). The direct absorption of hydrogen produced radiolytically requires much higher temperatures and dose rates than those achievable within a planned Canadian waste vault (Shoesmith et al. 1992). Westerman and coworkers (Westerman et al. 1982, Westerman and Telander 1986; Nelson et al. 1984) observed hydrogen absorption under basaltic conditions at 250°C only for gamma dose rates $>10^2$ $Gy{\cdot}h^{-1}$ compared to maximum expected temperatures and dose rates of ~90°C and 50 $Gy{\cdot}h^{-1}$ under Canadian waste vault conditions (Johnson et al. 1994b).

Atmospheric corrosion has been studied at elevated temperatures but not at temperatures as low as 100°C. Moroishi and Shida (1980) studied the oxidation of commercially pure Ti (CPTi, equivalent to grades 1-4 Ti, Table I) in air saturated with steam at 0.1 MPa (1 atm) for 24-101 d at temperatures between 400 and 550°C. The rate varied from 2.6 to 45 $mm{\cdot}a^{-1}$ over that temperature range and breakaway corrosion was only observed at 550°C. Extrapolation of their data to lower temperatures suggests a corrosion rate of 0.005 $mm{\cdot}a^{-1}$ at 100°C and <0.001 $mm{\cdot}a^{-1}$ at 25°C.

The corrosion performance of Ti and Ti alloys has also been investigated in contact with clay and in moist clay atmospheres. The majority of these studies were conducted on either commercially pure Ti (CPTi, equivalent to Ti-2) or the palladium-containing Ti-7 (Table I). No measurable differences in performance were observed between the two materials although Ti-7 was more universally tested than CPTi (Debruyn et al. 1990).

Tests were performed in direct contact with clay at both 90°C and 170°C for exposure periods up to 6 a. No significant weight change was observed, and optical microscopy and metallography showed no observable differences between unexposed specimens and those included in the tests. Auger spectroscopy on Ti-7 confirmed that the alloy was covered by the normal thin oxide. In humid clay atmospheres (15°C to 170°C) no evidence for corrosion damage was found, even in the presence of a radiation field (10^3 $Gy{\cdot}h^{-1}$).

Tests were also conducted in synthetic vapour environments to simulate the atmospheres expected in clays which may have undergone pyrolysis. These included tests at 50°C in a corrosion chamber containing water vapour (relative humidity 75%), SO_2 (100 $\mu g{\cdot}g^{-1}$) and a flow of 250 $L{\cdot}h^{-1}$ of air; and tests at temperatures from 13°C to 150°C in a furnace supplied with 3.5 cm^3 of moisture and 14.5 L of air per hour. A wide range of materials were tested. After 49 months at 50°C in the corrosion chamber only the titanium alloys

(CPTi, Ti6Al4V, Ti5Al2Sn) showed no evidence of pitting attack, and despite the formation of deposits there was no observable crevice corrosion. After 3 a of testing in the furnace no corrosion was observed and the metal remained covered by the thin protective oxide. In none of these tests did the formation of mineral deposits lead to observable localized corrosion.

5. PITTING

As for crevice corrosion (Shoesmith et al. 1995c), the vault conditions most likely to support pitting are warm and oxidizing, and the process will be limited by the duration of the oxidizing period (Figure 2). If it can be demonstrated that pitting cannot initiate during the early warm period then we can be assured it will not occur as cooler anoxic conditions are established, even though groundwater salinity may steadily increase with time of emplacement of the container in the vault, Figure 2.

The pitting of titanium has been studied in some detail (Posey and Bohlmann 1967 and references therein; Koizumi and Furuya 1973; Covington 1976; Beck 1973a,b; Petit et al. 1980; Watanabe et al. 1988; Shibata and Zhu 1994a,b, 1995a,b,c; Raetzer-Scheibe 1978; Casillas et al. 1994) and, with a few well-characterized exceptions, is not feasible with the materials considered as candidates for waste containers. While extremely rare, pitting has been observed in hot anhydrous organic solvent streams, in high temperature oxidizing bromide solutions, in hot salt evaporators at T > 130°C, and associated with embedded iron or steel particles. None of these situations, with the possible exception of the last, is relevant to the environment anticipated in a Canadian waste vault. Pitting due to embedded iron particles has been observed during hot (>80°C) brine exposure but is more appropriately considered as a special case of crevice corrosion (Covington 1976). It can be avoided by proper handling techniques or by the use of the alloys Ti-12, Ti-7 and Ti-16.

Two extensive studies of the pitting of Ti have been published (Posey and Bohlman 1967; Koizumi and Furuya 1973). Koizumi and Furuya (1973) measured pitting potentials (breakdown potentials, E_P) and dealt predominantly with the effects of environmental factors such as pH, chloride/bromide concentration, the effects of other anions and temperature. Posey and Bohlmann (1967) also measured values of E_P but investigated the effects of material composition and how these influence E_P as a function of temperature.

5.1 ENVIRONMENTAL FACTORS

The parameter which exerts the greatest influence on E_P is temperature. For low temperatures ($\lesssim$ 50°C) E_P is >10 V, even in concentrated chloride solutions, Figure 6, and remains large up to $\gtrsim$100°C. Even for the maximum expected vault temperature of $\gtrsim$90°C, E_P should be $\gtrsim$7 V. E_P does not vary much with either pH or chloride concentration. For a change in pH from neutral (7) to acidic (1) E_P shifts to more active

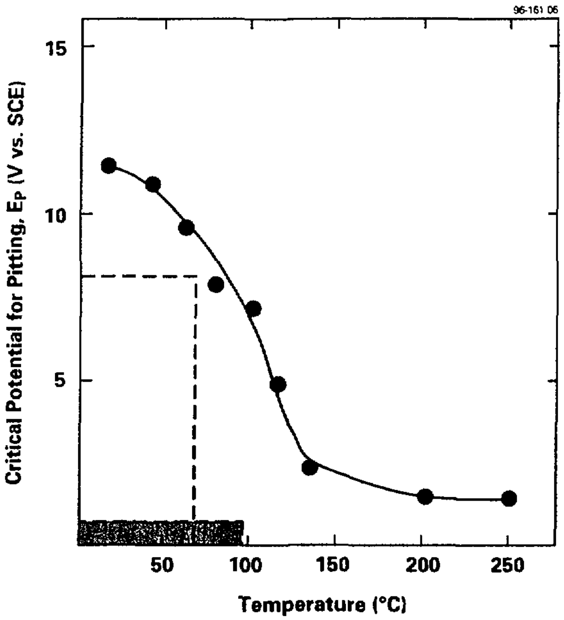

FIGURE 6: Effect of Temperature on the Critical Potential for Pitting Measured in 0.53 mol·L^{-1} NaCl (from Koizumi and Furuya 1973). The horizontal dashed line indicates the potential above which film growth accelerates after proceeding by a HFIC process at lower potentials. The vertical dashed line indicates the temperature above which a similar change in film growth process occurs. The shaded area shows the ranges of temperature and corrosion potential expected over the lifetime of a Canadian waste vault.

values by only ~0.2 V. Koizumi and Furuya (1973) determined the relationship between E_P (vs. SCE) and [Cl$^-$] at 200°C over the range 0.04 to 2.00 mol·L^{-1} (at pH = 3) and found the relationship

$$E_P = 1.4 - 0.10 \log[\mathrm{Cl}^-] \tag{2}$$

Providing this dependence applies for lower temperatures, then the anticipated increase in groundwater chloride concentration with time of container emplacement in the vault (Figure 2) would exert no significant influence on the resistance of Ti to pitting. The presence of other potential groundwater anions would not undermine this resistance since most have been shown to inhibit the initiation of pitting. The order of ability to inhibit is

$$SO_4^{2-} > NO_3^- > PO_4^{3-} > CO_3^{2-} . \tag{3}$$

The horizontal dashed line in Figure 6 shows the potential above which film growth is accelerated after thickening linearly with potential via a high field ion conduction (HFIC) process at lower potentials (Ohtsuka et al. 1985). This increase in growth rate was attributed to the completion of film breakdown/recrystallization and an increase in density of grain boundaries which provide short diffusion paths for the ions involved in film growth (Appendix A). As noted in Appendix A, TiO_2 is a network-forming oxide which tends to grow predominantly by the inward diffusion of oxygen but without incorporating anions from the electrolyte. This inability to incorporate anions has been demonstrated by Auger electron spectroscopy (AES) for Br^-, an anion with the ability to induce pitting even at low potentials (Casillas 1993) (see below). Consequently, while growth by HFIC is proceeding, the chloride incorporation into the oxide, which would lead eventually to the initiation of pitting, does not occur. After film breakdown/recrystallization, the presence of a large density of grain boundaries effectively allows Cl^- transport to the metal interface without the need for its incorporation into the structure of the oxide. A description of the processes which could be involved in the chloride-induced initiation of pits has been given recently by Burstein and Mattin (1995). That E_P is predominantly determined by film properties and is not particularly dependent on $[Cl^-]$ is consistent with this reasoning.

A similar explanation can be advanced to explain the large change in E_P as T rises above 70°C (indicated by the vertical dashed line in Figure 6). As for high potentials, once T exceeds 70°C, the rate of film growth accelerates due to the breakdown/ recrystallization of the oxide and the introduction of a high density of grain boundaries. Consequently, only for $T \gtrsim 70°C$ would Cl^- ions be capable of reaching the metal oxide interface in sufficient quantity to initiate pits. The increased absorption of water at higher T which conferred improved passivity and resistance to pitting in tests subsequently performed at low T (Shibata and Zhu 1995b) is apparently ineffective in doing so at temperature.

Also shown in Figure 6 is a shaded area encompassing the range of redox conditions (based on corrosion potential measurements) and temperatures expected in a Canadian waste vault over 10^6 a of container emplacement. The margin of safety between the expected conditions and those required for pitting to be possible is very large, and we can confidently rule out the possibility that pitting will occur.

One anion which can induce pitting at much lower potentials is Br^-. Figure 7 compares values of E_P measured in NaBr solutions to those measured in NaCl (Koizumi and Furuya 1973). At high temperatures, when film breakdown/recrystallization processes are complete and film properties are expected to be most important in determining E_P, values are not that different in the two electrolytes. However, the radical improvement in pitting resistance in chloride solutions as temperature decreases is not observed in bromide solutions. While significant quantities of Br^- are not expected in a waste vault, it is interesting to determine as far as is possible, why Br^-, and to a lesser degree I^- (Raetzer-Schiebe 1978; Beck 1973a,b), induce pitting at such low potentials.

A number of authors have attempted to explain why pit initiation in Br^- solutions occurs at potentials below that at which film growth switches from an HFIC process to a grain boundary transport-controlled process (Raetzer-Schiebe 1978; Beck 1973a,b; Petit et al. 1980; Casillas et al. 1994). However, only a few attempts have been made to investigate directly the nature of the pit sites initiated in Br^- solution. Using ion beam analyses, Petit

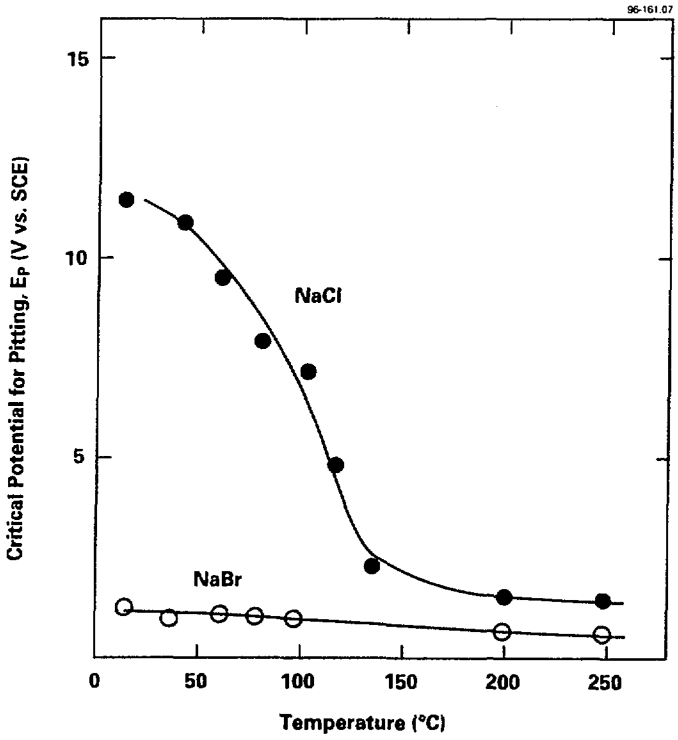

FIGURE 7: Effect of Temperature on the Critical Potential for Pitting in 0.53 mol·L^{-1} NaCl and 1.0 mol·L^{-1} NaBr (from Koizumi and Furuya 1973).

et al. (1980) identified a low density of Br$^-$ enriched sites at $E < E_P$. That these sites were metastable micropits was then demonstrated by the topographical agreement between their location and that of the pits subsequently developed at $E > E_P$. It was claimed that pit nucleation in Br$^-$ solutions involved the formation of $TiBr_4$ molecules on surface defects.

The most thorough investigation has been undertaken by Casillas et al. (1994). Using scanning electrochemical microscopy (SECM) to measure a current attributable to Br-oxidation, it was shown that a small number of sites with sufficient conductivity to support such an electron transfer reaction existed on the passive Ti surface. While their nature remained elusive, it was clearly shown they were the sites at which stable pits eventually grew. The current through these defects flows at potentials between 1 and 2 V (vs. SCE), Figure 8, i.e., at potentials much less than the ~2.5 V required to achieve anodic surface degeneracy. This confirms that these currents are associated with defects in the oxide. Oxide thickening by anodic oxidation in acidic sulphate solutions prior to the measurement of E_P in Br$^-$ solutions showed these defects were eliminated in thicker oxides, Figure 8, leading to an increase in E_P (Shibata and Zhu 1994b). The involvement of the Br$^-$ ion, coupled with the dependence of E_P on oxide thickness, suggests a potential-dependent chemical dissolution of the outermost oxide layers is involved in the initiation of pits.

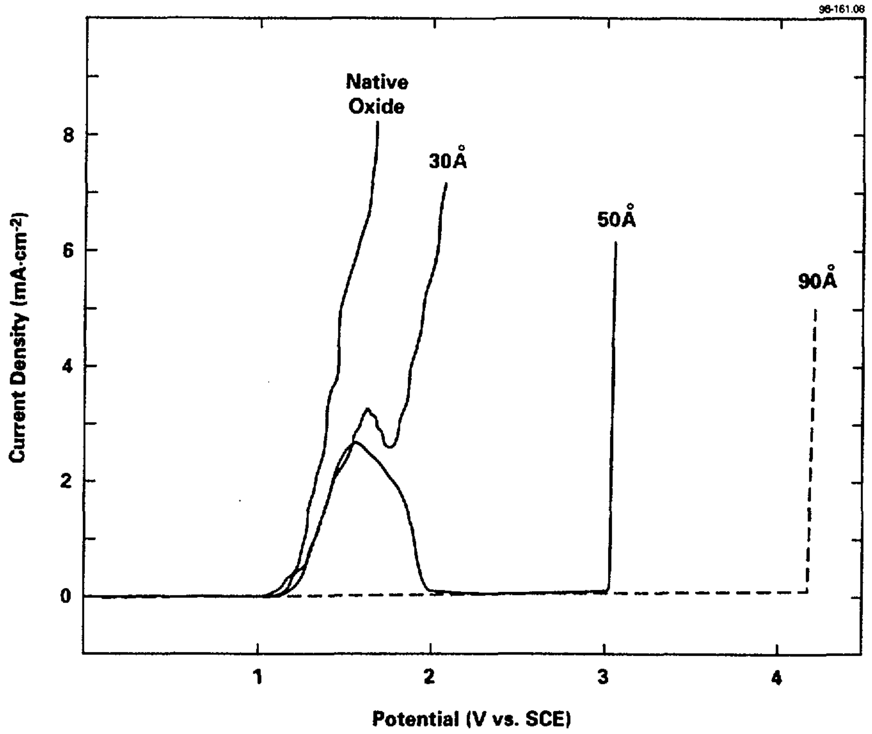

FIGURE 8: Voltammetric Responses (at 1 mV·s^{-1}) of Ti Electrodes as a Function of Passive Oxide Thickness in a Solution Containing 1 mol·L^{-1} KBr and 0.05 mol·L^{-1} H_2SO_4 (pH = 1.05) (from Casillas et al. 1994).

That the Cl$^-$ ion cannot induce dissolution and pit initiation at these defects is apparent in the large values of E_P measured in Cl$^-$ solutions (Figures 6 and 7). That the process of pit initiation is quite different in the presence of the two anions is clearly indicated in the different temperature dependencies of E_P (Beck 1973a,b).

Further evidence in support of titanium's resistance to pitting in Cl$^-$ solutions is clear in the microelectrode studies of Burstein and Souto (1995). In acidic Cl$^-$ solution (1.5 mol·L^{-1} NaCl) there is evidence for a small number of infrequent metastable pitting events in the passive region (Figure 9A). In these transients film breakdown is inevitably followed by repassivation (Figure 10A), and only a very limited number of transients show minor pit propagation before repassivation (Figure 10B). In neutral Cl$^-$ solutions (1.0 mol·L^{-1}), similar to those anticipated in a waste vault, only oxide growth with no observable metastable pitting transients was observed, Figure 9B.

5.2 MATERIAL FACTORS

Posey and Bohlmann (1967) found the same dependence of E_P on T as Koizumi and Furuya (1973) but investigated the effects of alloying additions to the metal rather than environmental factors. The influences of such additions were observable but small, (Figure 11). Additions of ~1% Al, Sn or Ni lead to a significant increase in E_P for

(A)

(B)

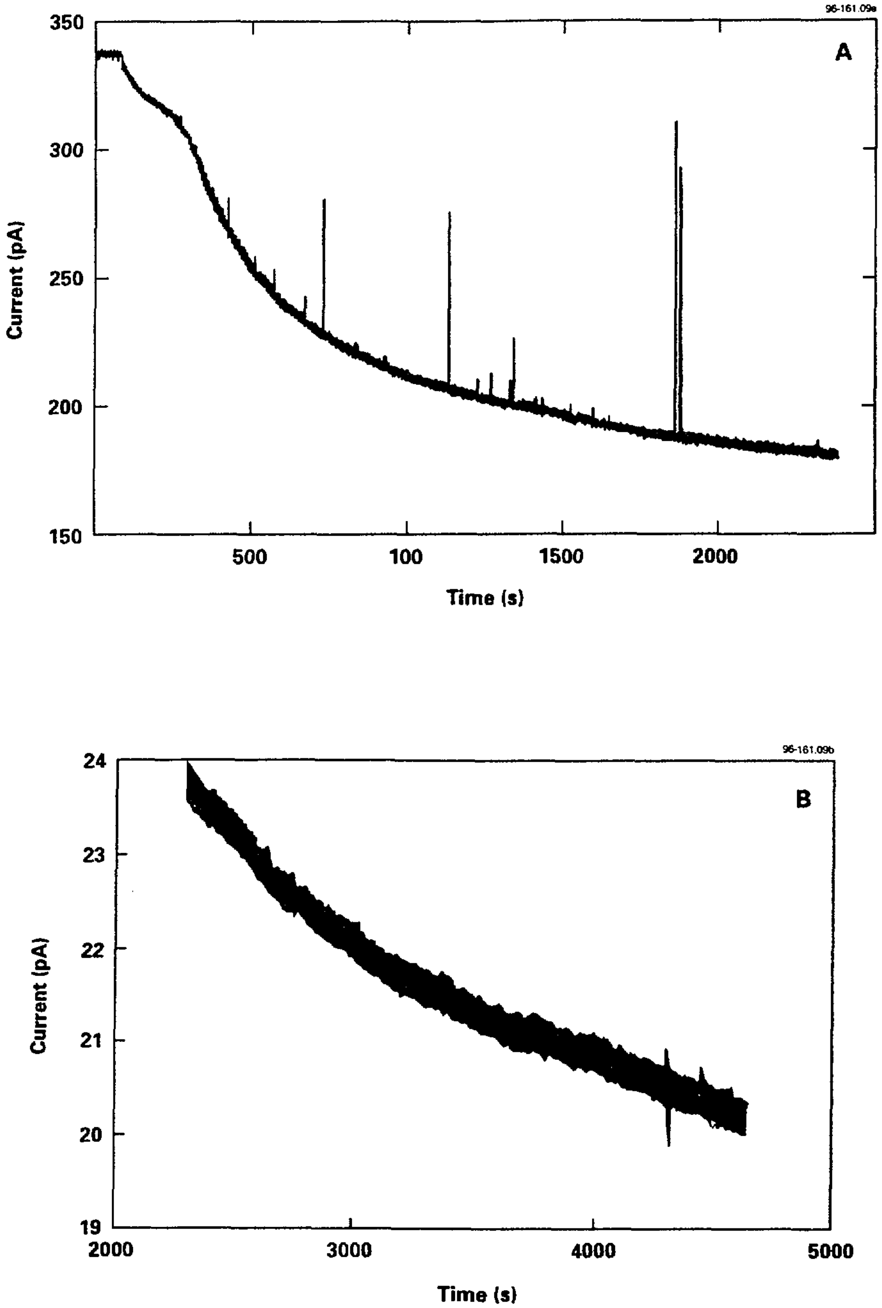

FIGURE 9: A. Current as a Function of Time for a Ti Microelectrode Polarized in 1.5 mol·L^{-1} HCl at a Potential of 0.9 V (vs. SCE).

B. Current as a Function of Time for a Ti Microelectrode Polarized in 1.0 mol·L^{-1} NaCl at a Potential of 0.9 V (vs. SCE) (from Burstein and Souto (1995)).

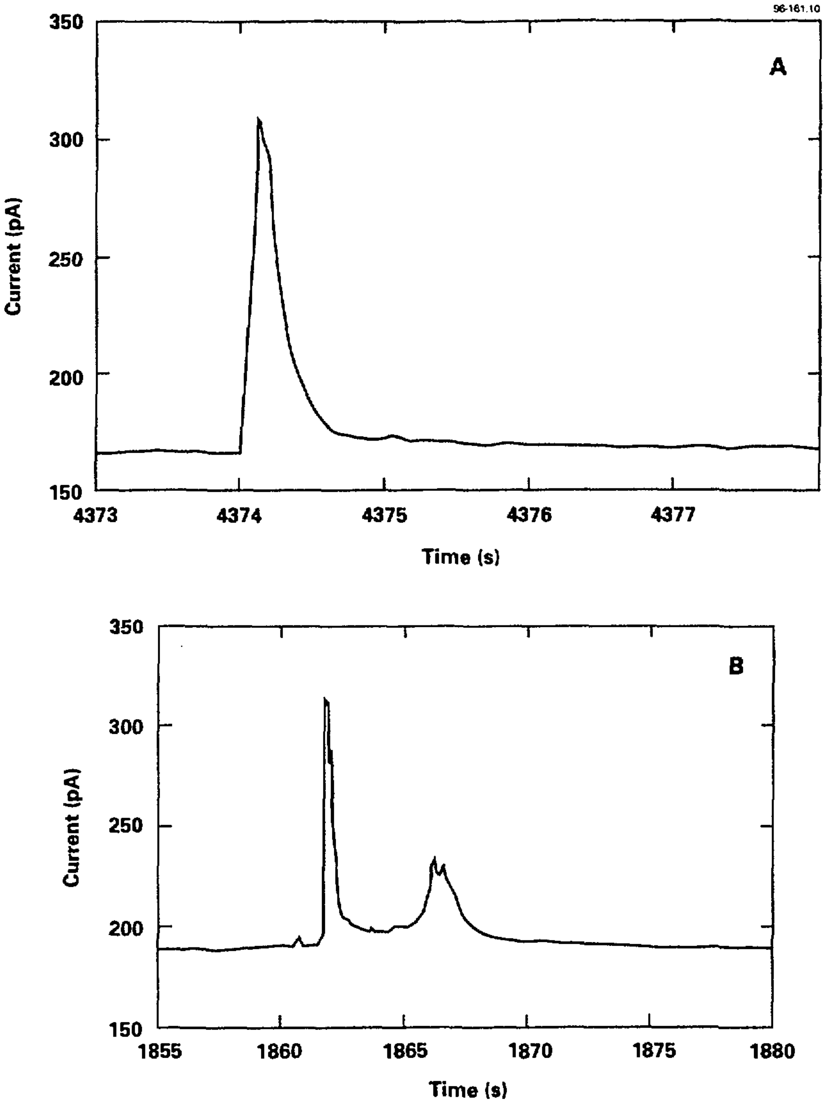

FIGURE 10: A. Anodic Current Transient Showing Film Breakdown Followed Immediately by Repassivation.
B. Anodic Current Transient Showing Film Breakdown Followed by Minor Propagation Before Eventual Repassivation.
Transients recorded on a Ti microelectrode at 0.9 V (vs. SCE) in 1.5 mol·L^{-1} HCl (from Burstein and Souto (1995)).

T < 100°C in 1.0 mol·L^{-1} NaCl. By contrast, the addition of ~1% Mo has little effect below 125°C but leads to an increase at higher temperatures (>3 V at 200°C, Figure 11). Of those alloying elements present in candidate container materials (Ni, Mo, Pd), (Table I), none will lead to a decrease in E_P for waste vault temperatures. An attempt to summarize these influences is shown in Figure 12. E_P is shown to be normally distributed around a conservatively low mean value of 7 V with a σ value of ~1 V (Shibata and Zhu 1994b). Also shown is the range of E_{CORR} values expected under waste

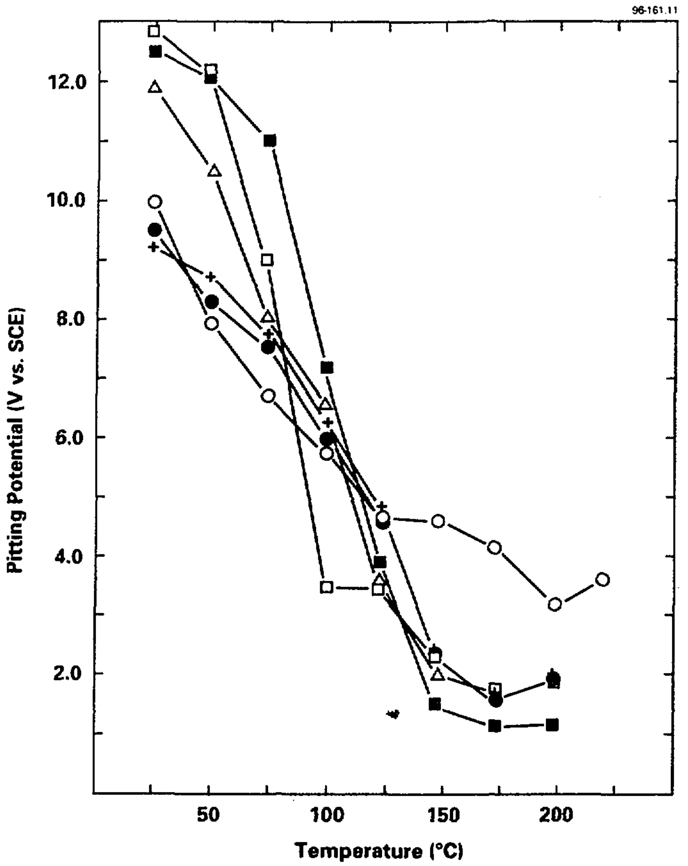

FIGURE 11: Effect of Small Percentages of Alloying Elements on the Pitting Potential of Titanium Recorded in 1.0 mol·L^{-1} NaCl; (●) CPTi; (+) Ti + 0.15% Pd; (□) Ti + 1% Al; (○) Ti + 1% Mo; (■) Ti + 1% Sn; (△) Ti + 2% Ni (from Posey and Bohlmann (1967)).

vault conditions. This comparison is made for a T of 100°C, the maximum attainable under vault conditions and clearly indicates the insignificant effect of these alloying additions on the pitting resistance of Ti.

One alloying addition which can significantly reduce the value of E_P is a combination of $\gtrsim$4% Al plus either Mn, Sn, V or Nb/Ta. Figure 13 indicates that E_P for the alloy Ti6Al4V (Ti-5) is as low as 1.5 V in 1.5 mol·L^{-1} NaCl at 100°C. While the difference between E_P and E_{CORR} may still be sufficient to claim no susceptibility to pitting under waste vault conditions, the very large difference in E_P for Ti-5 compared to those containing small amounts of Ni, Mo, Pd suggests a radically different pitting mechanism. The more complicated alpha and alpha-in-beta phase structure, as well as the possibility of microstructural effects due to segregation could be responsible. Microstructural, compositional and morphological examinations of the oxide films on Ti-5 have shown that it possesses a more heterogeneous texture/microstructure than that on Ti-2 (Ask et al.

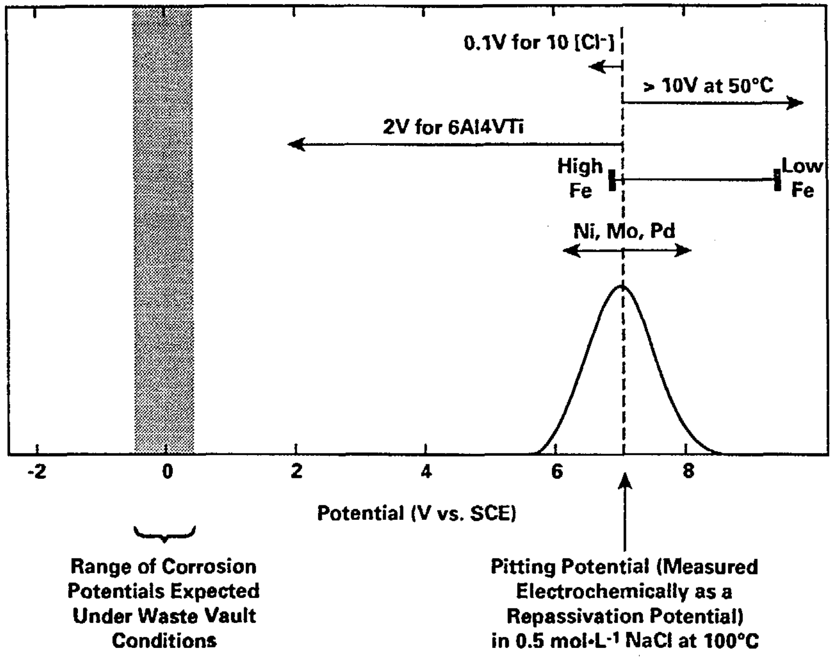

FIGURE 12: Summary of the Effect of Various Parameters on the Pitting Potential for Ti.

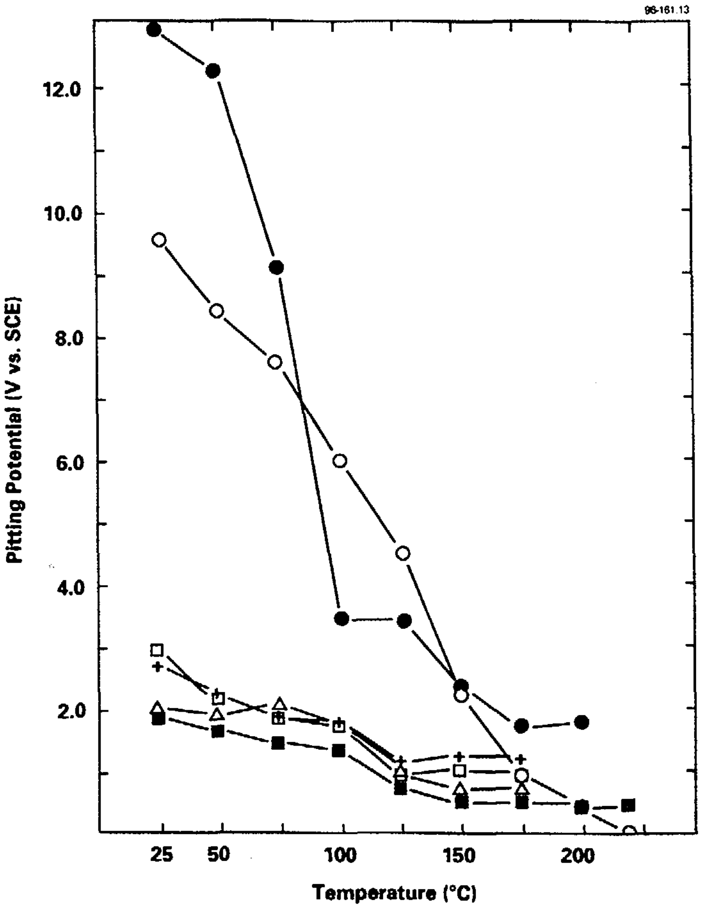

FIGURE 13: Pitting Potential for Ti-Al Alloys in $1.0\ \mathrm{mol{\cdot}L^{-1}}$ NaCl; (○) CPTi; (●) 1% Al; (□) 4% Al and 4% Mo; (■) 5% Al and 0.5% Sn; (†) 6% Al and 4% V; (Δ) 8% Al, 2% Nb and 1% Ta (from Posey and Bohlmann (1967)).

1989, 1990; Lausmaa et al. 1990). The porosity of the oxide appears higher and the V has a strong enrichment factor (1.5 to 2) in the oxide grown on the alpha-in-beta phase.

One of the most common impurities found in Ti alloys is Fe, which we have shown can have a major impact on the propagation rate of crevice corrosion in commercially pure Ti (Ti-2) (Ikeda et al. 1990, 1994). When present with small amounts of Ni in intermetallic particles it suppressed crevice propagation, but when distributed more dilutely in β-phase or altered microstructural features such as martensite or twinned structures it appears to offer anodic sites at which crevice corrosion can propagate preferentially.

Watanabe et al. (1988) have shown that the Fe content also has an influence on the pitting behaviour of Ti-2. For T < 100°C, E_P values decrease with Fe content (Figure 14), but still remain around 6-7 V at 100°C. For "pure" Ti ([Fe] = 9 $\mu g \cdot g^{-1}$) and Ti with a low Fe content (<300 $\mu g \cdot g^{-1}$), E_P decreases markedly above 70°C consistent with the predominance of film properties in determining pitting behaviour, as discussed above. For [Fe] > 300 $\mu g \cdot g^{-1}$, E_P is significantly lower and decreases steadily with T. Our own measurement of E_P at 150°C (Shoesmith et al. 1995a) shows this trend is maintained up to 150°C, Figure 14. The analyses of Watanabe (1988) show that the iron content is enriched at specific sites (possibly intermetallics), which dissolve preferentially under anodic polarization and act as pit nucleation sites. The loss of any dependence of E_P on Fe content at T > 70°C is consistent with the predominant influence of film characteristics in the pit initiation process at these higher temperatures (Section 3). The dependence of

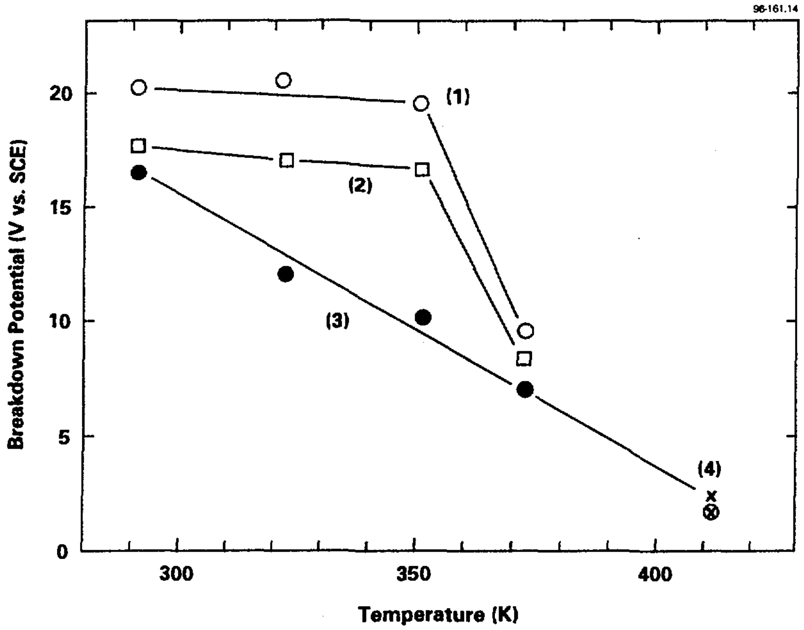

FIGURE 14: Effect of Temperature on the Pitting Potential of Ti Specimens Containing Various Iron Contents Recorded in 30% NaCl Solution (from Watanabe et al. 1988): (1) 9 $\mu g \cdot g^{-1}$ Fe; (2) 238 $\mu g \cdot g^{-1}$ Fe; (3) 342 $\mu g \cdot g^{-1}$ Fe; (4) data from Shoesmith et al. (1995a).

E_P on T once the Fe content exceeds that required for the segregation of Fe to occur suggests that a change in the mechanism of pit initiation to one involving precipitates has occurred. While observable, these effects will have an insignificant influence on the resistance to pitting of Ti under waste vault conditions (Figure 12).

6. MICROBIALLY INFLUENCED CORROSION (MIC)

The potential for MIC will be strongly influenced by the evolution of vault conditions. The combined effects of heat, gamma radiation and desiccation of the buffer material will prevent microbial growth close to, or biofilm formation on, the container at short emplacement times (King and Stroes-Gascoyne 1995). The preponderance of available evidence suggests that the lack of water may be the critical feature in producing this "sterile" zone which could extend some tens of centimetres from the container surface. However, microbial activity remains possible at locations beyond this zone where the water activity will be higher and the gamma field lower. If this period of desiccation is of long enough duration (Section 4 and Figure 2) then it is possible that anoxic conditions could be established before rewetting of the container occurs, and the consideration of the effects of aerobe activity would no longer be necessary. Once cool and anoxic conditions become established in the vault, the potential for microbial activity will increase, but the formation of a biofilm on the container is a process likely to be made very difficult by the relative dimensions of the microbes (>0.1 μm) and the pore size of the buffer (0.01 - 0.05 μm). However, the products of microbial action remote from the container could produce species (e.g., sulphide, organic acids) which would be subsequently transported to the container surface (King 1996).

A case has been made for the resistance of titanium to MIC (Schutz 1991). Here, we will deal predominantly with the bacterial activity expected in natural, brackish and sea waters since these are likely to be most representative of those anticipated in a waste vault.

The chemical changes expected at a metal surface under a biofilm formed in aerated natural waters have been reviewed by Dexter and Chandrasekaran (1996) and Dexter (1996). While the biofilm itself may be patchily distributed on the metal surface, sharp gradients of both $[O_2]$ and pH exist within the biofilm which becomes aerobic and near neutral in the outer layers but acidic and low in O_2 close to the metal surface. The pH close to the metal surface can fall to <3 and direct measurements using Ir-IrO_2 micro-pH electrodes have recorded values approaching 1 within marine biofilms grown on Pt. Hydrogen peroxide at millimolar levels has been detected within the films and is thought to be both produced and limited by bacterial enzymes during the aerobic respiration process. Peroxide helps to maintain a low pH by oxidizing heavy metal cations which then hydrolyze to maintain the low pH close to the metal/biofilm interface. These processes are illustrated schematically in Figure 15.

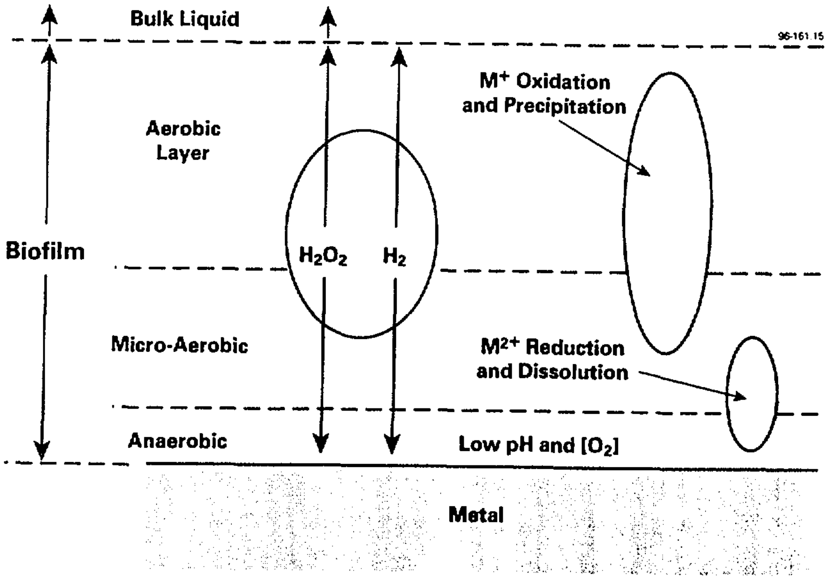

FIGURE 15: General Model for Biofilm Chemistry Causing Enhancement of the Cathodic Reaction on Passive Metal Surfaces Immersed in Natural Waters (from Dexter 1996).

This chemical combination leads to the ennoblement (a shift in E_{CORR} to more positive values) of passive metals and alloys such as stainless steels, superalloys and titanium (Dexter and Zhang 1990). An example for a number of stainless steels is shown in Figure 16 (Little and Mansfeld 1995). This shift has been shown to occur in natural waters (Dexter and Zhang 1990) of all salinities as long as the biofilm provides a nominal coverage in excess of ~40% (Dexter 1995). The ennoblement suggests that the probability for localized corrosion has increased, and there has been extensive discussion on whether this is attributable to thermodynamic or kinetic effects. Thermodynamically, a positive shift in the reversible potential of the O_2 electrode due to local acidification could account for ennoblement. Kinetically, an increase in the exchange current density for the oxygen reduction reaction would produce the same effect.

The importance of a thermodynamic effect has generated some dispute (Dexter and Chandrasekaran 1996, Dexter 1996, Little and Mansfeld 1995), but it is generally acknowledged that the generation of a low pH is insufficient to account for the up to 0.5 V shifts in E_{CORR} observed (Little and Mansfeld 1995), particularly on high molybdenum stainless steels and superalloys. An increase in the exchange current for O_2 reduction due to catalysis by biopolymer metal complexes could lead to ennoblement and the presence of a biofilm has been shown to accelerate cathodic reaction kinetics (Chandrasekaran 1995), a shoulder of increased current being observed on the low potential edge of cathodic polarization curves (Motoda et al. 1990, Zhang 1993), Figure 17. The explanation of catalysis of O_2 reduction by organometallics has been criticized, however, because ennoblement is also observed on Ti which lacks the

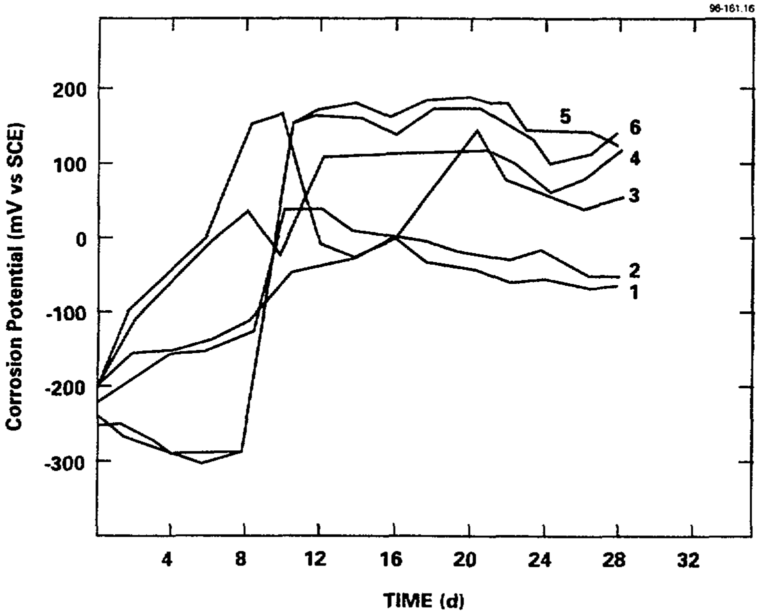

FIGURE 16: Corrosion Potential Measured on Freely Exposed Stainless Steel Specimens in Natural Seawater Flowing at a Velocity of 0.5 m·s^{-1}; (1) Sandvik SR 60; (2) SAF 2205; (3) Sanicro 28; (4) 254 SMO; (5) Monit; (6) 984 LN (from Little and Mansfeld 1995).

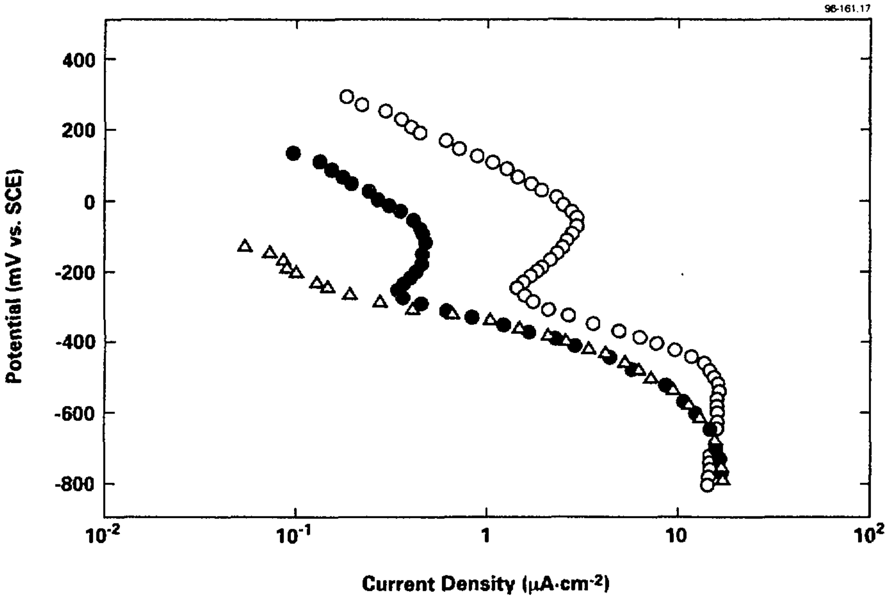

FIGURE 17: Cathodic Polarization Curves for 316 Stainless Steel After Immersion in Natural Seawater for 0 (Δ), 7 (●) and 14 (O) days (from Motoda et al. 1990).

transition metal elements thought to be necessary to form such catalysts (Mansfeld and Little 1989).

An equally likely possibility, and one that would explain the increased currents in O_2 cathodic reduction curves (Figure 17) is the production of H_2O_2, Figure 15. Peroxide in the biofilm can contribute to a noble shift in E_{CORR} thermodynamically, by virtue of its more positive equilibrium potential, and kinetically by changing the nature of the cathodic reaction (Dexter and Chandrasekaran 1996) from O_2 reduction to H_2O_2 reduction (Little and Mansfeld 1995). That the production of H_2O_2 is involved in the process of ennoblement is consistent with the attempts to chemically simulate the effect. A combination of low $[O_2]$, a $pH < 3$, and millimolar quantities of H_2O_2 were required to reproduce both the shift in E_{CORR} and other electrochemical observations (Chandrasekaran 1995).

Under biofilm conditions where ennoblement of stainless steels inevitably occurs it is generally, but not always (Little et al. 1993), observed for Ti. However, while a shift in E_{CORR} for stainless steel can be taken as an indication that the probability of localized corrosion is increased, this is not necessarily the case for Ti. The values of E_P (>8-9 V, Section 3) for Ti are so positive that a shift of E_{CORR} to values in the range of 0.5 V is insignificant. In fact, such a shift would lead to a thickening of the passive film and a decrease in number density of defects in it (Section 3).

While Ti can be considered effectively immune to biologically induced pitting, the threat of crevice corrosion is not quite so easily dismissed since it is a process which can initiate at potentials within the range achievable by ennoblement. This was acknowledged in modelling the failure of Ti waste containers by crevice corrosion when it was noted that the initiation of a crevice under a biofilm on the container surface had not been completely ruled out (Shoesmith et al. 1995a).

The effect of biofilms on crevice corrosion has been considered in some detail by Dexter (1996), and it has been claimed that initiation times should be decreased and propagation rates increased by ennoblement (Johnsen and Bardal 1985). Dexter et al. (1986) have shown that bacteria in crevice solutions can contribute to the depletion of O_2, a requirement for crevice initiation to occur. Whether or not more rapid initiation can be induced is debatable, but the evidence for the acceleration of crevice propagation when biofilms are present is more convincing. Dexter and Zhang (1995) and Zhang and Dexter (1995) have used remote crevice assemblies to show that the propagation of crevice corrosion is accelerated by biofilms on stainless steels with low and intermediate resistance to crevice corrosion in coastal waters. The biofilms had no effect on crevice corrosion resistance of high molybdenum alloys.

If biofilms are to force the initiation of crevice corrosion on Ti alloys, then a combination of low pH (<1) and high temperature (>70°C) is required, Section 3. This temperature is generally above the temperature regime of bacterial activity. While $pH \lesssim 3$ can be expected in biofilms due to the production of weak organic acids, such as butyric and acetic acids, this is not low enough to threaten the integrity of the TiO_2 passive film (Schutz 1991). Also, in the absence of heavy-metal cations, hydrolysis reactions to further reduce the pH cannot occur. The presence of substantial chloride concentrations would also be required for the initiation of crevice corrosion and, according to Schutz (1991), a 2% HCl solution is needed at 50 to 60°C if active corrosion is to be initiated on Ti-2.

The effect of temperature on the crevice corrosion of stainless steels in microbially active natural seawater has been studied by Mollica et al. (1988). As the temperature increased the probability of initiation and the propagation rates of crevice corrosion decreased. Kain and Lee (1985) found that increasing the temperature of natural seawater from 30 to 50°C decreased the corrosion current for stainless steel by nearly three orders of magnitude and Mollica and Trevis (1976) and Mollica et al. (1988) showed that the ennobling effect of a biofilm could be eliminated just by increasing the temperature of water to 40°C, a good indication that the main effect of T is to decrease the activity of aerobic bacteria.

It is clear from this discussion that the ennoblement of Ti under a biofilm is extremely unlikely to cause the initiation of crevice corrosion. This is not surprising since the passivity of Ti is more threatened under reducing conditions. For neutral pH a sufficient degree of negative polarization could lead to redox transformations in the oxide accompanied by hydrogen absorption (Section 3). If acidic conditions were to develop simultaneously, then reductive dissolution of the oxide could lead to the active conditions which prevail within a crevice.

A wide range of bacteria can produce molecular hydrogen as an end product from the fermentation of carbohydrates, and can contribute to electrolytic hydrogen production by the formation of acids such as acetic and butyric (Ford et al. 1990). The presence of sulphate-reducing bacteria (SRB) could present a particular problem by producing sulphides thereby promoting the formation of hydrogen atoms which could be subsequently absorbed by the metal.

If the hydrogen is to be absorbed by Ti, then a sufficiently negative E_{CORR} must be achieved. The industrial guideline for the threshold for hydrogen absorption is a potential of $\leq$ -0.7 V (vs. SCE) (Section 3). However, if we accept the flatband potential of ~-0.55 V (vs. SCE) (measured in acidic solutions (Torresi et al. 1987)) to be the threshold potential, then any hydrogen-producing bacterium must be able to polarize the Ti surface to a value cathodic of this.

Using the permeation technique developed by Devanathan and Stachurski (1962), Ford et al. (1990) measured the hydrogen produced in a biofilm that absorbed into Pd. E_{CORR} and the hydrogen production rate (measured as the permeation current) follow the bacterial growth curve, Figure 18, E_{CORR} decreasing as bacterial growth causes a decrease in the solution redox potential and produces organic acids. Once growth stops the potential increases again and the permeation current goes to zero. The most negative E_{CORR}

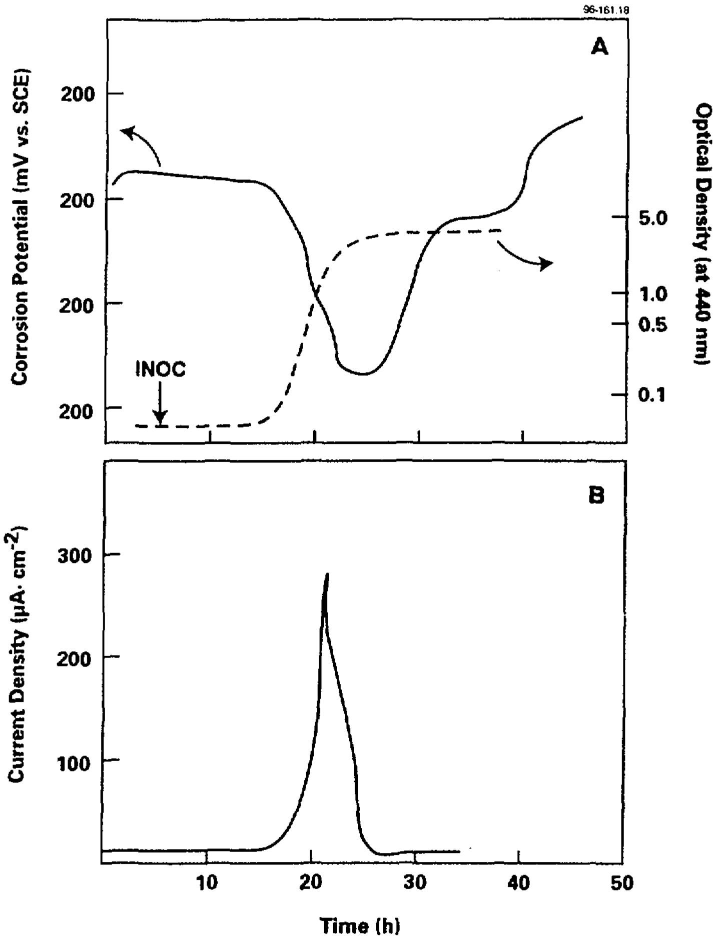

FIGURE 18: A. Corrosion Potential Measured on Pd During the Growth of *Clostridium Autobutylicum* and the Bacterial Growth Curve Measured as the Optical Density at 440 nm.

B. Corresponding Hydrogen Permeation Current Through the Pd. Measurements were made using the permeation technique developed by Devanathan and Stachurski (1962) (from Ford et al. 1990).

produced is in the range -0.470 V to -0.482 V (vs. SCE). While a passivated Ti surface is extremely unlikely to be so easily polarized to such negative potentials, even if it were, it would be insufficiently negative to exceed the hydrogen absorption threshold.

It is clear from the above discussion that the combination of high temperature and chloride concentration coupled with low pH and anoxic conditions required for localized corrosion are extremely difficult to achieve as a consequence of microbial activity. This has been confirmed by a number of studies of the corrosion performance of Ti in the presence of microbiological activity (Dexter and Zhang 1990; Mansfeld et al. 1990, 1992, 1994; Mansfeld and Little 1991; Little et al. 1992, 1993).

Mansfeld et al. (1990) have used electrochemical impedance spectroscopy (EIS) to study Ti exposed to natural Pacific Ocean seawater for periods up to 4 months under both open circuit and cathodically-polarized conditions (-850 mV vs. SCE). Both bacterial (open-circuit) and calcareous (cathodically polarized) deposits were formed, but while the growth and properties of the calcareous deposits could be determined by EIS, the growth of the biofilm could not. For the biofilm, changes in double-layer capacitance (C_{dl}) of stainless steel were taken as an indication that the metal/seawater interface was modified by its presence. By contrast, biofilm formation on Ti indicated no such modification, C_{dl} remaining constant over the 40-day exposure period. For calcareous deposits the EIS spectra exhibited two time constants which were analyzed in accordance with the model for porous polymer coatings on metals. For Ti, the formation of the tight deposit lead to increased protectiveness with exposure time as indicated by the steady increase in pore resistance.

A later study confirmed these results (Mansfeld et al. 1992) for Ti and the absence of a second time constant in the EIS spectra (when a biofilm was present) showed that the film could not be compared to either a thick porous-inhibitor film or a polymer coating. Whether or not the biofilmed specimens were exposed to natural light or to reduced light made little difference to the EIS behaviour. Dexter and Zhang (1990) confirmed that, despite some ennoblement, no observable MIC occurred on Ti-2 in natural seawater. A more wide-ranging study was undertaken by Little et al. (1992) using a dual-cell arrangement in which two electrochemical cells were separated by a semipermeable membrane and only one cell contained bacteria. The corrosion process was then followed by attaching a zero-resistance ammeter across two identical electrodes. The resistance of Ti and stainless steel was determined in the presence of both sulphur-oxidizing bacteria (SOB) and SRB, and of welded Ti in the presence of hydrogen-producing bacteria. No evidence of either localized corrosion or hydrogen absorption was observed in flowing seawater.

These experimental observations are consistent with practical experience, much of which is summarized in a recent review of the resistance of Ti to microbially influenced corrosion (Schutz 1991). Here we quote from this report:

> "A review of the literature and service experience fails to reveal a single titanium alloy component failure related to MIC (1-4,7). This record exists despite its extensive use in plate/frame and shell/tube heat exchangers, vessels, pumps, valves, and piping systems handling highly biologically active processes and raw cooling water streams over the past 30 years. These cooling water streams include all natural waters, especially seawater, and process cooling waters in treated and untreated conditions. Specific examples of Ti's extensive use in natural seawater worldwide include the following:
>
> - welded Ti-2 (UNS R50550) tubing in coastal power plant surface condensers (>1.5 x 10^5 km in service);

- Ti-1 (UNS R50250), Ti-2, Ti-12 heat exchangers in coastal chemical plants and oil refineries;
- Ti-1, Ti-2 and Ti-12 heat exchangers in coastal chemical plants and oil refineries;
- desalination plant welded Ti-2 heat exchanger tubing (>500 km in service);
- various Navy submarines, submersibles, and surface ship seawater components;
- Ti-2 service water piping systems in nuclear power plants in Sweden.

> Various test exposures of Ti alloy samples in the sea for periods as long as 20 years have demonstrated immunity to attack despite extensive micro- and macro-biogrowth on metal surfaces. Furthermore, the full resistance of Ti to all forms of biocidal treatments used to control component biofouling is also demonstrated. Since these methods are basically highly oxidizing, these alloys are fully compatible with chlorine gas or hypochlorite injection, bromination, ozonation, hydrogen peroxide, and copper/silver ion treatments. Full tolerance to various non-oxidizing, organic biocidal treatments, such as quaternary amines, glutaraldehyde, and isothiazolin, can be expected."

7. SUMMARY

The properties of the passive oxide film on titanium have been reviewed. For this oxide to be breached and localized corrosion to initiate either a combination of high T ($\gtrsim 70^{\circ}$C) and low pH ($\lesssim 1$) or cathodic polarization to >-0.7 V (vs. SCE) is required. Only under creviced conditions are such conditions achievable.

Extensive testing under unsaturated clay conditions showed no initiation of localized corrosion on Ti despite the formation of deposits under which crevice attack might have been expected. The lack of availability of water is expected to limit the radiolytic production of N-acids while conditions remain warm and oxidizing and capable of sustaining the propagation of localized corrosion. The direct absorption of radiolytically produced hydrogen has been shown to be insignificant at the dose rates and temperatures prevailing at the container surface.

The pitting potentials are many volts positive of the corrosion potentials achievable in a waste vault, making it possible to rule out pitting as a credible container failure mechanism. The dependence of E_P values on temperature and their insensitivity to Cl^- concentrations demonstrate that they are determined by film breakdown/recrystallization processes which only become significant for large anodic potentials (>8 to 9 V) or high temperatures (>70°C). No other environmental parameter, except Br^- concentration, has any significant influence on E_P. For reasons poorly explained at present, the oxidation of Br^- at a small number of conductive defects in the passive oxide leads to breakdown and pitting at much lower potentials. Providing alloys with >4% Al containing other alloying constituents (such as V in Ti-5 (Ti6Al4V)) are avoided, none of the alloying elements (Mo, Ni, Pd) or impurities (Fe) in the alloys considered lead to any significant decrease in E_P.

Many years of industrial application and testing have failed to reveal a single example of MIC on titanium. The generally potential ennobling tendency of biofilms on passive metals and alloys is insufficient to cause film breakdown. The possibility of crevice corrosion under a biofilm is extremely remote since the required combination of low acidity (pH ~ 1) and high T (>70°C) is not conducive to bioactivity. Bacteria which can produce both hydrogen and acidic conditions would appear to be the most threatening for Ti since only a relatively small cathodic polarization to <-0.7 V (vs. SCE) is required for hydrogen absorption. However, even for metals catalytic for H^+ reduction, such as Pt, the maximum achievable cathodic polarization is too small.

It is clear that the alloys of Ti considered for the construction of nuclear fuel waste containers (Ti-2, Ti-12, Ti-16) will not be susceptible to pitting, MIC, or corrosion in moist vapour atmospheres under the conditions expected in a Canadian nuclear waste vault.

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APPENDIX A

A.1 GENERAL OXIDE PROPERTIES

The oxide TiO_2 can occur in three polymorphic forms: rutile, anatase and brookite. The most stable of these is rutile which crystallizes in the tetragonal structure. The composition of the native oxide on titanium is TiO_{2-x} (Aladjem 1973). The oxide film present on open circuit exposure at room temperatures is generally amorphous. This is in keeping with the common tendency of most oxide-covered metals to form amorphous structures (Young 1961). The film thickness can be non-uniform and there is good evidence from tunneling spectroscopy (Casillas 1993) and capacitance measurements (da Fonseca et al. 1994) that the oxides are defective and spatially inhomogeneous.

According to Fehlner and Mott (1970), TiO_2 (along with the oxides of Si, Al, Zr, Nb) can be classified as a network forming oxide as opposed to a network modifying oxide (Fe, Ni, Cu, Pt). Network forming oxides have the metal cation predominantly in a common single oxidation state. During oxide growth the mobility of the anion is greater than that of the cation (Leach and Pearson 1988) and the growth process occurs close to the metal /oxide interface. This leads to the formation of dehydrated, very coherent and protective films that do not contain other anions incorporated from the electrolyte. The absence of adsorbed water in anodically-grown oxide films has been demonstrated using x-ray photoelectron spectroscopy (XPS) by Shibata and Zhu (1995).

The Ti ions in TiO_2 have a $Ti^{4+}(3d^0)$ electron configuration. In the absence of d electrons, the oxide possesses the characteristics of an insulator (or wide band-gap semiconductor) with a band gap of 3.05 eV. Deviations from stoichiometry (TiO_{2-x}) give the thin oxide film n-type characteristics. Torresi et al. (1987) have characterized the oxide on titanium as an n-type semiconductor with a band gap of ~3V and a flatband potential of ~-0.54V (vs. SCE) in acidic sulphate solutions.

These n-type characteristics can be attributed to a combination of oxygen vacancies and interstitial Ti^{3+} ions which lead to the trapping of electrons in a band orbital just below the conduction band edge (Jarjebski 1973). The presence of defects in the native oxide is clearly demonstrated by the higher density of surface electronic states at energies corresponding to what would be the band gap in crystalline rutile or anodically-grown films (Casillas 1993), and by the high donor densities measured by Mott-Schottky analyses (da Fonseca et al. 1994). XPS analyses show a clear correlation between the number of Ti^{3+} species detected and the defect donor density from capacitance measurements (da Fonseca et al. 1994). Films grown on open-circuit in neutral, as opposed to acidic, solutions do not appear to be as defective, Ti^{3+} species being hard to find by XPS (Noël et al. 1996a).

A.2 EFFECT OF APPLIED POTENTIAL

An n-type semiconductor with a band gap of 3V and a flatband potential (in 0.5 mol·L^{-1} H_2SO_4) of ~-0.54 V (vs. SCE), should only be able to support electron transfer reactions to soluble species in the electrolyte for applied potentials 2.4 V$\lesssim$ E $\lesssim$-0.6 (vs. SCE) when surface degeneracy should be achieved. Some evidence exists to support this. Both Ohtsuka et al. (1985) and Casillas et al. (1994) found that E $\gtrsim$ 2.5V was required for O_2 evolution to be observed. Torresi et al. (1987) also did not see O_2 evolution until ≥3V. However, for the oxide present on more compositionally-complex alloys of Ti (Ti-15Mo-3Nb-3Al, Ti-15V-3Cr-3Al-3Sn) Kolman and Scully (1993, 1994) found the onset of O_2 evolution at potentials as low as 1.4V (vs. SCE), a clear indication of the presence of electronically conducting defects in the oxide film.

The nature and distribution of these defects in both native and anodically-grown oxides have been investigated electrochemically in Br^- solutions using a combination of SECM and voltammetry (Casillas 1993). This combination clearly indicates that a relatively small number of defects (20 ± 10 pits·cm^{-2} for an open-circuit oxide ~2 nm thick) are present with a significantly higher conductivity than the general surface. Electron transfer at these sites leads to the oxidation of Br^- to Br_2. This process is reversed at the SECM tip and the variations in cathodic current as a function of the tip position, reflect local variations in the rate of Br^- oxidation on the TiO_2 surface. Subsequent examinations at more positive applied potentials show that pits nucleate at these sites.

Under anodic conditions the number of defects decreases and the film thickens by a high field ion conduction (HFIC) process as the potential increases. Ellipsometric results indicate that the oxide grows at a rate of ~2 nm·V^{-1} (Ohtsuka et al. 1985) up to ~7 V. For potentials up to ~5 V the absence of both a distinct diffraction pattern in TEM experiments and a Raman spectrum indicates that the film remains amorphous in this range (Shibata and Zhu 1995), although the results of electron diffraction and photoelectrochemical measurements have been interpreted to indicate the presence of a rutile structure (Tyler et al. 1987). The difference may be attributable to the rates of film growth, crystalline oxides being grown slowly under potentiodynamic conditions while amorphous oxides were grown more rapidly under potentiostatic conditions. The photoelectrochemical studies of McAleer and Peter (1980) also indicate a substantial increase in the degree of order in films grown potentiodynamically at low (1 mV·s^{-1}), as opposed to high (1 V·s^{-1}), sweep rates. This is consistent with the formation of a more crystalline oxide under slow growth conditions and is confirmed by the observation that film dissolution rates in acidic sulphate solutions are ~10 times slower for the more slowly grown oxide (Blackwood et al. 1988).

As the potential is increased and the oxide thickens the number density of electronically conductive precursor sites for oxide breakdown and pitting in Br^- solutions decreases. This is clearly demonstrated by the SECM results of Casillas (1993) and the capacitance measurements of da Fonseca et al. (1994) and Torresi et al. (1987), and confirmed by the analyses of pit generation and repassivation rates of Shibata and Zhu (1994a). Using a statistical model for the parallel birth and death of pits, Shibata and Zhu (1994a) showed that the pit generation rate decreased while the repassivation rate remained constant with an increase in oxide formation potential up to 6 V.

For E > 5V, clear evidence exists for the crystallization of the film initially to microcrystalline anatase (6 V) and eventually to well-developed crystalline particles of anatase, (Dyer and Leach 1978a; Ohtsuka et al. 1985; Shibata and Zhu 1995). These authors observed a roughening or rippling of the oxide film for E > 7.5 V consistent with a film breakdown process. Breakdown was accompanied by an accelerated thickening of the oxide with increasing potential. This was attributed to the film breakdown/ recrystallization process which lead to an increase in ionic currents at leakage sites and grain boundaries and, hence, the provision of short diffusion paths for the ions involved in film growth. The driving force for recrystallization is thought to be the build up of compressive stresses as the film thickens (Leach and Pearson 1988). Evidence in support of the importance of film stresses is offered by Shibata and Zhu (1995).

In the absence of adsorbed water, which is thought to form OH bridges at defective sites and to capture dissolved metal ions within the film, repassivation of the film at these potentials does not occur. This is consistent with the results of Shibata and Zhu (1994a), who showed that once film breakdown/recrystallization was underway (E > 6 V) the pit generation rate increased. By contrast, the film repassivation rate was independent of oxide formation potential showing that it is independent of film properties and probably controlled by transport processes.

A.3 CATHODIC POLARIZATION

The capacitance measurements of Dyer and Leach (1978b) demonstrate that polarization negative of the oxide flatband potential causes changes in the impedance properties of the oxide. These changes are accompanied by optical changes, observed in the ellipsometric parameters, the extinction coefficient and refractive index (Dyer and Leach 1978b, Ohtsuka et al. 1987), and lead to changes in the photoresponse (Weber et al. 1982). In neutral solutions at room temperature these changes begin at $E \leq -0.5$ V (vs. SCE) and are complete by -1.06 V and no dissolution of the oxide occurs. Potentiodynamic sweeps also show transitory cathodic currents in this range (Torresi et al. 1987). These changes are reversible and the optical and impedance properties return to their original values when the oxide is subsequently anodically reoxidized or allowed to relax on open-circuit.

Dyer and Leach (1978b) found a capacitance maximum within this range consistent with a redox change within the film. The capacitance maximum corresponds to the point at which the film impedance is a minimum and the redox change is 50% complete. On switching off the polarization the ellipsometric parameters relaxed at a rate from which a relative diffusion coefficient of $\sim 3 \times 10^{-13}$ $cm^2 \cdot s^{-1}$ was derived. This is too high for all but proton mobility within the oxide film (Dyer and Leach 1978c). That the reaction occurring is within the bulk of the oxide is indicated by the direct relationship between the film thickness and the size of the capacitance maximum (Dyer and Leach 1978b). Calculations of the amount of hydrogen absorbed from the electrochemical changes involved indicate one atom of hydrogen absorbed for each Ti atom in the film regardless of thickness (Ohtsuka et al. 1987). The combination of a capacitance maximum superimposed upon a capacitance steadily increasing with increasingly negative potential is an indication of a potential-dependent filling of the oxide with hydrogen coupled to a redox change within the oxide.

These observations were attributed to changes in film composition due to reduction of the oxide and the accompanying absorption of hydrogen according to the reaction,

$$TiO_2 + xH^+ + xe^- \rightarrow TiO_{2-x}(OH)_x$$

The introduction of hydrogen into the film increases the degree of OH bonding, resulting in a decrease in polarizability of O^{2-} ions and thus a decrease in the refractive index. The hydrogen in the film acts as an electron donor

$$H_{abs} \rightarrow H^+ + e^-$$

thereby producing a new absorption band in the bandgap region of the oxide leading to a decrease in both the film resistivity and the extinction coefficient. In reality, the situation may be more complex and other states of hydrogen appear to exist in titanium oxides (Weber et al. 1982).

The coupling of the proton reduction (to produce H_{abs}) and the redox transformation ($Ti^{IV} \rightarrow Ti^{III}$) within the oxide is consistent with the present understanding of proton reduction reactions occurring on oxide surfaces (O'Sullivan and Calvo 1987). It is difficult to imagine that significant electron transfer across the oxide/solution interface could occur on highly resistive TiO_2 layers without the increase in conductivity that accompanies the introduction of defect states in the form of reduced cation centres (Ti^{III}) within the oxide. For an n-type semiconductor like TiO_2 polarization negative of the flatband potential would be required for this to occur.

According to Ohtsuka et al. (1987), anodic reoxidation removes the hydrogen in two stages: a relatively rapid desorption of hydrogen within the film and a slower desorption of hydrogen assumed to be absorbed in the underlying metal. While it is possible that the slower desorption of hydrogen could be attributed to the difficulty of oxidizing hydrogen at irreversible trap sites within the oxide, Murai et al. (1977), in long experiments in artificial seawater (180 days), established that measurable absorption occurred for applied potentials $\leq$-0.6 V (vs. SCE). A similar threshold was obtained by Shimogori (1981) in deaerated 6% salt water at 100°C (60 days).

It would appear, therefore, that hydrogen absorption into the metal becomes feasible once proton discharge on the surface of the oxide becomes possible (i.e. for $E \leq E_{fb}$). This is consistent with the lower limit of impressed potential, -0.7 V (vs. SCE), imposed by practical experience (Schutz and Thomas 1987).

Beyond this threshold, the rate of absorption of hydrogen by the metal is almost independent of applied potential down to ~-1.0 V (vs. SCE). This is consistent with an adsorption process controlled by transport across an oxide barrier. For potentials ≤-1.0 V (vs. SCE) the current increases markedly with potential, hydrogen is evolved (Torresi et al. 1987), and the rate of absorption of hydrogen by the metal increases markedly (Murai et al. 1977). For polarizations of sufficient duration a layer of titanium hydride (TiH_2) is formed on the metal surface (Murai et al. 1977, Noël et al. 1996b).

A.4 EFFECT OF pH

The major interest is in the effects of decreasing pH since these conditions are the most likely to lead to oxide removal and the initiation of localized corrosion. For sufficiently acidic conditions, an active region is observed between -0.7 V and -0.3 V (vs. SCE) and a surface hydride layer forms during active corrosion. For E >-0.3 V passivity is maintained irrespective of the pH. Based on corrosion rates (from weight loss measurements) and polarization resistances (from impedance measurements) in chloride solutions, Watanabe et al. (1989) showed that a pH ≤ 0 was required for active behaviour to be observed.

The dissolution of passive oxide films on open circuit was shown to be chemical, as opposed to electrochemical (i.e. the autoreductive coupling of oxide dissolution and metal dissolution), and to proceed uniformly as opposed to locally (Blackwood et al. 1988). For very thin films dissolution is rapid and may not be uniform reflecting the inhomogeneous nature of such films (thickness, crystallinity) as determined by electron diffraction and spatially-resolved photocurrent measurements (Kozlowski et al. 1988). The dissolution rate was found to depend on the oxide formation conditions, the solution composition and temperature. Thus, an oxide grown slowly under potentiodynamic conditions ($1\ mV\cdot s^{-1}$), and hence expected to be more crystalline (Kozlowski 1988), dissolved ~10 times slower than one grown at $1\ V\cdot s^{-1}$ when a more amorphous structure is anticipated. The dissolution rates in H_2SO_4 range from $0.23\ nm\cdot h^{-1}$ to $2.23\ nm\cdot h^{-1}$ over the concentration range 0.02 to $3.0\ mol\cdot L^{-1}$ and are first order in proton concentration suggesting the dissolution reaction

$$TiO_2 + H_2O + H^+ \rightarrow Ti(OH)_3^+$$

Whether or not complexation by HSO_4^- (to produce species such as $Ti(OH)_3HSO_4$) is a factor is not clear. Surprisingly, the dissolution rate at pH = 14 ($1.0\ mol\cdot L^{-1}$ KOH) is greater than that at pH = 0. For pH > 1 the dissolution rate becomes very low («$1\ nm\cdot h^{-1}$)

even in media such as oxalic acid that are expected to complex Ti^{IV} ions. The values obtained in acidic solutions have been confirmed by measurements of oxide film thinning made by in-situ neutron reflectometry (Wiesler and Majkrzak 1994).

Cathodic polarization of the oxide-covered metal leads to electrochemical dissolution of the oxide according to the reaction

$$TiO_2 + 3H^+ + e^- \rightarrow Ti(OH)^{2+} + H_2O$$

in acidic solutions. The open circuit film thinning rates measured ellipsometrically (Ohtsuka et al. 1987) confirm the dissolution rate values measured in acidic sulphate solutions. They also show that dissolution is accelerated by cathodic polarization but cast doubts on the claim by Blackwood et al. (1988) that the oxide film is eventually totally removed. Under galvanostatic conditions, the current efficiency for oxide film reduction decreases as the potential falls to <-1.0 V (vs. SCE) and the complete removal of the oxide is difficult since the current becomes consumed mainly by hydrogen evolution and hydride formation. The persistence of the oxide at very negative potentials is not consistent with the claims of Arsov (1985), based on ellipsometric measurements, that the oxide was totally removed for E < -0.6 to -0.7 V (vs. SCE), but would explain the retention of distinct regions of different behaviour above and below -0.6V on both negative and positive going potentiodynamic sweeps (Nöel et al. 1996b).

A.5 EFFECT OF TEMPERATURE

Shibata and Zhu (1995) studied the effect of temperature on the structure and composition of films on Ti. At room temperature, films grown potentiostatically (in 0.5 $mol \cdot L^{-1}$ H_2SO_4 and generally at low applied potentials e.g., 1.5 V) were amorphous, as expected (Section A2). At 60°C films were still generally amorphous but contained small crystallites of anatase (~10 nm), consistent with electrochemical measurements which yielded a value of dielectric constant close to that expected for this phase, (Shibata and Zhu 1994b). Narrow elongated cracks were observed in the film confirming that recrystallization was accompanied by breakdown (Yahalom and Zahavi 1970; Dyer and Leach 1978 (a)). By 80°C no amorphous film was observed and a large number of crystallites (10 to 30 nm) of anatase and rutile were found. This change from amorphous to crystalline was confirmed by ex-situ Raman spectroscopy and XPS was used to show that the amount of bound water increases steadily up to 70°C and more rapidly at higher temperatures. Recrystallization and absorption of water is accompanied by a thickening of the oxide film as the density of grain boundaries, which provide short diffusion paths for the ions involved in film growth, increases (Shibata and Zhu 1995). XPS analyses of films grown under open circuit conditions in NaCl indicate a similar increase in amount of bound water as the temperature increases (Noël et al. 1996a).

The consequences of these changes in film properties with temperature have been investigated by measuring the pitting potentials (E_P) of oxides anodically grown at different temperatures in NaBr solutions at room temperature. The value of E_P decreased with increasing temperature up to ~70°C as a consequence of the recrystallization/ breakdown process. However, once the amount of adsorbed water (for T > 70°C) started to increase substantially, the pitting potential also increased dramatically, i.e., from ~3 V (70°C) to > 6 V (90°C) for films grown at 1.5 V. For films grown at 9 V the corresponding increase in E_P over this temperature range was from ~5 V to >9 V (Shibata and Zhu 1994b). This improvement in resistance to pitting for films grown at higher anodic potentials is consistent with the elimination of defects in thicker films observed by Casillas et al. (1994).

The increase in pitting potential with temperature was attributed to the formation of more compact, less defective films for T > 70°C when copious amounts of water are absorbed. Bound water in the film is thought to exist as a variety of bridging bonds which lead to the presence of a gel-like structure by trapping metal cations (Okamoto and Shibata 1970). This appears to improve passivity in two ways. The Ti-OH bridge bonds form at those active sites otherwise utilized as Br^- adsorption sites and hence inhibit the initiation of pits, and by trapping dissolved metal cations they facilitate repassivation.

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